



## 12 Treatment Technologies

The PFAS Team developed a training module video with content related to this section, it is the Treatment Technologies video.

This section provides information about treatment technologies for PFAS in environmental media. Treatment technologies for PFAS in environmental media are still evolving and it is prudent to use caution in implementing long-term remedies. Selection of remedial actions should prioritize protection of drinking water supplies and human health, with consideration of other objectives (such as reducing risk to ecological receptors and environmental resources, liability, source area mass, mass flux, generation of PFAAs from precursors). At some sites, it might be reasonable to take short-term site stabilization actions with the intent of applying more robust and cost-effective technologies as these are developed.

The treatment technologies described in this section are organized by degree of development and implementation, as well as current confidence in the technology based on peer-reviewed literature and the professional judgment of the authors. The levels are field-implemented technologies, limited application technologies, and developing technologies.

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### 12.1 Overview

Treatment technologies exploit a contaminant's chemical and physical properties to immobilize, remove, or destroy the contaminant. The stability and surfactant nature of PFAS make many treatment technologies ineffective, including those that rely on contaminant volatilization (for example, air stripping, soil vapor extraction) or bioremediation (for example, biosparging, biostimulation, bioaugmentation). Even aggressive technologies such as thermal treatment and chemical oxidation require extreme conditions beyond typical practices (for example, extreme temperatures, high chemical doses, extreme pH) to be effective or partially effective in destroying PFAS.

Treatment technologies can be employed either ex situ or in situ. For example, when groundwater is extracted via pumping from wells and treated, this would be considered an ex situ approach. In contrast, when treatment materials are injected into the subsurface to immobilize contaminants in groundwater under the surface, this would be considered an in situ approach. Because existing treatment technologies have generally shown to be inadequate, the unique chemical properties of PFAS often require new technologies or innovative combinations of existing technologies.

A range of unproven technologies exist for treatment of either liquids or solids that may be performed either in situ or ex situ. However, the most demonstrated technologies for treating PFAS in liquids are limited to the use of ex situ technologies.

Full-scale treatment of PFAS-impacted liquids or solids is currently limited to sequestration technologies that remove or bind PFAS but do not destroy them. Sorption using granular activated carbon and ion exchange media has been proven effective at full scale (see Table 12-1, provided as separate PDF, for references). Transformation or destruction technologies, including bioremediation, chemical oxidation, chemical reduction, and thermal technologies, are currently being tested. This section discusses both proven and emerging treatment technologies for liquids (waters, leachates, or other liquid wastes) and solids (soil, sediment, or other solid wastes).

The treatment technologies described in this section are organized by degree of development and implementation, as well as current confidence in the technology based on peer-reviewed literature and the professional judgment of the authors. Three levels of implementation/confidence are defined as follows:

- *Field-implemented technologies*—Technologies that have been demonstrated under full-scale conditions at multiple sites, by multiple practitioners and multiple applications, and are well documented in practice or peer-reviewed literature. Stakeholder concerns about the effectiveness of certain treatment technologies, including the testing and analytical approaches to measure efficiency, are presented in Section 13.1.20.
- *Limited application technologies*—Technologies that have been implemented on a limited number of sites, by a limited number of practitioners, and may not have been documented in peer-reviewed literature. These limited application technologies for liquids and solids are contained in the technology comparison Tables 12-1 and 12-2 (provided as separate PDF) and discussed in Section 12.5 and Section 12.6.
- *Developing technologies*—Technologies that have been researched at the laboratory or bench scale, but have not been field demonstrated. Often, these results are reported by only one group (for example, one university, practitioner, or vendor) or lack detailed validation of the treatment effectiveness or mechanisms. Experimental techniques to treat PFAS are under development, but only those technologies that have some level of publicly available documentation demonstrating effectiveness are included here.

The technology evaluations presented herein provide data for PFAS removal. This information varies widely among technologies and the data provided are based on the reported test conditions and results. Ultimately, the feasibility of a technology to meet applicable regulatory guidance values and standards often depends on site-specific conditions.

Currently in the United States, the regulatory standards for PFAS treatment are primarily driven by drinking water mitigation and focused on a small subset of PFAS. PFOS and PFOA are the only two compounds with federal regulatory guidelines

### **“Treatment” versus “Remedial Action”**

The term “treatment” refers to the application of certain technologies to specific impacted media to achieve desired remedial action goals or objectives.

As defined in the Superfund Amendments and Reauthorization Act (SARA), a “remedial action” is the actual construction or implementation phase of a site cleanup. Remedial action has a broader context that includes concepts surrounding targeted clean-up levels and monitoring but also addresses issues related to administrative elements, long-range planning, and remediation/restoration.

### **Technology Selection**

Selecting a technology to meet treatment targets is dependent on:

- an understanding of PFAS fate and transport
- a well-prepared conceptual site model
- proven remediation technologies
- defined (and achievable) treatment targets
- a stable regulatory environment.

(USEPA 2016c, d), and most regulatory discharge criteria for PFAS focus on PFOS and PFOA. Some states have guidelines, and several have regulatory criteria for additional PFAS, but precursor and short-chain PFAS are generally not considered in regulations or guidance, although that is changing. The technology evaluation information presented here provides data about all PFAS tested for a given technology. This information varies widely among technologies. Additional information on regulations is provided in Section 8.

### 12.1.1 Factors Affecting Technology Selection

Selection of a remedy, with confidence that treatment targets can be achieved, depends on a number of key factors, including the ability to reliably define the nature and extent of contamination, the availability of proven remediation technologies, and the capacity and tools to measure progress and compliance with desired regulatory criteria. A well-prepared CSM requires adequate information and is also fundamental to understanding and presenting the rationale and justification for the selected remedy.

Moreover, proven remediation technologies are limited in capacity and demonstrated ability to meet chosen treatment targets. The comprehensive discussions contained herein reveal many questions and uncertainties that must be addressed.

Factors affecting PFAS remedy selection include:

- **characteristics of PFAS.** The wide-ranging chemical and physical characteristics of PFAS affect the treatment effectiveness. Key factors include recalcitrance to common technologies due to the strength of the carbon-fluorine bond, ionic state (anionic, cationic, and zwitterionic), types of ionic groups (sulfonate or carboxylate), lipo- and hydrophobicity, chain length and branching, partitioning coefficients, phase behavior, volatility, solubility, acidity, total PFAS mass, and total concentration.
- **changes in PFAS properties.** Naturally occurring processes or remedial actions for other (commingled) contaminants, such as chlorinated solvents and petroleum hydrocarbons, can affect PFAS distribution and mobility in groundwater (McGuire et al. 2014). Example changes include:
  - The alkyl functional group of some PFAA precursors may be more readily subject to chemical or biological transformation than the fully fluorinated aliphatic chain (PFAAs).
  - Partial degradation of the carbon-carbon bonds in the aliphatic chain reported for some chemical remedies generates short-chain PFAS, which may be more mobile (Guelfo and Higgins 2013).
  - Modifications in aquifer properties (for example, redox or pH) during remediation of commingled contaminants results in a conversion of some precursors to the more stable and mobile PFCAs (McKenzie et al. 2015; McKenzie et al. 2016).
- **co-contaminants, organic matter, and geochemistry.** The presence of co-contaminants, total organic carbon, natural organic matter, minerals, and anions can significantly affect remediation. Some technologies that are designed and implemented to treat PFAS co-contaminants may transform perfluoroalkyl acid (PFAA) precursors into more stable perfluorocarboxylic acids (PFCAs) (McKenzie et al. 2015).
- **community acceptance.** Stakeholders, including community members, are often faced with trade-offs in terms of cost, level of cleanup, and residual contamination as part of remediation efforts.

For those directly engaged in assessing the suitability of PFAS treatment technologies, a structured process for systematic evaluation is currently under development via a SERDP-funded project (ER18-1633). The project focuses on five lines of evidence to evaluate technology performance and will provide resources to identify relevant information and data gaps and address key questions necessary for that assessment. Additional information is provided in Section 12.8.

### 12.1.2 Section Organization

The information presented in the following sections reflects the availability of performance results published, presented, or posted to the internet. Those technologies that have been implemented in the field at multiple sites, by multiple parties, and have peer-reviewed documentation of performance are discussed in Section 12.2 and Section 12.3. Projects funded by SERDP and the Water Research Foundation (WRF) are also highlighted. This section discusses the following key elements for each of these field-implemented technologies:

- *treatment description*—background and development of technology
- *treatment mechanism*—separation, sorption, or destruction
- *state of development*—applications and degree of commercial availability
- *effectiveness*—documented treatment effectiveness on PFAS and common co-contaminants along with water quality considerations and pretreatment need and options

- *design/operating considerations* –critical or unique operational or design needs
- *sustainability*–footprint, community enhancement, and cost.

Treatment case studies are presented in Section 15.2. Note that air treatment technologies are not included in this section because the current research is limited to liquid and soil treatment technologies and air exposures are not presently a regulatory priority.

## 12.2 Field-Implemented Liquids Treatment Technologies

These technologies have been implemented in the field by multiple parties at multiple sites and the results have been documented well in the peer-reviewed literature. The liquid treatment technologies in this section may be applied to a variety of PFAS-impacted media, including drinking water (regardless of source), surface water, groundwater, wastewater, or landfill leachate. At this time, all technologies that are considered “field-implemented” are ex situ treatment systems, meaning PFAS-impacted water is extracted and treated. Although some of the technologies described in this section have been applied in situ, they are not considered field-implemented at this time. Not all technologies would be appropriate for all applications. Site-specific evaluation is necessary to identify the best technology alternative for a given treatment media or scenario.

### 12.2.1 Sorption Technologies

Sorption technologies have been used for both ex situ and in situ water treatment applications. In situ applications are not covered in this section, because they are still considered “limited application or developing technologies” as defined in this document. Multiple sorption media types may be used in series for ex situ applications to optimize overall concentration reduction and removal capacity. Adsorption and ion exchange are two “sorption” mechanisms by which PFAS can be removed from water. Adsorption is a physical mass transfer process that uses Van der Waals and/or other weak ionic forces to bind the entire PFAS molecule to the surface areas of the adsorptive media. Ion exchange is the exchange of ions of the same charge. Ion exchange targets and binds to the hydrophilic ionized or functional end of the molecule (for example, the sulfonate in PFOS) while releasing an equivalent amount of an innocuous ion (for example, chloride) into the treated water. A number of influent water parameters can therefore be expected to impact the sorption efficiency for a specific PFAS compound. These include pH, ionic strength, the nature and concentrations of organic co-contaminants present (including naturally occurring organic matter [NOM]), competing inorganic ions normally present (for example, sulfate, nitrate, bicarbonate, and chloride), and any suspended solids or potentially precipitating impurities (for example, iron, manganese, calcium carbonate) that can foul and degrade the performance of the media. Pretreatment steps may be necessary to optimize the performance of such media, including coagulation, precipitation, filtration, pH adjustment, or oxidant removal. Ion exchange media used for PFAS removal from water use both the adsorption and ion exchange mechanisms. The use of two or more different media in series can be considered if the expected increase in overall removal efficiency can be used to justify the increased equipment cost.

Life cycle cost assessments can be used to compare the long-term cost-performance benefits of various sorption media types. Spent media management can be an important cost component. Common options used at the time of publication for spent media management are off-site disposal by thermal destruction (via commercial incineration or cement kilns), reactivation/regeneration for reuse, and landfilling.

Incineration and thermal reactivation/regeneration offer the possibility of destruction of PFAS waste streams, though incineration has received recent attention due to possible incomplete combustion and by-product generation and is the topic of current study to better understand the fate of PFAS. Incineration is discussed in Section 12.4.

#### **Key Cost Considerations for Sorption Media Selection**

- PFAS mix and competitive species
- pretreatment needs
- influent concentrations
- flow rate
- discharge criteria
- media change-out criteria
- media disposal

**Related Ongoing Research Funded by SERDP (ER) and Water Research Foundation (WRF)**

- ER18-1395 Electrically Assisted Sorption and Desorption of PFASs
- ER18-1417 Molecular Design of Effective and Versatile Adsorbents for Ex Situ Treatment of AFFF-Impacted Groundwater
- ER18-1052 Remediation of PFAS Contaminated Groundwater Using Cationic Hydrophobic Polymers as Ultra-High Affinity Sorbents
- ER18-1306 Combined In Situ/Ex Situ Treatment Train for Remediation of Per- and Polyfluoroalkyl Substance (PFAS) Contaminated Groundwater
- ER18-5015 Removal and Destruction of PFAS and Co-contaminants from Groundwater via Groundwater Extraction and Treatment with Ion-Exchange Media, and On-Site Regeneration, Distillation, and Plasma Destruction
- ER18-B3-5053: Evaluation and Life Cycle Comparison of Ex-Situ Treatment Technologies for Poly- and Perfluoroalkyl Substances in Groundwater
- WRF 4913: Investigation of Treatment Alternatives for Short-Chain PFAS

### 12.2.1.1 Granular Activated Carbon (GAC)

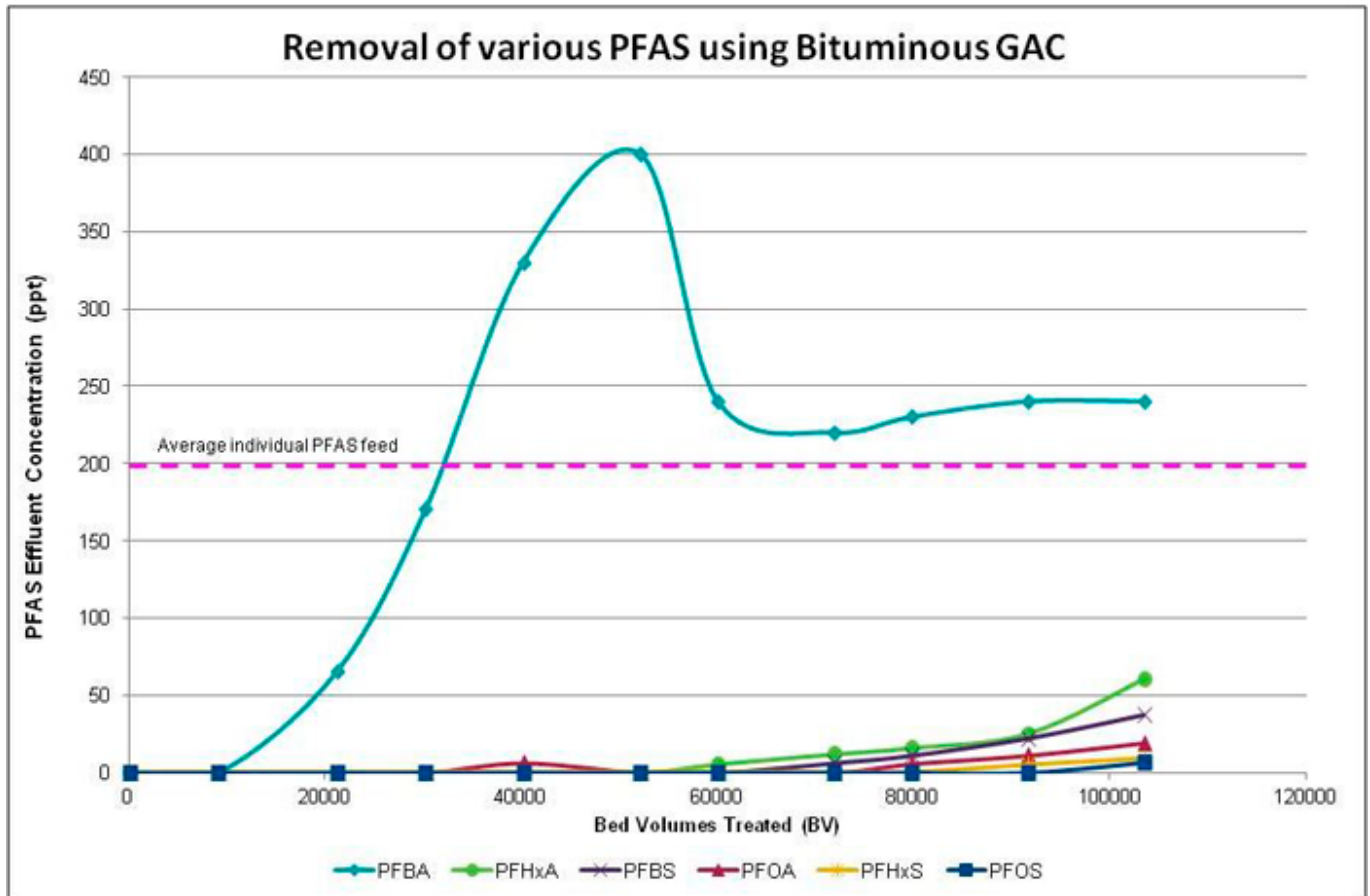
**Treatment Description:** GAC is an effective sorbent media for organics that has historically been used to reduce contaminants in a variety of water treatment applications. The information contained in this section describes ex situ GAC treatment in which water is extracted and transferred from the source of contamination and directed through the treatment system.

**Treatment Mechanism:** Removal of PFAS by GAC is a physical mass transfer process (refer to Section 12.2.1) from the aqueous phase onto solid media that does not involve or trigger any form of chemical degradation or transformation.

**State of Development:** GAC is an established water treatment technology proven to effectively treat long-chain PFAS (such as PFOS, PFOA, and PFNA). The application of GAC as a treatment technology for PFAS removal has been practiced for over 15 years at more than 45 military installations, as well as several industrial sites and publicly owned treatment works (Forrester 2018) involving private and municipal drinking water supplies.

**Effectiveness:** The following references were used to support the treatability effectiveness discussion presented below for long-chain PFAS by GAC: Appleman et al. (2013); Burdick et al. (2016); Cummings (2015); Dickenson (2016); Ochoa-Herrera and Sierra-Alvarez (2008); Szabo (2017) and Woodard, Berry, and Newman (2017). These references also include more comprehensive bibliographies if further details are needed on specific topics or studies. Literature and supporting column studies have shown that newly placed GAC can reduce effluent concentrations for PFAS listed in USEPA Method 537.1 (Shoemaker and Tettenhorst 2018) to below analytical detection limits until initial breakthrough begins to occur. The adsorption removal mechanism is not expected to transform precursors (for example, telomer alcohols) to terminal PFAS as would be the case when using advanced oxidation/reduction technology. Because GAC is generally used to treat many common groundwater contaminants, it is capable of also treating most organic co-contaminants that may be present, with the primary impact being increased GAC consumption due to greater loading per unit of time, which may require more frequent change-outs.

Individual PFAS have different GAC loading capacities and corresponding breakthrough times (often defined as the number of bed volumes treated prior to detection in the effluent) (Eschauzier et al. 2012). GAC removal capacity for PFOS is greater than PFOA, but both can be effectively removed (McCleaf et al. 2017). In general, shorter chain PFAS have lower GAC loading capacities and faster breakthrough times, but could be effectively treated if changeout frequency is increased. Figure 12-1 provides an example of removal curves and breakthrough information for a number of PFAS performed at a specific influent concentration based on vendor-supplied column studies.



**Figure 12-1. Example GAC removal curves at specific influent concentration (15-minute empty bed contact time).**

*Source: Used with permission from Calgon Carbon Corporation.*

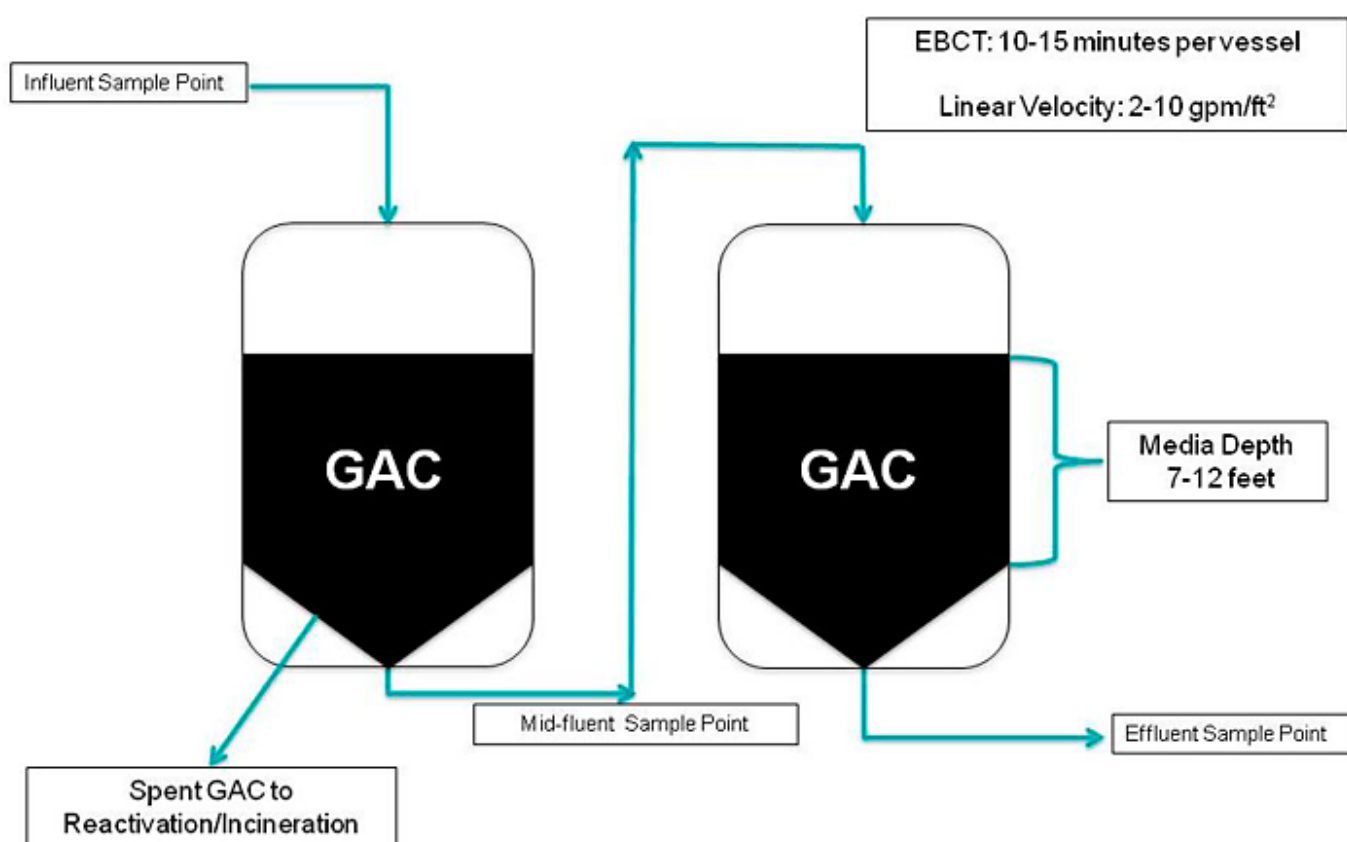
More studies are needed to confirm GAC treatment effectiveness for shorter chain PFAS or to identify complementary technologies/materials to supplement GAC removal capability. This may include studying the influence on sorption site competition from PFAS precursors that are often not quantified during the GAC system design. Recent accelerated column tests by vendors have shown the successful removal of a variety of PFAS, including the butyl (C4), pentyl (C5), and hexyl (C6) compounds (Appleman et al. 2013; Dickenson 2016; Brewer 2017). Functional groups also impact the ability of GAC to adsorb PFAS compounds. Compounds with sulfonate and sulfonamide groups are more readily adsorbed than those with carboxylates (Appleman et al. 2013; Dickenson 2016). Studies currently in the developmental stage involve the use of other materials that can modify GAC surfaces to improve removal capabilities. Mixtures of powdered activated carbon, kaolinite, and amorphous hydroxide have been tested at the bench- and pilot-scale and have shown high removal rates for shorter chain PFAS in raw AFFF-impacted groundwater (Chiang 2017; Kempisty, Xing, and Racz 2018).

Most GAC full-scale treatment system case studies to date are based on treatment of PFOA and PFOS in the impacted drinking water sources. As such, limited information is available regarding the treatment of other PFAS. The full-scale drinking water systems demonstrate that PFOA and PFOS can be removed to below analytical detection limits until breakthrough occurs. More information is available in Table 12-1 posted as a separate PDF. Treatment of groundwater impacted with PFAS from an AFFF release area contaminated with PFAS such as fire training areas (FTAs) may require complex pretreatment and more frequent change-outs (higher influent concentrations compared to influent for drinking water treatment systems) and higher operation and maintenance (O&M) costs.

**Design/Operating Considerations:** Laboratory treatability tests (for example, rapid small-scale column testing (RSSCT) and accelerated column test (ACT)) are useful for evaluating treatability and determining initial design parameters. Larger scale pilot demonstrations are recommended to establish site-specific design parameters such as adsorption bed depth; GAC consumption rate to meet a given treatment objective; empty bed contact times (EBCTs); projections of breakthrough (based on bed volumes treated); and corresponding change-out frequency/costs. Column studies can also be used to compare loading capacity/breakthrough performance for different types of GAC (for example, different materials, preparation methods, and pore size distributions) offered by various vendors. These studies should always use site water to

ensure that the effects of site-specific geochemical characteristics are assessed. Alternative analytical screening methods, for example, total oxidizable precursor (TOP) Assay (Section 11.2.2.2) and particle induced gamma ray emission (PIGE) (Section 11.2.2.3), can be used to better estimate potential total mass load during the GAC remedial design phase. Field performance of GAC systems often varies significantly from that predicted in the RSSCT and other bench tests. Proper monitoring is critical to demonstrate that the desired performance is being achieved, especially at system start-up and following media change-out events.

Temporary and permanent GAC systems can be rapidly deployed and require minimal operator attention, if intensive pretreatment is not needed. The GAC media are placed in packed-bed flow-through vessels generally operated in series (lead-lag configuration). EBCTs of 10-15 minutes per vessel are typical. PFAS breakthrough is monitored by testing the water, at a minimum, between the lead and lag vessels. Additional sampling ports can be added (for example, at 25%, 50%, and 75% of the depth of the media). When breakthrough exceeds identified change-out criteria, the lead bed is taken offline and the spent GAC is removed and replaced with either new or reactivated GAC. The spent media are disposed off site by thermal destruction or can be thermally reactivated for reuse. Treatment can be continuous if the lag bed is used as the lead bed while the media in the latter are changed out. Figure 12-2 depicts a simple process flow diagram for a GAC treatment system.



**Figure 12-2. Typical GAC treatment system process flow diagram.**

*Source: Used with permission from Calgon Carbon Corporation.*

Various GAC base materials (for example, bituminous coal, lignite coal, coconut shells) can be used for adsorption, though bituminous coal-based GAC has been used for the majority of existing sorption treatment systems for PFAS and current data show that bituminous-based products are more effective for PFAS removal (McNamara et al. 2018; Westreich et al. 2018). Specialized GAC formulations and coconut-based GAC can also be effective. Media selection and life cycle cost will depend upon a number of factors, including PFAS and co-contaminant concentrations, media availability, and pricing.

GAC treatment applications will evolve as analytical methods improve and regulatory concerns encompass an increasing number of PFAS. Shorter chain PFAS exhibit faster breakthrough times as mass loading rates increase (Appleman et al. 2013), so particular attention needs to be given to these compounds if their removal is required. Alternative design optimization approaches or use of other technologies in combination with GAC (for example, ion exchange (IX) resins discussed in Section 12.2.1.2) can address high O&M costs that can be incurred for GAC treatment involving high influent PFAS concentrations, especially if shorter chain PFAS must be removed. As discussed in Section 12.2.1.2, specialty single-

use and regenerable IX resins have been developed that have higher loading capacities for shorter chain PFAS. GAC and IX can also be used in series to optimize removal capacity and minimize O&M costs, generally with GAC ahead of IX to remove non-PFAS organics and longer carbon chain PFAS, followed by IX to remove the shorter carbon chain PFAS. This approach has been implemented in the field and is presented in a case study in Section 15.2.2.1.

Spent GAC that contains PFAS can be thermally reactivated and reused, which may result in a lower cost media replacement option versus new GAC. However, some regulatory agencies may not allow the use of reactivated GAC for drinking water systems. NSF/ANSI standards require that the use of reactivated GAC for drinking water systems involve only media generated by the treatment system owner/operator and cannot include a mixture of GAC that originated from other sources. The management of spent media should be planned during the life cycle assessment phase and be documented as the treatment system is executed. Commercial facilities are available for thermal reactivation of spent GAC, which currently are not available for other sorption media and can offer a potential life cycle cost benefit for spent media disposal. Based on vendor feedback (Mimna 2017), commercial thermal GAC reactivation is performed at higher operating temperatures than steam or nitrogen regeneration systems, and may be capable of complete desorption and destruction of PFAS from spent GAC (Watanabe et al. 2016; Yamada et al. 2005). However, similar to incineration, additional studies are needed to investigate the fate of PFAS in the GAC reactivation process.

**Sustainability:** GAC ex situ PFAS water treatment systems have unique sustainability considerations as well as considerations in common with other ex situ PFAS sorption media water treatment systems (treatment complex construction, utilities, water collection and pumping, and discharge infrastructure). Major sustainability considerations unique to GAC systems are associated with:

- raw material collection and transportation
- GAC manufacturing and transportation
- larger media vessels relative to IX due to longer EBCTs
- larger treatment complex size due to larger vessels
- spent media transportation followed by reactivation, destruction, or disposal.

Multiple resources are available for performing sustainability assessments for sorption remedial designs (Amini et al. 2015; Choe et al. 2013; Choe et al. 2015; Dominguez-Ramos et al. 2014; Favara et al. 2016; Maul et al. 2014; Rahman et al. 2014; Ras and von Blottnitz 2012).

### 12.2.1.2 Ion Exchange Resin

**Treatment Description:** IX is an effective sorbent for other contaminants and has historically been used for a variety of water treatment applications (for example, nitrate, perchlorate, arsenic). To date, IX for PFAS removal from water is limited to ex situ applications.

IX resin options for removal of PFAS include single-use and regenerable resins. Single-use resins are used until breakthrough occurs at a pre-established threshold and are then removed from the vessel and currently disposed of by high temperature incineration or by landfilling, where permitted. Regenerable resins are used until breakthrough but are then regenerated on site using a regenerant solution capable of returning the full exchange capacity to the resin. Temporary and permanent IX systems can be rapidly deployed.

#### **Related Ongoing Research Funded by SERDP (ER) and Water Research Foundation (WRF):**

- ER18-1027 Ex Situ Treatment of PFAS Contaminated Groundwater Using Ion Exchange with Regeneration
- ER18-1063 Regenerable Resin Sorbent Technologies with Regenerant Solution Recycling for Sustainable Treatment of PFASs
- ER 18-5015 Removal and Destruction of PFAS and Co-Contaminants from Groundwater via Groundwater Extraction and Treatment with Ion-Exchange Media, and On-site Regeneration, Distillation, and Plasma Destruction
- ER 18-1306 Combined In Situ/Ex Situ Treatment Train for Remediation of Per- and Polyfluoroalkyl Substance (PFAS) Contaminated Groundwater
- ER18-5053: Evaluation and Life Cycle Comparison of Ex-Situ Treatment Technologies for Poly- and Perfluoroalkyl Substances in Groundwater
- WRF 4913: Investigation of Treatment Alternatives for Short Chain PFAS

**Treatment Mechanism:** Removal of PFAS by IX is a physical mass transfer process from the aqueous phase onto solid



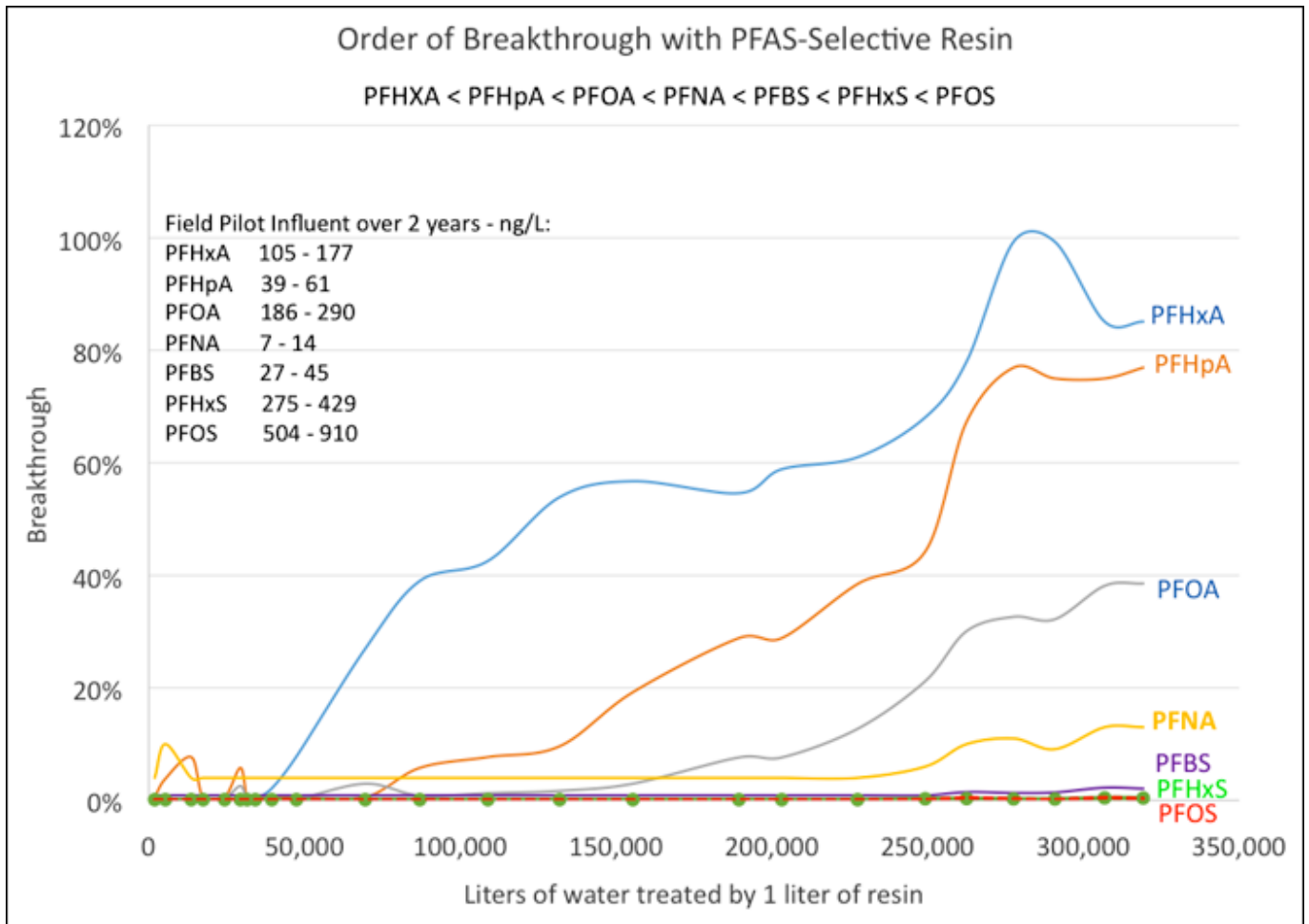
media that does not involve any form of chemical degradation or transformation. IX resins with positively charged functional groups can readily remove negatively charged PFAS compounds from water by forming ionic bonds (the sulfonic and carboxylic acid heads of PFOS and PFOA are negatively charged at the typical range of pH values found in natural water). Simultaneously, the hydrophobic end of the PFAS structures can adsorb onto the hydrophobic surfaces of the IX resins. This dual removal mechanism can exhibit higher selectivity versus other sorption media that function largely by adsorption alone.

**State of Development:** Ion exchange technology has been used since the late 1930s for common water treatment processes like softening, demineralization, and selective contaminant removal. The development and use of selective resins for PFAS removal is relatively new but already well established. As of 2019, a limited number of regenerable IX systems have been installed in full-scale applications after successful pilot testing. Collection of data on longer term treatment and on-site regeneration of the IX resin is ongoing at a case study site (Section 15.2.2.2). In general, the removal capacity of the single-use resin is higher than that of regenerable resin, and single-use resin can be more fully exhausted in a lead-lag vessel configuration than regenerable resin. The relative efficiency of regenerable and single-use resins depends upon PFAS and co-contaminant influent concentrations and treatment goals.

**Effectiveness:** Selective IX has been demonstrated to reduce concentrations for a broad suite of PFAS at the bench and field scale for influent concentrations as high as 100s of parts per billion (ppb) total PFAS to below analytical detection limits in effluent (Kothawala et al. 2017; McCleaf et al. 2017; Woodard, Berry, and Newman 2017). The affinity of such resin for common subgroups of PFAS generally follows the order PFSA > PFCA. Within each subgroup, affinity increases with increasing carbon chain length, and are not necessarily sequential (that is, longer chain PFCA may be adsorbed better than shorter chain PFSA).

In general, IX resin systems being used for PFAS removal are not installed with the intention of removing co-contaminants. Co-contaminants (including organic and inorganic compounds) may significantly reduce the removal capacity of IX for PFAS, although this depends on the selectivity of the IX resin. Because of the variability in resin behavior, as well as groundwater chemistry, influent characterization is needed to assess potential pretreatment options to remove co-contaminants. Pretreatment is necessary to preserve resin capacity for PFAS removal, particularly in the context of remediation where complex co-contaminant chemistry is expected. Pretreatment needs for drinking water applications may be simpler or not required.

Single-use PFAS-selective IX resins are well-suited to treat low-concentration PFAS such as is typically encountered in potable water treatment systems, where media change-out would be infrequent. Figure 12-3 provides an example of removal curves and breakthrough information for a number of PFAS at the specified influent concentrations (in the legend) based on vendor-supplied data for a full-scale single-use system.



**Figure 12-3. Example of IX removal curves at specific influent concentrations (2.5-minute EBCT).**

*Source: Used with permission from Purolite Corporation.*

Regenerable resins are better suited for removal of higher concentration PFAS where the savings realized from reusing the treatment media outweighs the cost of frequent replacement of nonregenerable media. Depending on the treated water discharge goals, evaluation of regenerable resin could be warranted once influent concentrations exceed 10 ppb total PFAS, such as would be encountered in groundwater remediation at or near PFAS release areas. Regenerable resins can be more efficient for treating higher ppb influent levels of PFAS where the cost of the regeneration system may pay for itself over time as compared to disposal and replacement cost for single-use resin. An example of typical breakthrough curves for regenerable resin system is shown in Figure 12-4. On the graph the y-axis is sample concentration/original concentration ( $C/C_0$ ), also note the influent PFAS concentrations (in the legend) in Figure 12-4 are higher (reported in ppb) than presented in Figure 12-3 (reported in ppt). Additional details on a regenerable resin system are provided in a case study in Section 15.2.2.2. The cost effectiveness for regenerable resin systems increases significantly when a central regeneration facility can be shared amongst multiple PFAS removal systems. The application of single-use versus regenerable resins must be evaluated on a site-specific basis.

Example Breakthrough Characteristics  
 Regenerable IX Media - 2.5 min EBCT; Total PFAS ~ 90 ppb

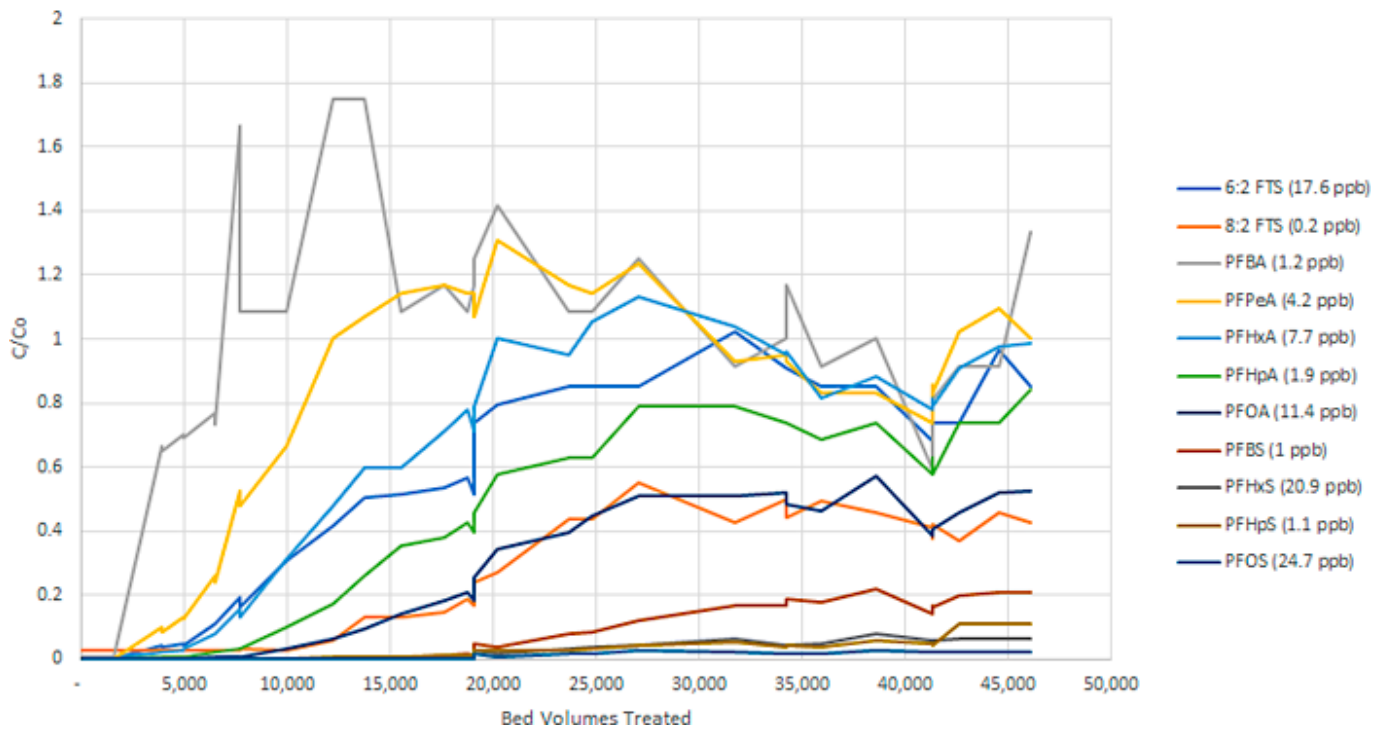
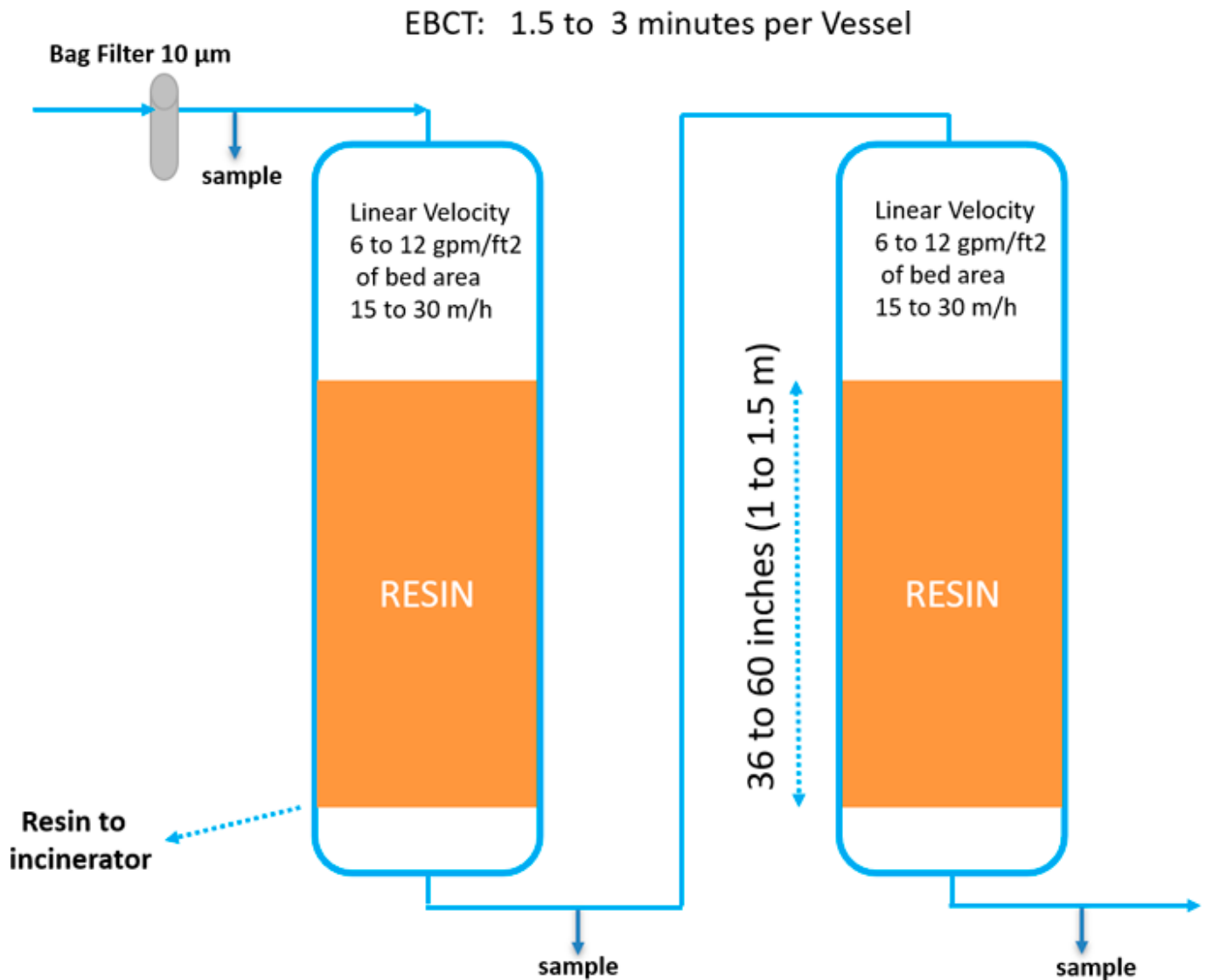


Figure 12-4. Example of regenerable IX removal curves at specific influent concentrations (2.5-minute EBCT).

Source: Used with permission from ECT2.

**Design/Operating Considerations:** IX treatment systems are configured similarly to GAC systems. Refer to Section 12.2.1 for a description of GAC systems that also applies to IX systems. Figure 12-5 depicts a simple process flow diagram for a single-use IX treatment system.



**Figure 12-5. Single-use IX process flow diagram.**

*Source: Used with permission from Puroilite Corporation.*

IX technology features include:

- high selectivity—single-use IX resins can be used to selectively target more mobile PFAS (for example, shorter chain PFAS), although results will depend on water chemistry
- greater capacity, faster kinetics, and lower EBCT compared with GAC, resulting in smaller vessel size and potentially less frequent media change-out
- ability to consistently reduce PFAS to low ppt levels
- simultaneous removal of ionic co-contaminants
- for regenerable resins, the possibility of reduced operating and disposal costs as compared to single-use IX.

Selective IX requires a relatively short EBCT of 1.5–5 minutes per vessel of resin (Boodoo 2017), hence smaller resin volumes and smaller, less costly treatment vessels for a specific application. Selective IX resins have shown high operating capacities when removing trace levels of PFAS (for example, 200,000–300,000 bed volumes; refer to Figure 12-5), resulting in fewer change-outs of spent IX resin and reduced O&M costs.

Selective IX resins show much higher selectivity for PFAS compounds than for common anions in water such as sulfate ( $\text{SO}_4^{2-}$ ), nitrate ( $\text{NO}_3^-$ ), chloride ( $\text{Cl}^-$ ), and bicarbonate ( $\text{HCO}_3^-$ ). However, these common anions are generally present in water at about three orders of magnitude higher than PFAS and will be the main competitors for the ion exchange sites on the resin. As such, they will largely determine the operating capacity of such resins. The choice between single-use and regenerable resins will in part be determined by the expected service period before the resin must be either replaced (single-use) or regenerated.

Regenerable IX resin can be reused for many years if protected from contact with strong oxidizing agents, foulants, and chemical/mechanical stresses. To date, insufficient operating data are available for PFAS regenerable systems to understand the long-term durability of regenerable resin because the first regenerable IX systems were installed in 2018. IX regeneration is a chemical process. The only field-demonstrated regeneration method capable of fully restoring PFAS removal capacity is a proprietary process using a solvent-brine solution, where the brine dislodges the ionic head of the PFAS molecule and the solvent desorbs the fluorinated carbon chain (or “tail”) from the IX resin (Woodard, Berry, and Newman 2017; Amec Foster Wheeler 2017). For a regenerable IX system, it is possible to concentrate the regenerant solution and reuse it by distillation (Nickelsen and Woodard 2017). The distillate residue then contains a concentrated PFAS waste that can be super-loaded onto specialized resin to create a small volume of solid waste that can be managed by off-site disposal or potentially through on-site destruction using other technologies currently under development and discussed in Table 12-1 (provided as separate PDF) (for example, plasma or electrochemical destruction).

**Sustainability:** Resin ex situ PFAS water treatment systems have unique sustainability considerations in addition to those shared with other ex situ PFAS sorption media water treatment systems. Major sustainability costs unique to resin systems are associated with;

- raw material collection and transportation
- resin manufacturing and transportation
- regeneration of multiple-use resin
- generation, use, and disposal or destruction of regeneration residuals
- spent single-use and, eventually, multiple-use media transportation followed by destruction or disposal.

### 12.2.2 Reverse Osmosis (RO)

RO is a technology used to remove a large majority of contaminants (including PFAS) from water by pushing the water under pressure through a semipermeable membrane as described below. The most common membrane module configuration is spiral-wound, which consists of flat sheet membrane material wrapped around a central collection tube.

**Treatment Description:** RO membranes are effective in removing most organic and inorganic compounds from water solutions. In recent years, new polymer chemistry and manufacturing processes have improved efficiency, lowering operating pressures and reducing costs. As a result, RO membranes are increasingly used by industry to concentrate or remove chemicals. RO is commonly used around the world in household drinking water purification systems, the production of bottled mineral water, self-contained water purification units (for example, for branches of the U.S. military), and industrial applications (for example, water supply to cooling towers, boilers, and deionized water). The largest application of RO is in desalination.

**Treatment Mechanism:** RO removes compounds from water solutions by passing pressurized water across a semipermeable membrane. Treated water (permeate) passes through the membrane and the rejected water (concentrate) is collected for disposal or discharge, depending on the nature of the compounds present.

**State of Development:** RO has been studied in bench-scale studies and pilot plants for wastewater and drinking water applications, offering the opportunity to compare both treatments operating simultaneously (Tang et al. 2006; Tang et al. 2007; Flores 2013; Glover, Quiñones, and Dickenson 2018; Dickenson 2016; Merino et al. 2016; Appleman 2014; Snyder 2007). This allows for an understanding of the effectiveness of traditional drinking and wastewater treatment methods alongside PFAS-specific technologies.

**Effectiveness:** Pretreatment is important when working with RO membranes. Membranes are highly susceptible to fouling (loss of production capacity) because some accumulated material cannot be removed from the membrane surface. Therefore, effective pretreatment to remove suspended solids is a necessity for any RO system. Pretreatment technologies would be specific to the RO feedwater quality.

RO removal of PFAS from various waters (for example, semiconductor wastewater, drinking water, surface water, and reclaimed water) has been studied and several studies have combined RO with nanofiltration (NF). NF is discussed in Section 12.4.3. PFOS removal > 99% was achieved using four different types of membranes over a wide range of feed concentrations (0.5–1,500 ppm [mg/L]) (Tang et al. 2006). Another study by Tang et al. (2007) tested five RO and three NF membranes at feed concentrations of 10 ppm PFOS over 4 days. The PFOS rejection and permeate flux performances were > 99% for RO and 90–99% for NF (note that 99.9993% removal would be required to reduce 10 ppm to the USEPA health advisory of 70 ppt). The use of RO and NF as advanced drinking water treatments is still limited, but both technologies have

been shown to be successful for the removal of longer chain (> C5) PFAAs (Loi-Brügger et al. 2008; Tang et al. 2006).

Thompson et al. (2011) studied the fate of perfluorinated sulfonates (PFSAs) and carboxylic acids (PFCAs) in two water reclamation plants that further treat water from wastewater treatment plants (WWTPs) in Australia. One plant (Plant A) used adsorption and filtration methods alongside ozonation; the other (Plant B) used membrane processes and an advanced oxidation process to produce purified recycled water. At both facilities, PFOS, perfluorohexane sulfonate (PFHxS), perfluorohexanoate (PFHxA), and PFOA were the most frequently detected PFAS. Comparing the two reclamation facilities, Plant A showed some removal during the adsorption/filtration stages. Overall, however, Plant A failed to completely remove PFOS and the PFCAs shorter than PFNA in chain length. All PFAS present were removed by RO at Plant B from the finished water to concentrations below detection and reporting limits (0.4–1.5 ng/L).

**Design/Operating Considerations:** This section refers to design and operating considerations for both RO and NF systems. In the process of planning and implementing a membrane filtration system, there are several important issues that affect system design and operation and could impact system performance and thus PFAS removal. These issues include membrane flux, water quality, and temperature.

- **Membrane Flux:** One of the major challenges in the application of membrane technology is fouling (significant flux loss due to continuous accumulation of colloidal and organic matter, precipitation of inorganic salts, and/or microbial growth). There are several ways to avoid fouling: (1) changing operating conditions, (2) modifying the membrane, and (3) modifying the feed by adding antifoulants prior to filtration system (pretreatment) (Roux et al. 2005). Adequate pretreatment and appropriate membrane selection can slow the fouling rate, but the membrane cleaning is an essential step in maintaining the performance of the membrane process. Membrane replacement is a necessary part of plant operation to maintain the quality of the produced water (Abdul-Kareem Al-Sofi 2001). Although there are a number of cleaning techniques, such as physical or chemical or a combination of both, only the chemical cleaning methods are widely used by NF and RO industries for membrane cleaning and regeneration. Spent cleaning solution may contain PFAS and would need to be managed properly.
- **Water Quality:** Because water quality can have a significant impact on membrane flux, feedwater quality is also a primary design consideration for membrane filtration systems. Poorer water quality will require lower fluxes, which in turn increase the necessary membrane area and required number of modules, adding to both the cost and the size of the system. However, pretreatment can often improve feedwater quality at a lower cost than additional membrane area.
- **Temperature:** Like other water quality parameters such as turbidity and total dissolved solids (TDS) (for NF/RO systems), the temperature of the feedwater also affects the flux of a membrane filtration system. Water becomes increasingly viscous at lower temperatures; thus, lower temperatures reduce the flux across the membrane at constant transmembrane pressure or alternatively require an increase in pressure to maintain constant flux. Because rejection decreases as membrane pores expand at higher temperatures, more leakage of PFAS across the membrane could occur at higher operating temperatures.

**Sustainability:** The environmental footprint for this technology includes energy source and consumption during treatment system operation, as well as manufacturing/disposal of pretreatment/treatment media (examples may include solids from upstream precipitation/coagulation or microfiltration, used cartridge filters, and worn RO membrane modules) and cleaning solutions to maintain the membrane. RO requires power for high-pressure pumps and the management of concentrate, which can be energy-intensive.

An issue inherent to contaminant removal by membrane processes is the disposal of the PFAS-enriched concentrate, which must be carefully considered. Development of effective treatment methods for the concentrate entails evaluating significant parameters, such as volume generated, concentration, characteristics of the feedwater, and operational conditions, and using well-verified analytical methods to detect trace amounts of contaminants. Recycling concentrate to main treatment units is not the only option, and further research on integrated treatment systems must be performed (Joo and Tansel 2015). The reject stream will contain PFAS-enriched concentrate, which needs to be appropriately managed through treatment, permitted discharge, or disposal.

### 12.2.3 Drinking Water Applications

Remedial actions for PFAS-impacted drinking water from private wells and municipal supplies can include providing alternative drinking water sources, such as bottled water, new nonimpacted source wells or surface water, point of entry

(POE) treatment (also referred to as POET), and point of use (POU) treatment. POE treats water as it enters a home or building (for example, immediately after a pressure tank for a private well system) and POU treats water at one or more specific locations (for example, at a kitchen faucet where water is typically directly ingested or used for cooking). POE systems provide “whole supply” treatment while POU provides selected usage point treatment.

NSF International has developed a testing method and protocol, P473: Drinking Water Treatment Units-PFOA and PFOS, to verify the ability of a water treatment device to reduce PFOA and PFOS to achieve the USEPA health advisory levels of 70 ng/L (NSF International 2018). This method does not evaluate the removal of other PFAS or other organics, metals, and nonorganic compounds that also may adversely impact water supplies. Current systems with this certification are mainly small-scale POU systems such as sink faucet filters, refrigerator water filters, and pour-through filters. It should be recognized that although this certification exists, it is not required. This means that other POU systems as well as POE systems (larger well head or large public-serving systems) may not be certified under NSF P473 but may be acceptable for treatment of PFOA and PFOS. Public serving system components are required to be certified through NSF 61, which certifies that they are acceptable for potable water use. Treatment for PFAS in these systems typically uses adsorbents, GAC (Section 12.2.1.1) or IX (Section 12.2.1.2) or RO (Section 12.2.2).

## 12.3 Field-Implemented Solids Treatment Technologies

Field-implemented technologies are those that have been implemented in the field by multiple parties at multiple sites and the results have been documented well in the peer-reviewed literature. The technologies in this section may be applied to a variety of PFAS-impacted media, including soil, sediments, or sludge. Site-specific evaluation is always needed to identify the best technology alternative for a given treatment scenario. As with water treatment, solids treatment can be performed ex situ (for example, excavation or dredging) or in situ (for example, injection or reactive capping). At present, field-implemented solids treatment has been performed almost entirely ex situ. There are currently two known field-implemented technologies for treating soil contaminated with PFAS: sorption/stabilization and excavation/disposal.

### 12.3.1 Sorption and Stabilization

**Treatment Description:** Amendments are added to the soil and sediment to reduce the potential for PFAS to mobilize from soil and sediment to groundwater and surface water. For sorption purposes, PFAS-adsorbing materials (for example, activated carbon) can be applied through in situ soil mixing or ex situ stabilization (for example, pug mill mixing) to reduce the leachability of PFAS from contaminated soil/sediment through physical and/or chemical bonding.

Sorption and stabilization (considered “immobilization” or “chemical fixation” technologies) is a relatively quick, simple, and low-cost (relative to off-site disposal) way to reduce ongoing PFAS contamination transport to waterways and groundwater from source zones. The main disadvantage is that these technologies do not destroy the contaminants, but rather bind or immobilize them. For some amendments, established test methods have shown the binding to be stable over the long-term (see below).

**Treatment Mechanism:** Amendments adsorb or stabilize PFAS to reduce their release from soil. This occurs primarily through electrostatic interactions between the negative charge on the PFAS functional group and the positive charges on the sorbent and hydrophobic interactions between the amendment and the electronegative carbon-fluorine chain on the PFAS. Typical amendments that have been demonstrated in the field include activated carbon and composite materials such as a blend of aluminum hydroxide, kaolin, and carbon specifically designed to treat anionic, cationic, and zwitterionic long- and short-chain PFAS (Kempisty, Xing, and Racz 2018).

**State of Development:** Sorption and stabilization techniques using carbon-based amendments are considered field-implemented technologies. Various amendments have been applied to soil/sediment both in situ and ex situ. Different delivery methods for amendments, such as injection or in situ mixing (ISM), may provide different results depending on geology and objectives. Carbon amendments have been modified to enhance their sorption of PFAS. One patented amendment consists of activated carbon enhanced with amorphous aluminum hydroxide, kaolin clay, and other proprietary additives (USEPA 2017p). This amendment has been used to immobilize PFAS-impacted soil at field-scale in Australia and Europe and at laboratory-scale in the United States. In 2015, a large-scale project involved the ex situ treatment of 900 tons of PFAS-impacted soil from an airport site in Australia (Stewart 2017).

**Effectiveness:** Carbon- and mineral-based sorption and stabilization techniques vary in their effectiveness according to site conditions, PFAS types, and mixing approaches. The PFAS characteristic that determines sorption is length of carbon-fluorine chain, with longer chains having increased sorption (Xiao, Ulrich, et al. 2017).

Some specifically designed amendments have the ability to bind short- and long-chain compounds using different mechanisms (Stewart, Lawrence and Kirk 2016). The carbon component binds to the hydrophobic backbone of longer chain PFAS, while the negatively charged functional groups of the PFAS anions bind electrostatically to the positively charged surfaces of aluminum hydroxide. Furthermore, the amorphous form of aluminum hydroxide presents a relatively high surface area of positive charges, and the pKa of around 9.1 means that these surfaces remain positively charged over a wide environmental pH range (~pH 3 to pH 9.1). The kaolin component contains some negatively charged surfaces that theoretically have the ability to sorb PFAS cations and zwitterions (Stewart, Lawrence and Kirk 2016; Kempisty, Xing, and Racz 2018). However, standard analytical methods do not quantify cations and zwitterions, and actual field performance on these PFAS compounds is generally undemonstrated.

The charge on the PFAS compounds affects sorption (for example, cations sorb more readily than zwitterions and anions). Aquifer and soil chemistry also affect the sorptive ability of PFAS onto the amendments. High organic content in soil can reduce effectiveness (NGWA 2017). Low pH, the presence of polyvalent cations in the soil, or treatment amendment also increases sorption, retardation, and metals precipitation. An independent study at the University of Adelaide, Australia, showed that environmental ranges of pH and ionic strength did not adversely affect the binding of a specialized amendment to PFOA (Lath et al. 2018). Co-contaminants also play a role in the effectiveness of PFAS sorption. A recent review article (Li, Oliver, and Kookana 2018) showed that the organic carbon component of natural soils and sediments plays less of a role in PFAS sorption than once thought; the mineral component of the soil/sediment and the pH conditions play a more important role in PFAS adsorption.

A patented amendment consisting of activated carbon blended with amorphous aluminum hydroxide, kaolin clay, and other proprietary additives has been field-implemented and was used to successfully immobilize 28 PFAS analytes in more than 14 different contaminated soils in a lab-based trial from fire training grounds across Australia (Stewart and MacFarland 2017). At average addition rates of around 2.5-5%, PFOS and PFOA in soil leachates were reduced by 95% to >99% following a 48-hour treatment process.

Sorption and stabilization do not destroy PFAS, and these technologies have not been implemented for enough time to demonstrate long-term stability of amendments for PFAS. However, in independent studies, the Multiple Extraction Procedure (MEP; USEPA Method 1320) has been used to successfully demonstrate the simulated long-term stability of immobilized PFAS in amended soils (Stewart and MacFarland 2017). The MEP is designed to simulate 1,000 years of acid rain conditions in an improperly designed sanitary landfill. In another independent study, the accumulation of PFAS in earthworms and plants was reduced by >90% in soil treated by carbon-based immobilization compared to untreated soils (Bräunig 2016; Kempisty, Xing, and Racz 2018). The amended soil can be mixed with concrete and other stabilizers to improve performance; however, the concrete increases pH and may influence binder performance (Ross et al. 2018).

**Design/Operating Considerations:** To establish design and application parameters for implementation of sorption and stabilization technology in soils, it is necessary to perform site-specific laboratory and/or pilot treatability tests. Information and quantity of amendment material required (dose rates) for materials can be determined with either simple beaker or jar-type lab treatability tests. These studies are most applicable if site soils and water are used to ensure that the effects of site-specific geochemical characteristics are assessed. Once the dose of amendment material is determined, field pilot studies are often conducted to validate lab data and design for full-scale implementation.

For in situ soil mixing, the amendments are added to soils at the design dose or application rate under controlled conditions with specific types of equipment designed to perform mixing. In situ soil mixing can be performed on soils in place with a wide range of standard construction equipment, including excavators, large diameter augers, and in situ blenders. In addition, with in situ soil mixing, soils can be removed and mixed in equipment such as a pug mill or other similar mixing systems.

After implementation of in situ soil mixing, it is important to perform postconstruction quality assurance and quality control to verify design endpoints. This may include leachability (Toxicity Characteristic Leaching Procedure (TCLP), USEPA Method 1311; Synthetic Precipitation Leaching Procedure (SPLP), USEPA Method 1312; or Multiple Extraction Procedure (MEP), USEPA Method 1320), hydraulic conductivity (ASTM D5084), and strength tests (various).

**Sustainability:** The environmental footprint for sorption and stabilization includes emissions from earthwork equipment, manufacturing, and transporting amendment material. This footprint can be smaller than excavation if the treated soil is reused on site. Community impacts include hindrance of redevelopment due to land use restrictions. However, if the land use is not expected to change, such as on active government-owned aviation or military sites, stabilization with



amendments and reuse of the soil may be a viable and cost-effective approach.

Resources are available for performing a sustainability assessment for sorption and stabilization remedial design, relating to other contaminants (Goldenberg and Reddy 2014; Hou et al. 2016; Kuykendall and McMullan 2014).

### 12.3.2 Excavation and Disposal

**Treatment Description:** This approach involves removing contaminated soil/sediment for off-site disposal. The contaminated material is disposed of at a permitted landfill, then the excavated area is filled with clean backfill. Treatment with stabilizing agents can reduce PFAS leachability from excavated soils and should be considered prior to landfilling. Sometimes, excavated soil/sediment can be treated on site using the sorption and stability approach or thermal treatment (as discussed in the next section) followed by soil reuse or off-site disposal.

**Treatment Mechanism:** This method is intended to remove PFAS from the source location. Transportation and disposal in a lined landfill is an option for excavated soil; however, leachate management should be a consideration at these facilities.

**Soil Containment**The focus of this section is to summarize the state of various remediation technologies. Containment is not listed as a specific technology but is commonly utilized for other contaminants and may be suitable for PFAS depending on site-specific conditions.

Containment could include capping to prevent infiltration or exposure, construction of a slurry wall (or similar isolation barrier), addition of sorptive media to prevent migration, or landfill disposal (discussed further in this section and in Section 2.6.3.1). Containment options will depend on site-specific considerations, nature of PFAS materials, and local regulatory requirements.

**State of Development:** Soil excavation and disposal is a well-demonstrated, proven technology. However, PFAS have been reported in landfill leachate (Lang et al. 2017), although the source for PFAS in leachate may be consumer product waste containing fluorochemicals. In some states, the leachate is not analyzed or regulated for PFAS. Disposal of PFAS waste to landfills potentially adds to the PFAS contaminant load in the landfill leachate. Some nonhazardous waste landfills do not accept PFAS waste.

**Effectiveness:** Excavation and disposal of PFAS-contaminated soil effectively removes a source area that may otherwise serve as a continuing source of groundwater contamination but does not result in destruction of the PFAS unless the soil is incinerated. Disposal of PFAS-impacted soils or wastes into unlined landfills should be avoided as unlined or improperly lined landfills can be sources of PFAS to the environment.

**Design/Operating Considerations:** Difficulties in finding landfills willing to accept the waste, coupled with rapidly changing regulations regarding whether PFAS are hazardous or not, make this option less straightforward than one would expect. Case-by-case inquiries to landfill facility owners is likely the best course of action. Overall, issues related to disposal of PFAS in landfills are similar to issues commonly encountered with other contaminants. See Section 2.6.3, Solid Waste Management, for additional discussion on this topic.

**Sustainability:** The environmental footprint for excavation and disposal includes earth-moving equipment emissions, transporting contaminated soil and backfill, and resource extraction (such as borrow area fill material) of backfill material. Incineration of the contaminated soil and investigation-derived waste (IDW) is energy-intensive and remains a topic of current study to better understand the fate of PFAS, see Section 12.4.

Truck hauling traffic affects the local community by creating additional traffic congestion, noise, and particulate matter emissions. The cost for this approach is high, but the solution is generally permanent and for smaller treatment volumes may be cost-competitive. Guidance is available for performing a sustainability assessment for an excavation and disposal remedial design (Cappuyns and Kessen 2013; Goldenberg and Reddy 2014; Söderqvist et al. 2015; Song et al. 2018).

## 12.4 Incineration

**Treatment Description:** Incineration is defined as destruction (mineralization) of chemicals using heat. Heat is applied directly to the PFAS-contaminated solids (soil/sediment/spent adsorbents/waste) or liquids (water/wastewater/leachate/chemicals). Vaporized combustion products can be captured (precipitation, wet scrubbing)

and/or further oxidized at elevated temperature.

**State of Development:** Incineration is a mature technology that has been used for various solid and liquid wastes.

**Effectiveness:** Incineration is one of only a few technologies that can potentially destroy PFAS. However, at the time of publication, this is an active area of research to evaluate effective destruction temperatures and treatment time, the potential to generate products of incomplete combustion, stack gas analyses, deposition onto land, and other risk factors.

**Design/Operating Considerations:** Waste incinerators are fixed facilities. Federal and state permits dictate the materials processed, core incinerator operations (for example, temperature and time, turbulence), and control of process air, liquid, and solid wastes. Permit and design/construction similarities reduce the operational and performance differences between individual incinerators.

When considering waste disposal options, transportation costs, energy costs, regulatory approvals, and final disposition of process waste residues should be evaluated, as these differ among incineration facilities.

**Sustainability:** The environmental footprint for incineration includes transportation and supplemental fuel for the incineration process. Incineration of contaminated soil, liquid wastes, and IDW is energy-intensive and PFAS emissions, including potential PFAS combustion byproducts, from incinerators are currently not well understood (USEPA 2020e). Truck hauling traffic affects the local community by creating additional traffic congestion, noise, and particulate matter emissions. The cost for this approach is high, but the solution may be cost-competitive for smaller treatment volumes.

## 12.5 Limited Application and Developing Liquids Treatment Technologies

The treatment technologies presented in this document are provided in a hierarchy defined in Section 12.1, which is based on level of implementation and confidence derived from widespread, well documented implementation. The three development levels include field-implemented technologies, limited application technologies, and developing technologies. Both in situ and ex situ technologies are included. It is not always clear if a limited application or developing technology may be effective in situ, ex situ, or both; therefore, further distinction is not made in this section.

The field-implemented technologies described in the preceding sections have been applied at multiple sites and are well documented in the available literature. In addition to these well-demonstrated technologies, many technology approaches have been tested in academic and other research laboratories at the bench scale or have progressed as far as field pilot tests or limited field applications. These limited application technologies are briefly summarized Table 12-1 for liquids, Table 12-2 for solids (provided as a separate PDF), and appropriate references are provided. Additional information is provided in the following summary sections.

### 12.5.1 Sorption Summary

#### 12.5.1.1 In Situ Remediation with Colloidal Activated Carbon

Colloidal activated carbon (CAC) consists of colloidal-sized particles (2 microns diameter on average) in aqueous suspension (the consistency of black-colored water), which can flow into aquifer flux zones upon gravity-feed or low-pressure injection. After injection, CAC particles will attach strongly to the aquifer matrix, where they can act as passive sorbents for organic contaminants, including PFAS. This sorption mechanism is detailed in the Section 12.2.1. Due to the small size of the particles, the kinetics of PFAS sorption on colloidal carbon are much faster than can be achieved with GAC, resulting in higher removal efficiencies (Xiao, Ulrich, et al. 2017). The primary function of injectable CAC is to immobilize contaminants and prevent their further horizontal and vertical migration in groundwater, thereby eliminating the risk to downgradient receptors. By flowing CAC into the flux zones of an aquifer, contaminants moving through the aquifer, as well as those contaminants back-diffusing from lower permeability zones, are captured and taken out of solution.

CAC may be injected in situ using a grid pattern in source zones to immobilize contaminants, or it may be injected in a transect pattern perpendicular to the width of a plume to mitigate contaminant flux. Direct push or vertical wells can be used to inject CAC into the subsurface. The longevity will be dependent upon PFAS composition, rates of mass discharge, presence of co-contaminants, and groundwater geochemistry.

McGregor (2018) discussed the in situ injection of CAC at a site in central Canada to mitigate mass flux of PFOS and PFOA from the source zone. Fire training exercises were carried out at the site in the 1970s and 1980s. Prior to CAC injection,

PFOS and PFOA were measured in groundwater monitoring wells at concentrations up to 1,450 ng/L and 3,260 ng/L, respectively. Monitoring wells at the site were screened in a shallow, thin silty sand overburden unit at depths of approximately 5–10 feet below ground surface. CAC was injected into the source zone at low pressure through temporary wells installed using direct push technology. Postinjection core sampling indicated that CAC was measured at distances of up to approximately 15–20 feet from the injection wells.

Carey et al. (2019) performed modeling with respect to the above site to predict the theoretical longevity and performance of the CAC. The study noted that longevity of performance could be extended by increasing the CAC dose, increasing the thickness of the treatment zone perpendicular to flow, or by additional injection upon breakthrough.

### **12.5.1.2 Coated Sand**

Polymer-coated sand is an adsorbent material that has high affinity for organic contaminants. Cyclodextrin molecules are polymerized by a cross-linking agent and form inclusion complexes with many organics. The adsorbent material has two components: (a) polymer coat (active component that removes the contaminants) and (b) support base (inactive component); the combination of both provides an adsorbent with high selectivity and mechanical stability.

#### **Related Ongoing Research Funded by SERDP:**

- ER18-1652 Destruction of PFAS and Organic Co-Contaminants in Water and Soil Present in Investigation-Derived Waste at DoD Sites Using Novel Adsorbent and Ultrasound

The adsorbent showed similar performance in removing PFOA and PFOS as GAC, but one of the key features of this technology is the high regenerability of the adsorbent (filter) for reuse (Bhattarai, Manickavachagam, and Suri 2014). Another important feature of the technology is that it can remove other organic pollutants such as chlorinated solvents (for example, trichloroethene (TCE), perchloroethylene (PCE), hexavalent chromium, and others (Badruddoza, Bhattarai, and Suri 2017). Surface modification has been shown to improve the adsorption of PFOS (Zhou, Pan, and Zhang 2013) by using organic polymeric surfactants.

### **12.5.1.3 Zeolites/Clay Minerals (Natural or Surface-Modified)**

Zeolites are naturally occurring aluminosilicate compounds that are widely used in chemical separation and purification due to their high surface area and small uniform pore size among other properties (Tao et al. 2006). Zeolites are also being increasingly considered as a medium for the sorption of various pollutants, including cationic heavy metals, ammonium, and some volatile organic compounds, due to the aforementioned properties, as well as their high ion exchange capacity and low cost (Delkash, Ebrazi Bakhshayesh, and Kazemian 2015). Clay minerals, including natural and surface-modified (see below), are also used as adsorbents and are similar to zeolites in composition but have different crystalline or chemical structure.

Both zeolites and clay minerals can be used *ex situ* (that is, pump and treat) by being placed in packed-bed flow-through vessels or *in situ* via injection into aquifers. *In situ* applications are currently lacking in study or field application.

Zeolite and clay minerals use both ion exchange and adsorption mechanisms to remove PFAS from water. For removal of PFAS, these natural materials have been shown to be inferior to activated carbon or ion exchange resins (Du et al. 2014). However, synthetic processing of zeolite can create highly siliceous material (Baerlocher 2007) or can incorporate cationic surfactants into the surface structure (aka surface-modified zeolites-SMZ) (Jiménez-Castañeda and Medina 2017). One study indicated that engineered zeolites with a high Si/Al ratio were effective at adsorption of PFOS, presumably due to hydrophobic interactions rather than ion exchange (Ochoa-Herrera and Sierra-Alvarez 2008). Surface-modified clay materials are broadly considered organoclays.

Most available literature is limited to academic laboratory experiments (Ochoa-Herrera and Sierra-Alvarez 2008; Punyapalukul et al. 2013; Zhou, Pan, and Zhang 2013; Zhou et al. 2010). Du et al. (2014) and Arias Espana, Mallavarapu, and Naidu (2015) provided comprehensive literature reviews. Two modified clay-based adsorbent products are identified as being used in field pilots or small-scale field trial applications (Arias (Arias et al. 2013) et al. 2013; (Arias Espana, Mallavarapu, and Naidu 2015) to treat PFOA and/or PFOS.

High silica materials, such as H-form synthetic mordenite (HSM) and Y-form sodium zeolite (NA-Y80), and hydrotalcite clay provided adsorption capacities that were equivalent or exceeded powdered activated carbon (PAC). Surfactant-modified clays also performed as well as or better than PAC. It should be noted that none of these studies were conducted in flow-through column experiments, so applicability to *ex situ* treatment systems cannot be assessed. Arias Espana, Mallavarapu, and Naidu (2015) stated that organoclays, clay minerals, and highly siliceous materials have fast kinetics (0.4–3 hr to reach

equilibrium), making them suitable for remediation applications.

#### **12.5.1.4 Biochar**

Biochar is a hybrid word rooted in the words “biomass” and “charcoal.” Biochar is a carbon-rich porous solid that is synthesized by heating biomass, such as wood or manure, in a low oxygen environment (Ahmad et al. 2014). This material has primary applications for carbon sequestration, improvement of soil fertility, and most recently as an adsorbent for pollutant removal. Biochar is characterized to have high affinity for organic contaminants, which is dependent on both the pore structure and the surface functional groups of the biochar material (Guo et al. 2017).

Some of the key factors controlling the properties of biochar (for example, pore size composition and hydrophobicity) include the temperature of pyrolysis and biomass feedstock, among others. In many respects, the properties of biochar are similar to but generally lower than those of GAC for sorptive purposes.

The available literature is limited to academic laboratory batch experiments on the bench-scale (Chen et al. 2011; Inyang and Dickenson 2017; Kupryianchyk et al. 2016; Rahman et al. 2014; Xiao, Ulrich, et al. 2017), with one published study reporting pilot-scale column operation (Inyang and Dickenson 2017).

#### **12.5.2 Precipitation/Coagulation/Flocculation Summary**

Precipitation/coagulation/flocculation is a common pretreatment approach used in wastewater treatment plants for removing various particles and dissolved constituents. Coagulants, either commodity or proprietary chemicals, can be added to water (conventional technology) or generated by anode-cathode reactions of metal plates inserted into the water (electrocoagulation). Common examples include:

- inorganic cationic coagulants (for example, alum, iron-based)
- commodity (for example, polyDADMAC) and specialty (for example, Perfluorad) polymers
- electrochemical precipitation

Coagulants assist in the formation of solids. Flocculation is typically conducted by adding a soluble polymer and slowly mixing to allow the particles to agglomerate and grow. Upon solid formation, constituents such as PFAS can be physically incorporated into, or sorbed onto, the flocculated particulate (which is known as co-precipitation). The precipitated solids are then separated from the water by sedimentation and/or filtration processes. The solid material containing the PFAS requires disposal, see Table 12-2 for solids (provided as a separate PDF). See Section 12.3.2 for solids disposal options.

Current literature documents only bench-scale study results on treating PFAS via precipitation, flocculation, or coagulation; therefore, this is considered a partially developed technology. Evaluations have focused on conventional commodity chemical coagulation (for example, aluminum or ferric salts) and nonconventional coagulation (for example, proprietary chemical coagulants or electrocoagulation). Pilot- and full-scale applications have not been documented in the United States (Birk 2017).

Nonconventional precipitation (for example, electrocoagulation or advanced chemical precipitants) has shown more potential for direct PFAS treatment, but has very limited data. High-affinity cyclodextrin polymer has been tested in bench-scale reactors and was found to have superior removal capacity to GAC (Xiao, Ling, et al. 2017).

#### **Related Ongoing Research Funded by SERDP:**

- ER-2425 Development of a Novel Approach for In Situ Remediation of PFC-Contaminated Groundwater Systems
- ER18-1026 Rational Design and Implementation of Novel Polymer Adsorbents for Selective Uptake of PFASs from Groundwater

Electrocoagulation reactors, which range from basic to very sophisticated designs, have been reported to be highly efficient, compact, relatively low cost, and completely automatable (Baudequin et al. 2011; Lin et al. 2015). Recent studies have found that PFAAs, such as PFOA and PFOS, can be quickly sorbed on the surface of zinc hydroxide particulates generated by electrocoagulation (Lin et al. 2015).

#### **12.5.3 Nanofiltration (NF)**

NF is a form of membrane technology that is pressure-driven and shown to be effective in the removal of PFAS (Tang et al. 2007). This method of filtration provides high water flux at low operating pressure (Izadpanah and Javidnia 2012).

Nanometer-sized membrane pores are used to remove compounds in a process similar to RO, but NF does not remove smaller ions such as chloride and sodium. The most common membrane module configurations are spiral-wound (consisting of flat sheet membrane material wrapped around a central collection tube); however, hollow fiber NF modules may also be available for applications with higher fouling potential.

Available data on the removal of PFAS via NF consist of laboratory-scale tests performed on flat sheet membrane coupons (laboratory-scale sections of the membranes to be tested) and one full-scale drinking water treatment plant using an NF treatment train. Therefore, variations in performance due to fouling, flux, and concentration distributions in standard spiral-wound membrane configurations have not been characterized (Boo et al. 2018).

NF membranes tested include the DuPont (formerly Dow FilmTec) membranes NF-270, NF-200, and NF-90, and the SUEZ (formerly GE Water & Process Technologies) DK membrane. Reported rejections were generally > 95% for PFAS with molecular weights ranging from 214 grams per mole (g/mol) to 713 g/mol, though some compounds had lower rejections (PFPeA at 70% and perfluorooctane sulfonamide at 90%) (Steinle-Darling and Reinhard 2008; Appleman et al. 2013). Effective full-scale removal of PFAS by NF membranes was confirmed based on nondetectable PFAS concentrations (<4 ng/L) in NF permeate (Boiteux 2017). Salt passage for PFOS was reported to range from < 1% for the tighter NF-90 membrane to about 6% for the looser NF-270 and DK membranes (Tang et al. 2007). As mentioned in Section 12.2.2, an appropriate disposal or treatment of the membrane concentrate stream needs to be considered, especially the application of high-pressure membranes for inland communities.

#### **12.5.4 Redox Manipulation Summary**

Redox manipulation includes chemical oxidation and reduction technologies. These have been summarized in more detail in Nzeribe et al. (2019). Chemical oxidation for PFAS is a technology approach that is achieved via the delivery of liquid, slurry, or gaseous oxidants to transfer electrons from a reactive oxidant species to a target (PFAS) and affect the cleavage of atoms in the PFAS molecular structure. Carboxylic or sulfonic group “heads” (functional groups) of PFAS are commonly more susceptible to redox transformation than the fluorinated carbon chain “tails.” There is currently a lack of robust evidence of defluorination via chemical oxidation processes. The mechanisms involving multiple species of free radicals that trigger PFAS oxidation are not well understood. PFAA precursors are also known to be oxidized to form persistent and terminal PFAAs without further oxidation (Houtz and Sedlak 2012; Anumol et al. 2016). Consequently, care should be taken to monitor site and plume conditions and understand potential formation and transport of transformation products.

Additional mechanistic studies are needed to develop chemical oxidation as a feasible PFAS remediation approach and to further assess factors that may promote or limit this technology. Common oxidants that have been documented to treat PFAS and other organic contaminants (for example, chlorinated solvents) include ozone, catalyzed hydrogen peroxide, and persulfate, as discussed further below.

##### **12.5.4.1 Ozone-Based Systems**

Ozone can be coupled with other oxidants such as hydrogen peroxide and persulfate to promote the generation of a suite of aggressive free radicals capable of degrading PFAS. An ozone-based system was implemented for the treatment of PFAS in a single field-scale test by Eberle, Ball, and Boving (2017) using combined ozone and activated persulfate.

The main pathway and mechanism behind the ozone-based system tested by Eberle, Ball, and Boving (2017) is unknown, as detailed mechanistic studies have not been performed. However, they suggested that PFAS reduction in groundwater after treatment was not limited to partial degradation, but it is possible that sorption also had a role to play in the declining aqueous PFAS concentration. They postulated that activated persulfate could lead to a decline in pH, thereby increasing sorption of PFAS to soil due to increased protonation.

This approach has been partially demonstrated in one field-scale setting, and results are encouraging for application using ex situ or in situ approaches. However, because there is an absence of supporting mechanistic data, it is likely that other factors could come into play that may promote or limit this technology.

The application of the ozone-based system for the treatment of PFAS has also been evaluated in bench studies (Lin, Panchangam, et al. 2012; Kerfoot 2014; Huang et al. 2016; Eberle, Ball, and Boving 2017). Lin, Panchangam, et al. (2012) used an ozone system without and inclusive of hydrogen peroxide addition in an alkaline environment, and Kerfoot (2014) used hydrogen peroxide and ozone bubbles for a bench-scale test of groundwater from a monitoring well foam firefighting site in Canada. Huang et al. (2016) combined ozone with photolysis to produce hydroxyl radicals and photogenerated electrons.

In the field demonstration, PFAS concentrations in groundwater were reduced by 21–79% after treatment. Also, an initial pilot test at a fire training area using ozone and peroxide has shown removal of 98.5% and 92.3% for PFOS and PFOA, respectively, in groundwater and over 80% for PFOS on saturated soil with proportional release of fluoride (Kerfoot 2016).

In bench-scale studies, Eberle, Ball, and Boving (2017) decreased PFAS by 99.9% using PFAS-contaminated site groundwater and spiked deionized water. Eberle, Ball, and Boving (2017) also reported that the system was not sensitive to other groundwater organics. Kerfoot (2014) reported 89.8% removal of PFOS and > 80% for other PFAS (PFPeA 89.8%, PFHxA 86.2% and PFHxS 98.1%). These studies, however, do not confirm destruction through mass balance and analysis of byproducts.

Each of these approaches and test conditions used different water matrices and starting concentrations. It is difficult to state whether current regulatory levels can be achieved in practice with these technologies, but in general they appear to be effective as a polishing technology to achieve low part-per-trillion treatment requirements.

#### **12.5.4.2 Catalyzed Hydrogen Peroxide (CHP)-Based Systems**

CHP is one of the strongest oxidant systems used in environmental remediation. It involves reaction of hydrogen peroxide with a catalyst to predominantly generate hydroxyl radicals. Some CHP systems produce nucleophiles and reductants, including superoxide and hydroperoxide (Mitchell et al. 2014). Common catalysts include transition metals such as iron (Fenton and Fenton-like reaction) or manganese, chelated metals, and naturally occurring minerals (for example, (Watts et al. 2005; Teel et al. 2007).

Hydroxyl radicals attack the alkyl groups of both PFCAs and PFSAs, but do not attack the perfluoroalkyl chain. As a result, PFCA and PFSA precursors are transformed to PFCAs of related perfluorinated chain length (Bruton and Sedlak 2017). Mitchell et al. (2014) demonstrated that superoxide and hydroperoxide (which are nucleophiles and reductants generated as a reaction in CHP but are not chemical oxidants) generated in alkaline pH CHP systems mineralize PFOA but did not elucidate a mechanism.

Bench-scale testing has been successfully demonstrated. Field deployment of hydroxyl radical-based CHP systems may be limited due to decomposition of PFAS precursors to PFOA and other PFCAs as unreactive transformation products (Bruton and Sedlak 2017).

CHP systems that predominantly generate hydroxyl radicals partially transform PFAAs to their PFCAs of related perfluorinated chain length, which are not further transformed (Houtz and Sedlak 2012; Bruton and Sedlak 2017). Systems that generate superoxide and hydroperoxide have been demonstrated at the bench test level to mineralize PFOA (Mitchell et al. 2014), but effectiveness with other PFAS is unknown.

#### **12.5.4.3 Activated Persulfate**

Persulfate anion ( $S_2O_8^{2-}$ ) is activated to generate reactive radical species, primarily sulfate radicals (2.6 volts, or V) and hydroxyl radicals (2.7 V). Methods to activate persulfate include transition metals, high pH, and heat activation (Siegrist, Crimi, and Simpkin 2011). Hydroxyl radicals are the predominant radicals formed at high pH conditions (Furman et al. 2011), while at acidic pH there is greater yield of sulfate radicals (Siegrist, Crimi, and Simpkin 2011).

PFCAs are attacked by sulfate radicals under acidic conditions, initiating a decarboxylation reaction, where cleavage of the carbon-to-carbon (C-C) bonds occurs between PFCAs and the carboxyl group (-COOH), forming unstable perfluoroalkyl radicals ( $C_nF_{2n+1}$ ) (Hori et al. 2010; Lee et al. 2012; Yin et al. 2016). A stepwise series of decarboxylation and hydrogen fluoride (HF) elimination reactions continues to form shorter chain PFCAs until all PFCAs are mineralized to fluoride and carbon dioxide. PFSAs such as PFOS are unreactive with sulfate radicals (Park et al. 2016; Bruton and Sedlak 2017). Hydroxyl radicals attack the alkyl groups of both PFCAs and PFSAs, but do not attack the perfluoroalkyl chain. As a result, PFCA and PFSA precursors are transformed to PFCAs of related perfluorinated chain length (Bruton and Sedlak 2017). Under alkaline pH conditions the sulfate and hydroxyl radicals are reactive with the alkyl groups but similarly unreactive with the perfluoroalkyl chain, which is the basis of the TOP method (Houtz and Sedlak 2012).

#### **Related Ongoing Research Funded by SERDP:**

- ER-2423 In Situ Treatment Train for Remediation of Perfluoroalkyl Contaminated Groundwater: In Situ Chemical Oxidation of Sorbed Contaminants (ISCO-SC)
- ER201729 Field Demonstration to Enhance PFAS Degradation and Mass Removal Using Thermally Enhanced

Persulfate Oxidation Followed by Pump-and-Treat

- ER18-1545 Innovative Treatment of Investigation-Derived Waste Polluted with Per- and Polyfluoroalkyl Substance Contaminants and Other Co-Contaminants.

Activated persulfate under acidic conditions has proven effective for PFOA (PFCAs) with nominal 100% degradation, but PFOS is not transformed. Sulfate radicals and hydroxyl radicals generated by alkaline persulfate activation transform PFCA and PFSA precursors to PFCAs of related perfluorinated chain length (Bruton and Sedlak 2017).

#### 12.5.4.4 Sonochemical Oxidation/Ultrasound

The sonochemical process relies on the propagation of acoustic waves in liquids at frequencies ranging between 20 kHz and 1,000 kHz (Furuta et al. 2004), which results in cavitation. Operating parameters such as frequency (Campbell and Hoffmann 2015), power density (Hao et al. 2014), solution temperature, sparge gas, and initial concentration of PFAS (Rodriguez-Freire et al. 2015) play a significant role in the sonochemical degradation and defluorination rate of PFAS.

Sonochemical degradation occurs via two mechanisms: localized thermal treatment and free radical destruction (Rayaroth, Aravind, and Aravindakumar 2016). During cavitation, cyclic formation, growth, and collapse of microbubbles result in an intense increase in temperature and pressure (5000 Kelvin (K) and 2000 atmosphere (atm)), along with the generation of free radicals (Furuta et al. 2004; Chowdhury and Viraraghavan 2009).

Sonochemical oxidation has been successfully applied for rapid degradation of PFAS to fluoride (F<sup>-</sup>), sulfate (SO<sub>4</sub><sup>2-</sup>) and carbon dioxide (CO<sub>2</sub>). Vecitis et al. (2008) reported a complete recovery of SO<sub>4</sub><sup>2-</sup> and >90% defluorination of PFOA and PFOS with initial concentrations of 0.24 μM and 0.20 μM, respectively, for a field-scale application to treat groundwater from below a landfill. At bench scale, sonolysis has been reported in the literature as one of the most effective treatment processes for PFAS-contaminated water, because they almost immediately mineralize to SO<sub>4</sub><sup>2-</sup>, CO<sub>2</sub>, carbon monoxide (CO), and F<sup>-</sup> after cleavage of their C-C/C-S bond. Studies have reported >90 percent degradation and defluorination for PFOA and PFOS (Moriwaki et al. 2005; Vecitis et al. 2008; Cheng et al. 2008, 2010). Gole et al. (2018) demonstrated removal and defluorination of AFFF in a 91-L sonolytic reactor.

#### 12.5.4.5 Photolysis/Photochemical Oxidation

A thorough review of photolysis/photochemical oxidation technology for PFAS decomposition is reported in Wang, Yang, et al. (2017). Chen, Zhang, and Liu (2007) and Giri et al. (2011) reported removal of PFAS by direct photolysis at 185 nm. Hori et al. (2004) and Chen, Zhang, and Liu (2007) reported that direct photolysis at 254 nm alone is not very effective because PFAS do not absorb light at wavelengths >220 nm due to their chemical structure. Chemical reagents/catalysts such as Fe<sup>3+</sup>, S<sub>2</sub>O<sub>8</sub><sup>2-</sup>, TiO<sub>2</sub>, heteropolyacid photocatalyst (H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>), CO<sub>3</sub><sup>2-</sup>, and IO<sub>4</sub><sup>-</sup> when combined with ultraviolet (UV) (>220 nm) light can effectively decompose PFAS (Hori et al. 2005; Chen and Zhang 2006) (Zhang, Pan, and Zhou 2016; Hori et al. 2007; Wang et al. 2008; Cao et al. 2010). This is due to generation of strong and reactive oxidative species such as OH<sup>•</sup>, H<sup>•</sup>, CO<sub>3</sub><sup>•-</sup> and PFAS-Fe complexes. Photochemical oxidation of PFAS is said to be dependent on the light source (UV or vacuum ultraviolet), initial concentration of PFAS, environmental matrix, temperature, pH, and type of reagent used (Lin, Panchangam, et al. 2012; Giri et al. 2012; Lyu et al. 2015b, a; Xu et al. 2017).

#### Related Ongoing Research Funded by SERDP:

- ER18-1595 A Combined Photo/Electrochemical Reductive Pathway Towards Enhanced PFAS Degradation
- ER18-1513 Effective Destruction of Per- and Polyfluoroalkyl Substances in Water by Modified SiC-Based Photocatalysts
- ER18-1515 A Cost-Effective Technology for Destruction of Per- and Polyfluoroalkyl Substances from DoD Subsurface Investigation-Derived Wastes
- ER18-1599 Pilot Scale Assessment of a Deployable Photocatalytic Treatment System Modified with BiPO<sub>4</sub> Catalyst Particles for PFAS Destruction in Investigation-Derived Wastewater

The major degradation pathways involved in the photochemical oxidation of PFAS are direct photolysis and free radical reactions. The C-C bond between PFAS is cleaved with the COOH group to form perfluoroalkyl radicals (Hori et al. 2003; Hori et al. 2008), which then react with water and undergoes hydrogen fluoride elimination to form shorter chain compounds. These then undergo hydrolysis to form subsequent shorter PFAS (losing CF<sub>2</sub> units). During direct photolysis, the C-C and C-S

bonds of PFAS are broken by photoelectrons to generate perfluoroalkyl radicals and carbon dioxide (Wang, Yang, et al. 2017).

#### **12.5.4.6 Electrochemical Treatment**

Electrochemical treatment occurs via anodic oxidation; a variety of materials have been used as anodes. The treatment effectiveness of PFOS and PFOA using different anodes can vary significantly. Most research on PFAS, particularly PFOS and PFOA removal, has been conducted using a boron-doped diamond (BDD) electrode due to its mechanical, chemical, and thermal stability (Trautmann et al. 2015; Schaefer et al. 2017). Some other electrodes, such as lead dioxide ( $\text{PbO}_2$ ), titanium oxide ( $\text{TiO}_2$ ), titanium suboxide ( $\text{Ti}_4\text{O}_7$ ), and tin oxide ( $\text{SnO}_2$ ), also have the ability to treat PFAS-contaminated water (Ochiai et al. 2011; Zhou et al. 2012) (Zhao, Gao, et al. 2013; Liang 2017; Liang et al. 2018). Operating conditions and parameters such as pH (Lin, Niu, et al. 2012) (Zhou et al. 2012), current density, electrolyte type (Song et al. 2010; Zhuo et al. 2012), electrode distance (Lin, Niu, et al. 2012), initial PFAS concentration, and temperature are important factors that influence electrochemical oxidation of PFAS (Niu et al. 2016).

Electrochemical treatment proceeds via direct and indirect anodic oxidation (Radjenovic and Sedlak 2015; Niu et al. 2016; Schaefer et al. 2018). In direct electrolysis, contaminants are adsorbed onto and degraded directly at the electrode, while in indirect electrolysis, contaminants are degraded in the bulk liquid in reactions with oxidizing agents (that is, hydroxyl radicals) formed at the electrode (Radjenovic and Sedlak 2015).

Bench-scale studies have shown success in the degradation and defluorination of PFAS, including short-chain, long-chain PFAAs as well as PFAA precursors (Chiang 2018). Electrochemical oxidation of precursors may lead to the transient generation of perfluorinated carboxylates (Schaefer et al. 2018). Ultimately, fluoride is released, with typical recoveries ranging from 60 to 80%; the fate of the remaining fluoride is unknown, but studies have suggested that losses due to volatile perfluorinated alkanes may occur. Currently, technology has not been tested for PFAS-laden water with low PFAS concentrations. However, it has been tested as a stand-alone technology for PFAS concentrations at ppb levels and as a destruction technology to destroy concentrated PFAS waste streams generated from other treatment technologies such as ion exchange resin and ozofractionation (Liang et al. 2018; Chiang 2018). It has been partially demonstrated as an ex situ treatment of PFAS. But in situ application is also being considered and funded in the SERDP program. The issue of perchlorate formation as a byproduct during electrochemical oxidation of PFAS has been addressed by Schaefer et al. (2017) using a biological treatment polishing step. The issue can also be minimized by not using sodium chloride as the electrolyte (Chiang 2018).

The technology has been demonstrated via bench studies and pilot-scale reactor to be very effective for treatment of short-chain, long-chain PFAAs, as well as most commonly detected PFAA precursors in spike water systems and several remediation-derived waste streams laden with high PFAS concentrations.

#### **Related Ongoing Research Funded by SERDP:**

- ER-2424 Investigating Electrocatalytic and Catalytic Approaches for In Situ Treatment of Perfluoroalkyl Contaminants in Groundwater
- ER-2718 Synergistic Treatment of Mixed 1,4-Dioxane and PFAS Contamination by Combining Electrolytic Degradation and Electrobiostimulation
- ER18-1320 Electrochemical Oxidation of Perfluoroalkyl Acids in Still Bottoms from Regeneration of Ion Exchange Resins
- ER-2717 A Novel Reactive Electrochemical Membrane System for Treatment of Mixed Contaminants
- ER18-1491 Reactive Electrochemical Membrane (REM) Reactors for the Oxidation of Perfluoroalkyl Compound Contaminated Water

#### **12.5.4.7 Solvated Electrons (Advanced Reduction Processes)**

Advanced reduction processes (ARP) has been investigated for the reductive degradation of groundwater contaminants. ARP involves the combination of activation methods such as ultrasound, ultraviolet, microwaves, and electron beam with reducing agents (reductants) such as ferrous iron, sulfide, sulfite, iodide, and dithionite to generate very reactive reducing radicals and the hydrated electrons ( $e^{-aq}$ ) that mineralize contaminants to less toxic products (Vellanki, Batchelor, and Abdel-Wahab 2013). The reducing hydrogen radical ( $\text{H}^{\cdot}$ ) and the hydrated electron are strong reductants that react easily with halogenated organic compounds (Buxton et al. 1988). ARP-induced degradation rates depend on initial solution pH and



reductant concentration (Vellanki, Batchelor, and Abdel-Wahab 2013). Bentel et al. (2019) described insights gained from a structure-activity relationship analysis of the mechanisms involved in the reaction of solvated electrons with PFAS.

The degradation pathway of PFAS using ARP differs from that of oxidizing agents in that the hydrated electron (Song et al. 2013) cleaves the C-F bond adjacent to the functional group of the PFAS rather than the C-C or C-S bond. Qu et al. (2014) proposed that hydrated electrons lead to the reductive cleavage of the C-F bonds, resulting in fluorine elimination from PFOA. Furthermore, they proposed that under UV irradiation, cleavage of the C-C bond between the COOH group and the perfluoroalkyl group occurred as shorter chain intermediates were detected in solution. Qu et al. (2014) therefore concluded that two reactions are responsible for the reductive defluorination of PFOA: (1) direct photolysis by UV irradiation, and (2) photoreduction by hydrated electrons.

Reductive processes have proven feasible for degradation of most PFAS, especially PFOS. It should be recognized that electrons will be scavenged by oxygen, nitrate, and chlorides, and this should be considered for treatment application. Recent research using UV-activated sulfite demonstrated effective generation of hydrated (aka solvated) electrons. Laboratory tests showed >50% defluorination of both PFOS and PFOA within 24 hours (Strathmann 2018).

#### **Related Ongoing Research Funded by SERDP:**

- ER-2426 Quantification of In Situ Chemical Reductive Defluorination (ISCRD) of Perfluoroalkyl Acids in Ground Water Impacted by AFFFs
- ER18-1526 Complete Reductive Defluorination of Poly- and Perfluoroalkyl Substances (PFASs) by Hydrated Electrons Generated from 3-Indole-acetic-acid in Chitosan-Modified Montmorillonite

#### **12.5.4.8 Plasma Technology**

Plasma technology is a promising destructive PFAS treatment technology. Plasma is formed as a result of an electrical discharge from the addition of sufficient energy to gas (Jiang et al. 2014) and is classified into two major groups based on temperature and electronic density: thermal plasma (local thermal equilibrium) and nonthermal plasma (nonequilibrium plasma) (Bogaerts 2002). Due to lower energy requirements and selectivity, nonthermal plasma is most often used in water treatment processes (Jiang et al. 2014). In water treatment plasma applications, electrical discharges can be discharged above the liquid surface, directly to the liquid, or in the form of bubbles in liquids (Locke, Lukes, and Brisset 2012) (Stratton et al. 2017). These electrical discharges diffuse in liquids to initiate various chemical and physical effects, including high electric fields, intense UV radiation, shock waves, and formation of strong oxidative and reductive reactive species ( $H^{\bullet}$ ,  $O^{\bullet}$ ,  $OH^{\bullet}$ ,  $H_2O_2$  aqueous electrons,  $H_2$ ,  $O_2$ ,  $O_3$ ), which are effective for the treatment and removal of contaminants (Lukes, Appleton, and Locke 2004; Lukes et al. 2005; Stratton et al. 2017).

Determination of plasma treatment mechanisms and degradation pathways for PFAS is currently a research focus, and several mechanisms and pathways have been proposed. Takeuchi et al. (2013) proposed that the main reaction pathway for PFOA by plasma treatment is by thermal cleavage of the C-C bonds resulting in direct decomposition to gaseous products without formation of shorter chain PFCAs. Others have proposed that PFAS decomposition is due to conversion to unstable radicals during interaction of PFAS with the most energized ions in the plasma (Hayashi et al. 2015; Obo, Takeuchi, and Yasuoka 2015), or with positive ion(s) generated by the plasma (Yasuoka, Sasaki, and Hayashi 2011) at the bubble gas-liquid interface. The unstable radicals produced during PFAS decomposition can result in a sequential loss of one carbon within the chain.

Plasma effectively degrades PFAS in a relatively short period of time (30-minute treatment) in both synthetic water and groundwater. It has been reported that plasma treatment provided 90% degradation of PFOA and PFOS, with only about 10% of the destroyed PFOA and PFOS being converted to shorter chain PFAAs (Stratton et al. 2017). The degradation rate is not affected by the presence of co-contaminants. This is an environment-friendly technology, because there is no demand on pressure or temperature and it does not require significant input of chemicals. Plasma also generates a broad range of reactive species.

#### **Related Ongoing Research Funded by SERDP:**

- ER18-1306 Combined In Situ/Ex Situ Treatment Train for Remediation of Per- and Polyfluoroalkyl Substance (PFAS) Contaminated Groundwater
- ER18-1624 Plasma Based Treatment Processes for PFAS Investigation-Derived Waste

- ER18-1570 Application of Non-Thermal Plasma Technology for the Removal of Poly- and Perfluorinated Substances from Investigation-Derived Wastes
- ER18-5015 Removal and Destruction of PFAS and Co-contaminants from Groundwater

#### 12.5.4.9 Zero-Valent Iron (ZVI)/Doped-ZVI

ZVI is an inexpensive groundwater remediation technology. It is the most commonly used reductant for in situ groundwater remediation. It is a strong reducing agent capable of successfully reducing major groundwater contaminants such as chlorinated solvents. Recently nanoscale zero-valent iron (nZVI) has had increased attention due to its higher reactivity, surface area, and potential in situ injectability compared to the micro-sized ZVI.

In general, the removal of PFAS by ZVI in reductive processes involves the mass transfer of contaminants to the ZVI surface, and their adsorption and reaction (transformation of contaminants into less toxic/nontoxic species) on the ZVI surface, followed by the desorption and mass transfer of byproducts into solution (Arvaniti et al. 2015). Because the reduction of contaminants by ZVI is a surface-mediated electron transfer process, the surface properties of ZVI influence contaminant reactivity. (Arvaniti et al. (2015)) found that PFOS removal using Mg-aminoclay-coated nZVI occurred via adsorption of PFOS to the ZVI surface followed by reduction. A similar decomposition mechanism for PFOS using ZVI in subcritical water was reported by Hori et al. (2006), who suggested that adsorption of PFOS onto ZVI played a major role in PFOS decomposition, as fluoride was detected in the treatment solution after treatment.

This technology is highly effective for the removal of PFOS, reacts relatively quickly, and has proven feasible for degradation of most PFAS.

#### 12.5.4.10 Alkaline Metal Reduction

Alkaline metal reduction involves the use of alkali metals (that is, the reductant) to reduce organic compounds to their anion radical. Reductive degradation of branched PFOS has been reported with vitamin B<sub>12</sub> as a catalyst and Ti(III)-citrate or nanosized zero-valent zinc as a bulk reductant (Ochoa-Herrera et al. 2008; Park, de Perre, and Lee 2017) where degradation rates increase with increasing solution pH, bulk reductant dose, and temperature.

The degradation pathway of PFAS by alkali metal reduction as postulated by Ochoa-Herrera et al. (2008) suggests that destruction of branched PFOS isomers occurs via chemical reductive dehalogenation. Park, de Perre, and Lee (2017) suggested that the ability of vitamin B<sub>12</sub> to reduce branched PFOS isomer and not linear is because the branched PFOS isomers possess greater electron density differences that are absent in linear PFOS isomers. Bench-scale studies have shown success for branched PFOS isomers and have proven to be efficient (greater than 70% removal; see (Ochoa-Herrera et al. 2008)). In situ applications have not been tested. Removal and defluorination are lower for PFHxS relative to PFOS. Polyfluorinated sulfonate intermediates (C<sub>5</sub>-C<sub>8</sub>) are the final products (Park, de Perre, and Lee 2017).

### 12.5.5 Biodegradation Summary

A limited number of studies have tested microbial degradation of PFAS and many conflicting reports exist, all suggesting that more work needs to be performed to fully understand the biotic transformations of these compounds.

Microbial degradation of PFAS has been observed to occur only with polyfluoroalkyl substances (Butt, Muir, and Mabury 2014), which contain some carbon-hydrogen bonds instead of C-F bonds (Buck et al. 2011). Recent research documented the aerobic biotransformation of fluorotelomer thioether amido sulfonate (FtTAoS) over a 40-day period to produce 4:2, 6:2, and 8:2 fluorotelomer sulfonate (FTS), 6:2 fluorotelomer unsaturated carboxylic acid (FTUCA), 5:3 fluorotelomer carboxylic acid (FTCA), and C4 to C8 perfluorinated carboxylic acids (Harding-Marjanovic et al. 2015). An unintended consequence of biologically mediated transformations is the conversion of precursors (polyfluorinated) to perfluorinated compounds.

PFOA and PFOS have been shown to be resistant to microbial biotransformation under a variety of growth conditions (Liu and Mejia Avendaño 2013). However, other PFAS, including chemicals in AFFF with nonfluorinated alkyl groups (polyfluorinated substances), are likely amenable to biotransformation. Most recently, defluorination of PFOA and PFOS were observed using an ammonium oxidizing autotroph (Huang and Jaffé 2019). Upon addition of PFOA or PFOS (0.1 mg/L and 100 mg/L, respectively) to the A6 culture, shorter chain perfluorinated products and acetate were observed. Incubations with hydrogen as a sole electron donor also resulted in the defluorination of up to 60% of PFOA and PFOS during 100-day incubations, while total fluorine (organic plus fluoride) remained constant. Reductive defluorination of perfluoroalkyl substances may be possible, as observed when using vitamin B12 and Ti(III)-citrate (Ochoa-Herrera et al. 2008). There are no known reports of biotransformation occurring under aerobic and anaerobic conditions.

A limited number of studies have tested microbial degradation of PFAS and many conflicting reports exist, all suggesting that more work needs to be performed to fully understand the biotic transformations of those compounds.

Research on the fungal degradation of PFAS has been ongoing due to the wide spectrum of substrate reduction catalyzed by extracellular ligninolytic enzymes. Experiments with white-rot fungus showed limited degradation of PFOA in microcosm studies under certain conditions (Tseng 2012). The innovative delivery of fungal enzymes for PFAS treatment requires further research.

The biodegradation of PFAS has been reported in a few studies as described above and in the following: 8:2 FTOH (Wang et al. 2009), 6:2 FTOH (Liu, Wang, et al. 2010), 6:2 FTSA (Wang et al. 2011), and N-ethyl perfluorooctane sulfonamidoethanol (Rhoads et al. 2008; Rhoads et al. 2013). Recently the PFOA-degrading strain YAB1 was isolated from soil that had been impacted by perfluorinated compounds through acclimation and enrichment culture, where perfluorooctanoic acid (PFOA) was amended as the sole carbon source (Yi et al. 2016). This strain was preliminarily identified as *Pseudomonas parafulva* based on colony morphology, physiological and biochemical features, and 16S rRNA gene sequencing. Using shaking flask fermentation, the maximum tolerable concentration of YAB1 on PFOA was found to be 1,000 mg/L, and the optimal PFOA concentration for the growth of YAB1 was 500 mg/L. After 96 hours of culture, the PFOA degradation rate was 32.4%. When 1 g/L glucose was added to the inorganic salt culture medium, the degradation rate increased to 48.1%. Glucose was the best exogenous carbon source for the degradation of PFOA (Yi et al. 2016).

#### **Related Ongoing Research Funded by SERDP:**

- ER-2422 Bioaugmentation with Vaults: Novel In Situ Remediation Strategy for Transformation of Perfluoroalkyl Compounds
- ER-2127 Remediation of Perfluoroalkyl Contaminated Aquifers using an In Situ Two-Layer Barrier: Laboratory Batch and Column Study

### **12.5.6 High-Energy Electron Beam (eBeam)**

High-energy electron beam (eBeam) is a high efficiency, flow-through, nonthermal, chemical-free technology that utilizes electron accelerators to generate large numbers of highly energetic electrons from electricity (Cleland 2011; Pillai and Shayanfar 2016). The technology has been commercialized globally for pasteurizing foods, sterilizing medical devices, cross-linking polymers, and eliminating insects and pests from fresh produce (Cleland 2011; Pillai 2016; Pillai and Shayanfar 2016; Zembouai et al. 2016). It provides a form of ionizing irradiation that does not involve the use of radioactive isotopes. The amount of energy from eBeam that is absorbed by an irradiated material per unit mass is called dose. The absorbed dose during eBeam treatment depends on the type and thickness of the material, the beam power, and the length of time the material is exposed to the electron beam (Waite 1998).

eBeam is applicable for use on soil and liquid matrices for many purposes: disinfection of sewage sludge (Praveen et al. 2013; Waite 1998); remediation of heavy hydrocarbon-contaminated soils (Briggs 2015); and remediation of volatile organic compounds (VOCs) and semivolatile organic compounds in liquid wastes such as groundwater, wastewater, and landfill leachate (USEPA 1997b). During irradiation of water, three primary reactive species are formed: solvated electrons and hydrogen radicals, which are strong reducing species, and hydroxyl radicals, which are strong oxidizing species. This creates both advanced reduction and oxidation processes without the addition of any chemicals. The absolute concentration of radicals formed during irradiation is dose- and water quality-dependent, but it has been measured at greater than millimolar (mM) levels in potable, raw, and secondary wastewater effluent (Waite 1998).

Researchers at Texas A&M University recently demonstrated defluorination of PFOA in aqueous samples by eBeam technology (Wang et al. 2016). The study measured defluorination efficiency as a function of molar concentration of free fluoride ions and initial

#### **Related Ongoing Research Sponsored by SERDP:**

- ER18-1620 Ex Situ Remediation of Investigation-Derived Wastes containing PFAS by Electron Beam Technology

molar concentration of PFOA to be treated. Final defluorination efficiencies ranged from 34.6 to 95% under various increasing concentrations of nitrate, alkalinity, and fluvic acid. The defluorination is possibly due to the formation of aqueous electrons and the formation of secondary radicals (Wang et al. 2016). An additional study further demonstrated eBeam-mediated defluorination of PFOS and PFOA with decomposition efficiencies of 95.7% for PFOA and 85.9% for PFOS in an anoxic alkaline solution (pH = 13). Radical scavenging experiments indicated that the aqueous electron and hydrogen radical were important in the eBeam degradation of PFOA and PFOS (Ma et al. 2017). Further evaluation of this technology for treating other PFAS (polyfluorinated precursors and other long- and short-chain PFAAs) in soil and water, as well as testing over a range of concentrations, will be necessary to further understand treatment performance potential and to identify any deleterious byproducts.

### **12.5.7 Surface Activation Foam Fractionation**

The surfactant nature of PFAS make them prone to accumulation at surface interfaces. Surface activation foam fractionation (SAFF) is a process that generates fine air bubbles rising through a narrow water column. PFAS that accumulate at the top of the column as foam are vacuumed off for separate disposal. Using hundreds of columns, PFAS is progressively stripped out until drinking water standards have been achieved. The process reduces the volume of PFAS-contaminated water. The base technology was developed and built in Australia and is currently operating at full-scale for the Australian Department of Defence, Army Aviation Centre Oakey (AACO) base near Toowoomba, Queensland. The AACO water treatment plan was commissioned on May 13, 2019 and treats 66,000 gpd.

A small one-day field trial in Williamstown, New South Wales, has also been applied in situ in an existing downhole groundwater monitoring well using compressed air introduced at the base of the well and harvesting of PFAS-rich foam at the top of the well (Phillips et al. 2018). This trial demonstrated that  $\geq C6$  PFAS molecules could be removed from the treatment well annulus where hydrogeology could replenish the treatment well with a continuous supply of impacted groundwater. Further research to optimize the downhole foam fractionation engineering design is warranted.

### **12.5.8 Deep Well Injection**

A potential alternative to treatment may be the use of on-site or off-site underground injection waste disposal wells for liquids containing PFAS. This approach eliminates discharges to surface water and groundwater, which could be a consideration given the present climate of varying discharge limitations for PFAS. Class I wells, as defined by USEPA, are acceptable for both hazardous and nonhazardous liquid wastes (USEPA 2019a). The USEPA has published guidance on the requirements for the use of injection wells, which include siting, construction, operation, monitoring, testing, record keeping, reporting, and closure (USEPA 2019a). The USEPA has also studied the risks associated with underground injection wells (USEPA 2001), and these risks should be considered for the use of underground injection wells for PFAS-laden water. This option may be most attractive as a disposal option for high concentration liquids, such as RO reject water, anion exchange regeneration fluids, wastewater from manufacturing sites, and landfill leachate.

## **12.6 Limited Application and Developing Solids Treatment Technologies**

The treatment technologies presented in this document are provided in a hierarchy defined in Section 12.1, based on level of implementation and level of confidence in the technology from peer-reviewed literature and extent of documented performance. The three development levels include field-implemented technologies, limited application technologies, and developing technologies. Where appropriate in the text both in situ and ex situ technologies are discussed. However, it is not always clear if a limited application or developing technology may be effective in situ, ex situ, or both, thus further distinction between in situ and ex situ is not made in this section. Table 12-2 (provided as separate PDF) presents limited application and developing technologies for solids, which may be applicable to soil, sediments, biosolids, or other solid

media, including PFAS-laden materials (for example, GAC, resin, scrubbers, filters). Thermal treatment warrants further discussion as a limited application technology because it has been field-demonstrated at multiple sites by multiple practitioners but has not been well documented in peer-reviewed literature.

### **12.6.1 Sorption and Stabilization/Solidification**

Limited application and developing materials being demonstrated or developed for sorption and stabilization include minerals (for example, organically modified clays) or stabilization agents (for example, Portland cement). Stabilization/solidification through mixing with cementitious materials (for example, Portland cement or other amendments) can be applied to encapsulate PFAS-impacted soil/sediment to restrict PFAS leaching or migration. In situ solidification is always performed with soils in place, and it is necessary to use specialized equipment and maintain careful control over the addition of amendments and water content. In situ solidification is intended to yield a high-compressive-strength monolith that has low permeability. A bench-scale study (Söregård, Kleja, and Ahrens 2019) indicated that solidification using a binder (combination of Portland cement, fly ash, and ground granulated blast-furnace base slag) at a ratio of 9:1 reduced leaching for 13 out of 14 PFAS (except for PFBS). Introducing additional additives (for example, activated carbon, surface-modified clays) at a 2% concentration can further reduce leaching of PFAS in solidification-treated soil.

### **12.6.2 Thermal Treatment**

Thermal treatment is defined as mobilization or destruction, or both, of chemicals using heat. This can be accomplished by thermal desorption or thermal destruction. Heat is applied directly to the PFAS-contaminated soil/sediment.

Ex situ thermal treatment has been demonstrated (450–954°C) at field pilot-scale studies by a few technology vendors and is considered a partially demonstrated technology (Endpoint Consulting 2016; Enviropacific 2017; Colgan et al. 2018; Grieco and Edwards 2019). The effectiveness depends upon the ability to deliver heat to achieve sufficient and evenly distributed temperature at field scale cost-effectively. The pilot studies conducted have reported >90% removal of PFAS from soil when high heat has been applied.

In addition, lower temperature thermal desorption has been demonstrated to be effective for PFAS at 350–400°C on the bench scale. During a recent proof of concept laboratory bench test, 99.99% removal of PFAS from soils was demonstrated while heating the target volume to 400°C (Crowover et al. 2019; DiGuseppi, Richter, and Riggle 2019).

No documented examples of in situ thermal treatment for PFAS-impacted soil have been identified. However, the ex situ testing at 350–400°C suggests that these temperatures are sufficient for desorption of PFAS and therefore in situ treatment is potentially feasible for PFAS. In situ thermal treatment for PFAS is an energy-intensive treatment method. Its environmental footprint includes the energy source and consumption during treatment system operation, as well as manufacturing and installation of heating system materials.

At bench, pilot, and field scales, limited data sets are available and data gaps still exist mainly regarding fate of PFAS and air emissions (Lassen et al. 2013; USEPA 2020e). Another concern is the volatilization of hydrogen fluoride, which could pose serious health and safety issues and could compromise equipment components. Hydrofluoric acid and other non-PFAS off-gas concerns can be managed through conventional off-gas treatment systems (scrubbers). Although air emissions from the thermal treatment of PFAS have not been thoroughly studied at the field scale to date, PFAS destruction via high temperature air incineration and subsequent acid-gas scrubbing is a common practice during carbon reactivation (Mimna 2017).

#### **Related Ongoing Research Funded by SERDP:**

- ER18-1501 Hydrothermal Technologies for On-Site Destruction of Site Investigation Wastes Contaminated with Per- and Polyfluoroalkyl Substances (PFASs)
- ER18-1556 Small-Scale Thermal Treatment of Investigation-Derived Wastes (IDW) Containing Per- and Polyfluoroalkyl Substances (PFAS)
- ER18-1572 Evaluation of Indirect Thermal Desorption Coupled with Thermal Oxidation (ITD/TO) Technology to Treat Solid PFAS-Impacted Investigation-Derived Waste (IDW)
- ER18-1593 Demonstration of Smoldering Combustion Treatment of PFAS-Impacted Investigation-Derived Waste
- ER18-1603 Field Demonstration of Infrared Thermal Treatment of PFAS-Contaminated Soils from Subsurface Investigations

## 12.7 Integrated Remedial Solutions

The information above focuses on in situ and ex situ technologies available to treat (that is, destroy, stabilize, or remove) PFAS in water and soil. There are also nontreatment remediation approaches that may be employed at PFAS sites, including source zone or plume containment or mass flux reduction, excavation and off-site disposal, underground injection, and institutional controls. These approaches can be used alone or together with one or more treatment methods. This discussion provides some examples of remedial strategies that incorporate multiple approaches.

### 12.7.1 Combined Technologies for Treatment of PFAS and Co-Contaminants

In a drinking water context, PFAS removal may be an isolated treatment objective without interference from co-contaminants; treatment may include a single technology such as GAC. However, for groundwater remediation, particularly associated with PFAS release/source areas, PFAS compounds are typically present with other contaminants. For example, plumes emanating from former fire training areas may consist of PFAS in addition to petroleum hydrocarbons and chlorinated solvents that require different treatment approaches. Natural groundwater geochemistry, such as high metals or organic carbon concentration, can reduce PFAS treatment technology effectiveness and efficiency. A combined remedy approach, using multiple technologies simultaneously or in series, is generally required to optimize PFAS removal in these situations.

For example, McGregor (2018) documented a case study in which CAC was successfully injected to mitigate the mass flux of PFOS and PFOA from a source zone at a site in Ontario. At the same time, a slow-release oxygen amendment was injected to facilitate the aerobic biodegradation of petroleum hydrocarbons that co-occurred with PFAS in one part of the site. This is also an example of applying combined remedies in different areas of the site.

In some cases, the remediation of co-contaminants has affected the fate of PFAS compounds in plumes. Precursor compounds may be transformed in situ to PFCAs or PFSAs through aerobic biological transformation or transformed in situ to PFCAs through chemical oxidation. For example, (McGuire et al. 2014) presented a case study of an AFFF release site where oxygen infusion is believed to have resulted in accelerated transformation of precursors to PFHxS and PFCAs in part of the plume. This indicates that it is important to consider the potential influence of co-contaminant remediation on PFAS transformation or transport.

### 12.7.2 Addressing Source Areas and Plume with Multiple or Combined Remedies Using Multiple Types of Treatment Alternatives

It may be necessary at some sites to address both mass flux from source areas into groundwater and to contain or control plume migration.

The most commonly used plume containment alternative for PFAS plumes involves groundwater extraction with ex situ treatment. Options for reduction in mass flux leaving a source zone are partly discussed in the (ITRC 2008) Enhanced Attenuation of Chlorinated Organics guidance manual, although many of these are applicable to PFAS sites also. Mass flux reduction strategies for PFAS sites may include:

- injecting CAC to mitigate flux from the source zone (McGregor 2018), or at one or multiple locations within a groundwater plume
- capping part of a site to reduce infiltration through a PFAS source zone above the water table
- excavating shallow soil (although this may not have much benefit if there is a PFAS source zone below the depth of excavation)
- engineering management of surface water runoff to mitigate nonpoint sources at or upgradient of a site (ITRC 2018b)
- upgradient interception/diversion of groundwater to reduce the flux through a source zone below the water table.

### 12.7.3 Combined Technologies for Efficient PFAS Treatment

Because ultimate destruction of PFAS requires high-energy processes, combining practices that concentrate PFAS followed by destruction offers an opportunity for more efficient and cost-effective treatment. Examples of concentration processes that enable follow-on destruction include, but are not limited to:

- pump and treat using a regenerable ion exchange resin

- foam fractionation
- membrane separation
- reverse osmosis

Examples of destructive processes that are able to destroy separated waste, many of which are under development or have had limited application to date, are provided in Sections 12.5.4 and 12.5.6. Incineration is an example of another destructive technology which is a demonstrated full-scale application, though incineration has received recent attention due to possible incomplete combustion and/or by-product generation and is the topic of current study to better understand the fate of PFAS, see Section 12.4.

## 12.8 Sustainability of PFAS Treatment

Federal and state environmental protection agencies have published myriad green remediation best management practice fact sheets and guidance documents covering a variety of remediation topics and emphasizing the minimization of environmental cleanup footprints (USEPA 2012d, 2018b), including methods to quantify the environmental footprint (USEPA 2019g). The best management practice fact sheets for excavation and surface restoration, implementing in situ thermal technologies, and (more generally) materials and waste management may offer supplemental sustainability information to that already included alongside the remediation technologies presented within this section (USEPA 2008, 2012c, 2013b).

Applying such a framework for PFAS cleanup projects, the environmental impact drivers for PFAS cleanup technologies that should be considered include the life cycle environmental footprint of all facets of the cleanup, including project site preparation; installation of the remedy; materials, equipment, and energy used to operate the remedy; waste materials generated by the cleanup technology; and demolition and deconstruction of the remedy. In alignment with greener cleanups, green and sustainable remediation recommends the “the site-specific employment of products, processes, technologies, and procedures that mitigate contaminant risk to receptors while making decisions that are cognizant of balancing community goals, economic impacts, and environmental effects” (ITRC 2011b)2011(ITRC 2011a, p. 3). Economic and quality of life impacts to the community can be alleviated by early incorporation of green and sustainable remediation best management practices, including meaningful stakeholder engagement, creation of employment opportunities, and advancement of the local community’s skill set to help manage treatment systems and public outreach (USEPA 2012b). Lastly, climate change vulnerability and adaptation measures of remedial technologies should also be considered to ensure resiliency in the implemented remedial action (USEPA 2013a, 2014a).

In alignment with sustainability principles, performance of early and meaningful risk communication can assist professionals in raising the community’s awareness of environmental hazards, empowering community participation in risk reduction measures, and increasing the quality of life for the community impacted by contamination and related risk management activities (USEPA 2007). Several environmental and public health regulatory agencies have prepared information documents to assist professionals in performing effective risk communication for PFAS sites (for example, see (ATSDR 2018a).

In addition, a communication plan can be developed to assist with information dissemination and stakeholder engagement (Emmett et al. 2009). Section 14 provides further in-depth guidance on risk communication planning and performance. A risk communication toolbox is also being developed to help decision makers through the planning process and provide tools to assist with meeting performance metrics at each planning step. Additional guidance on stakeholder concerns and engagement is provided within this document in Section 13.

## 12.9 Improving Evaluation of PFAS Treatment Technologies

Significant effort has been completed with respect to reviewing and compiling comparative information on PFAS treatment technologies. In a number of instances, proponents of innovative treatment technologies have claimed success in removing or destroying PFAS with limited confirmation of performance. For example, removal mechanisms may not have been proven, byproducts may not have been measured, and the effect of the technology in actual environmental matrices, at environmentally relevant concentrations, on PFAS mixtures, or with co-contaminants present may be unknown.

To guide future assessments and investments in developing PFAS treatment technologies, a SERDP project has prepared suggested lines of evidence, recommended metrics, and decision tools to assess the effectiveness of PFAS treatment technologies. These lines of evidence and decision-making tools can be used to identify priorities and next steps to advance a given technology, assess whether a technology is ready for field demonstration, and identify key areas of uncertainty regarding technology performance.

Further SERDP-funded work (ER18-5053) is focused on developing a comprehensive assessment framework for ex situ PFAS treatment technologies and generating data to compare established and emerging approaches on a life cycle assessment and costing basis.

**Related Ongoing Research Funded by SERDP:**

- ER18-1633 Lines of Evidence to Assess the Effectiveness of PFAS Remedial Technologies
- ER18-5053 Evaluation and Life Cycle Comparison of Ex Situ Treatment Technologies for Per- and Polyfluoroalkyl Substances (PFASs) in Groundwater

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