# Remediation Technologies and Methods for Per- and Polyfluoroalkyl Substances (PFAS)

## 1 Introduction

Remediation technologies exploit chemical and physical properties to immobilize, remove, or destroy the targeted contaminants. Certain PFAS have recently been the subject of regulatory actions and attempted soil, sediment, and water remediation. These compounds have unique chemical properties that require new remediation technologies or innovative combinations of existing technologies. The decision to remediate PFAS should be driven by applicable regulations and an appropriate risk assessment.

USEPA has compiled an online resource for PFAS that includes topics such as policy and guidance, chemistry and behavior, occurrence, toxicology, site characterization, and remediation technologies (USEPA 2017h). The National Groundwater Association (NGWA) has also published a resource on PFAS that includes information about remediation technologies (NGWA 2017).

### 1.1 PFAS Remediation Technologies Overview

Currently, full-scale PFAS treatment in water is limited to sorption using carbon, mineral media (for example, clay), or a combination of these. Additional pilot and bench-scale technologies are currently being tested. This fact sheet discusses the treatment technologies that have been successfully demonstrated through pilot testing at the field-scale. The accompanying tables summarize technologies that have only been tested in limited applications or in laboratory bench tests. Combining technologies may overcome limitations of any one given technology or expand the efficacy of each technology.

For each technology presented, this fact sheet discusses the following key elements:

- *Treatment Description* (according to each applicable media)

- *Treatment Mechanism* (for example, separation, sorption)

- *State of Development* – Is the technology at lab or bench-scale, field pilot-scale, or full-scale implementation? How many demonstration tests and what is the degree of commercialization for each technology?

- *Effectiveness* – Summary of demonstrated effectiveness on a broad range of PFAS (for example, Method 537 (Shoemaker, Grimmett and Boutin 2009) suite plus fluorotelomer sulfonates), a limited subset (for example, Third Unregulated Contaminant Monitoring Rule [UCMR3] list USEPA 2017f), or only perfluorooctane sulfonate (PFOS) and/or perfluorooctanoate (PFOA).

- *Sustainability Considerations* – Design considerations are evaluated including green remediation elements such as carbon footprint from energy usage, treatment media, and residual handling transport, as well as potential community impacts.

ITRC has developed a series of fact sheets that summarize the latest science and emerging technologies related to PFAS. The purpose of this remediation fact sheet is to:

- provide an overview of remedial technologies and methods for treatment of solids (for instance, soil or sediment) and liquids (for instance, groundwater, leachate, or surface water);

- describe processes for the treatment of PFAS that are now in use or are under development; and

- describe the challenges and limitations for each treatment technology.

The current state of full-scale PFAS treatment in water is limited to sorption using carbon and/or mineral media (for instance, clay).

Two supporting tables comparing PFAS remediation technologies are available in a separate Excel file: Table 1, Solids Comparison, and Table 2, Liquids Comparison. The tables present all reported treatment technologies, including those tested only at the laboratory/bench scale. To be included in the tables, a technology must have been documented in a publicly available document. Some technologies, however, are only documented in literature supplied by the inventor/researcher/vendor of that technology, with no independent confirmation or peer-review process—be aware of possible biases. ITRC periodically updates the supporting tables and maintains the most current version on its website.

Air treatment is not included in this fact sheet because the current research is limited, and this topic is less applicable to site remediation projects.

## 1.2 Factors affecting remedy selection

Site characteristics that affect PFAS remedy selection include the nature of the source, release pathways, affected receptors, and fate and transport in the environment (see *Site Characterization Considerations, Sampling Precautions, and Laboratory Analytical Methods; Environmental Fate and Transport;* and *Naming Conventions and Physical and Chemical Properties* fact sheets). Other site characteristics relevant to remedy selection may be identified as remedial technologies advance. Strategies for remediation of the broader class of PFAS may require complementary technologies, several of which are still being developed, as described in Tables 1 and 2.

Other factors affecting PFAS remedy selection include:

- **Characteristics of PFAS**. The wide-ranging chemical and physical characteristics of PFAS affect the remedy effectiveness. Key factors include ionic state (anionic, cationic, and zwitterionic), types of ionic groups (sulfonate or carboxylate), lipo- and hydrophobicity, nature and reactivity of alkyl groups, chain length and branching, partitioning coefficients, volatility, solubility, and acidity.

> Factors specifically challenging for PFAS remediation include:
>
> - Multiple ionic states
> - Variable isomers
> - Differing alkyl groups
> - Past remediation effects
> - Common co-contaminants

- **Changes in PFAS properties**. Chemical and physical properties resulting from naturally occurring processes or due to 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 PFAS may be more readily subject to chemical or biological transformation than the fully fluorinated aliphatic chain. This is the basis, for example, for the total oxidizable precursor (TOP) assay to estimate concentrations of precursor compounds (Houtz and Sedlak 2012).

  - 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, pH, or other geochemical characteristics) during remediation of comingled contaminants results in a conversion of PFAS to the more stable and mobile perfluorocarboxylic acids (PFCAs) (McKenzie et al. 2015, 2016).

- **Community acceptance**. Communities are often faced with trade-offs in terms of cost, level of clean-up, and residual contamination as part of remediation efforts. Stakeholder engagement and effective risk communication strategies are an important aspect of the overall remedial technology selection process, especially where off-site receptors are identified.

## 1.3 Technical Maturity

The treatment technologies described here are organized by degree of current confidence in the technology. Three levels of confidence are defined as follows:

- *Demonstrated Technologies*—Technologies that have been demonstrated under pilot or full-scale conditions and are well documented for multiple applications in peer-reviewed literature. These technologies are discussed in greatest detail.

- *Partially Demonstrated Technologies*—Technologies that have been documented in peer-reviewed literature by multiple researchers or practitioners but have only been executed at the laboratory or bench scale. These technologies are briefly mentioned.

- *Promising Technologies*—Technologies that have been demonstrated at the laboratory or field pilot-scale, but the results have not been rigorously peer reviewed. Often, these results are only reported by one group (for example, one university, practitioner, or vendor) or lack detailed validation of the treatment or mechanisms. These technologies are omitted from the text and presented only in the technology comparison tables (Tables 1 and 2).

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.

## 2 Technologies for Treatment of Solids

Several technologies are currently available to remediate PFAS in solids. Most of these technologies have been demonstrated on soils only but may also apply to saturated sediments or sludge treatment.

| Field-Demonstrated Treatment Technologies for PFAS in Solids |
| --- |
| • Excavation and off-site landfilling or incineration<br>• Sorption/stabilization through ex situ soil mixing<br>• Ex situ thermal desorption and off-gas destruction |

### 2.1 Capping

**Technology Description:** Capping places a cover over contaminated material such as landfill waste, contaminated soil, and sediments. Caps do not destroy or remove contaminants. The purpose of the cap is to prevent contact with the contamination and, depending on the design, to reduce or prevent further leaching of contaminants. For PFAS soil sites, the main purpose of a cap is to reduce or prevent further leaching of contaminants from soils to groundwater.

**Treatment Mechanism:** Caps isolate contaminants and prevent them from spreading and causing exposure by direct contact.

**State of Development:** Capping is a viable remediation method because it is simple technology that applies to most contaminants. Although capping has not been applied to a PFAS site, based on documented successes with other contaminants it offers promise for PFAS.

**Effectiveness:** Capping may prevent exposure and potentially reduce infiltration, but redevelopment options for the capped land surface may be limited. Caps are most effective when the seasonal high-water table is well separated vertically from the base of the contaminated solids. The PFAS contamination will remain at the site and therefore be a long-term liability. Contaminants could mobilize if site conditions change (for example, rising water table). Caps incur maintenance costs to maintain the integrity of the cap and require institutional controls to ensure the cap is not breached by future site uses or redevelopment.

**Sustainability Considerations:** The carbon footprint of capping includes earthwork equipment emissions and manufacturing and transporting capping material. Ecosystem restoration can be incorporated into the capping design (Lamb et al. 2014). Community impacts include truck hauling traffic and hindrance of redevelopment due to land use restrictions.

### 2.2 Excavation and Disposal

**Technology Description:** This remediation method includes removing contaminated soil and hauling it to a permitted landfill or incineration facility, then filling the excavated area with clean backfill.

**Treatment Mechanism:** This method isolates PFAS from receptors. Sometimes, PFAS-impacted soil is stabilized or solidified before disposal into a landfill. Disposal of PFAS-impacted soils or wastes into unlined landfills should be avoided. More studies are needed on interactions of PFAS with landfill linings.

Some states may require PFAS-contaminated solids to be treated at a Resource Conservation and Recovery Act (RCRA) permitted incinerator. The estimated temperature to destroy specific PFAS varies widely, from around 300° to greater than 1,000°C (Vecitis et al. 2008). Commercial incineration is often the only viable disposal option for media contaminated with PFAS.

**State of Development:** Solid wastes generated from environmental investigation and cleanup (for example, soil excavation, and investigation- and remediation-derived wastes) have been disposed at lined landfills, and therefore this is considered a well-demonstrated technology. PFAS have been reported in landfill leachate (Lang et al. 2017), although it is unlikely the source for these PFAS is investigation derived waste, as opposed to consumer product waste containing fluorochemicals. The combination of soil excavation and incineration is also considered to be a viable remedial option.

*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. Additionally, some nonhazardous waste landfills do not accept PFAS waste. Disposal of PFAS waste to landfills potentially adds to the PFAS contaminant load in the landfill leachate. In some states, the leachate is not analyzed or regulated for PFAS.

*Sustainability Considerations:* The carbon footprint for this approach includes earthwork equipment emissions, transporting contaminated soil and backfill, and manufacturing (such as resource extraction) of backfill material. Landfill incineration of the contaminated soil is energy intensive. Truck hauling traffic affects the local community. Guidance is available for performing a sustainability assessment for an excavation and disposal remedial design (Cappuyns and Kessen 2014; Goldenberg and Reddy 2014; Söderqvist et al. 2015; Song et al. 2018).

## 2.3 Sorption and Stabilization

*Technology Description:* Amendments added to the soil reduce or remove the potential for PFAS to mobilize from soil to groundwater.

> A few commercially available sorbents have been specifically developed to immobilize PFAS in soil.

*Treatment Mechanism:* Amendments adsorb or stabilize PFAS. These amendments include activated carbon and carbon nanotubes (CNTs), resins, minerals, biomaterials, and molecularly imprinted polymers. The amendments bind to PFAS and thus reduce their release from soil.

*State of Development:* Sorption and stabilization techniques using carbon-based amendments are considered partially demonstrated technologies. Both granular activated carbon (GAC) and powdered activated carbon (PAC) rapidly remove PFAS from groundwater and surface water and can be applied to soil, but efficacy is reduced in the presence of organic co-contaminants (NGWA 2017). Performance also depends on PFAS chain length and functional group (Xiao et al. 2017). Laboratory tests should be conducted using site specific soils and the stabilizing amendment before field application to ensure success. Carbon amendments can be modified to enhance their sorption of PFAS. One patented amendment is carbon enhanced with aluminum hydroxide, kaolin clay, and other proprietary sorbents (USEPA 2017p).

Sorption and stabilization techniques using non-carbon-based sorbents, such as iron oxide minerals and modified organoclays (such as montmorillonite [Mt], hydrotalcite, and palygorskite) are promising, but only limited tests have been conducted. Minerals such as clays, silica, iron oxides, and zeolites have been used as sorbents for removing contaminants from groundwater and soil (Zhu et al. 2016; Rattanaoudom, Visvanathan, and Boontanon 2012; Zhou et al. 2010; Zhou, Pan, and Zhang 2013). The surface of organoclays can also be modified for enhanced PFOS and PFOA sorption (Zhou et al. 2010; Kambala and Maidu 2013; Zhu et al. 2016). Additionally, an amine-modified palygorskite clay sorbent has been patented for the treatment of PFOS and PFOA (Kambala and Maidu 2013).

*Effectiveness:* Carbon- and mineral-based sorption and stabilization techniques vary in their effectiveness according to site conditions and PFAS type. An example of a site condition that can affect sorption is high organic matter in soil, which can foul carbon sorbents with competing compounds. PFAS type affects sorption in that PFAS often occur as mixtures, including PFAS of different chain lengths with varying sorption characteristics. Sorption capacity was assessed in one study where CNTs were mixed with sediments at 4% weight per weight (w/w), and the sorption capacity of the sediment increased in comparison to untreated sediment (Kwadijk, Valzeboer, and Koelmans 2013).

Organoclays are used because they are environmentally benign, have a high sorption capacity, and can be easily modified to enhance their sorption capacity with mesopores. Organoclays have also been proven to work on several classes of contaminants (Zhu et al. 2016; Espana, Mallavarapu, and Naidu 2015; Zhou et al. 2008). The surface of organoclays are hydrophilic, and therefore ineffective for sorption of hydrophobic organic compounds like long-chain PFAS; however, modification with cations changes the surface to lipophilic. For example, Mt often exists as Na-Mt with a sodium cation on the surface, which is lipophilic and may be effective for long-chain PFAS.

Biomaterials such as chitosan, straw, and quarternized cotton do not perform as well as other sorbents, and the biomaterials may eventually degrade (Du et al. 2014).

Sorption and stabilization do not destroy PFAS, and information on the long-term stability of amendments for PFAS remediation is a data gap that currently limits their use. The amended soil can be mixed with concrete and other stabilizers to better trap the PFAS.

*Sustainability Considerations:* The carbon footprint for sorption and stabilization includes emissions from earthwork equipment, manufacturing (for example, resource extraction), and transporting amendment material. Community impacts include hindrance of redevelopment due to land use restrictions. Resources are available for performing a sustainability assessment for sorption and stabilization remedial design (Goldenberg and Reddy 2014; Hou et al. 2016; Kuykendall and McMullan 2014).

## 2.4 Thermal

*Technology Description:* The mobilizing or destruction of chemicals using heat.

*Treatment Mechanism:* Heat is applied directly to the PFAS-contaminated soil. High temperatures can vaporize the chemicals or potentially destroy them. Vaporized chemicals can be captured and destroyed in off-gas treatment.

*State of Development:* Ex situ thermal treatment has been demonstrated at the field pilot-scale by a few technology vendors and is considered a partially demonstrated technology (Endpoint Consulting 2016; Enviropacific 2017). The use of this technology for PFAS-contaminated soil is still developing. Limited data sets are available, and several data gaps still exist. Additionally, no documented examples of in situ thermal treatment for PFAS-impacted soil have been identified.

*Effectiveness:* Results of one test indicated that the complete removal of a suite of nine PFAS was possible within 30 minutes but required temperatures over 900º C (Endpoint Consulting 2016). In another field pilot project, concentrations of 20 PFAS in soil were reduced to below reporting limits—greater than 99.9% reduction (Enviropacific 2017). At this time, it is unknown whether the pilot test resulted in volatilization or complete destruction. This test was performed at relatively lower temperatures (for example, approximately 450º C). There are still several data gaps related to thermal incineration of PFAS that should be considered when applying this technology. For example, the mass balance to assess whether PFAS are destroyed or simply mobilized is not completely understood.

*Sustainability Considerations:* Thermal treatment is an energy-intensive remediation method. Its carbon footprint includes the energy source and consumption during treatment system operation, as well as manufacturing and installation of heating system materials. Community impacts include managing the risks of potential vapor intrusion from volatile co-contaminants. Guidance is available for performing a sustainability assessment for thermal remedial design (Song et al. 2018; Vidonish et al. 2016).

# 3 Liquids Treatment

Several technologies are currently available for remediating PFAS in liquids. These technologies can be applied to drinking water supplies, groundwater, industrial wastewater, surface water, and other miscellaneous applications (such as landfill leachate). Influent concentrations of PFAS can vary by orders of magnitude for specific media or applications. These influent values, along with other general water quality parameters (for example, pH) can influence the performance and operating costs for the treatment technologies.

| **Field Demonstrated Treatment Technologies for Liquids** |
| --- |
| • Extraction and sorption with granular activated carbon or anion exchange resin |
| • Extraction and membrane filtration/reverse osmosis |
| • Extraction and precipitation/flocculation |

## 3.1 Sorption

Many organic compounds can be treated by passing contaminated water through special granular media. The mechanism of this technology varies depending on the media, contaminant, and influent concentrations. There are two broad categories of PFAS sorption treatment: adsorption onto carbon media and ion exchange.

### 3.1.1 Granular Activated Carbon

*Technology Description:* Granular activated carbon (GAC) is made from organic materials, such as coal and coconut, which serve as effective adsorbent media because they are highly porous and provide a large surface area for contaminant contact. GAC treatment can be used for any aqueous-based treatment application (for example,

municipal drinking water, groundwater, point-of-use residential, industrial wastewater, and landfill leachate). The GAC media is placed in packed-bed, flow-through vessels generally operated in series (lead-lag configuration). Either virgin or reactivated GAC can be used for most applications, but virgin GAC is the industry preference for more risk-averse drinking water applications. Commercial facilities in the United States conduct thermal reactivation of spent GAC, which can provide a more sustainable and less costly replacement option than virgin GAC and off-site disposal. To address concerns about using reactivated GAC, vendor bench-scale column studies can be performed prior to initial usage, and a quality control testing program can be implemented prior to delivery of each shipment.

**Treatment Mechanism:** Removal of PFAS from treated water by GAC is an adsorption process, as well as a physical mass transfer process from the aqueous phase onto solid media that does not involve any form of chemical degradation or transformation. Adsorption is a surface chemistry phenomenon by which an aqueous phase contaminant adheres to the surface of a granular media (via electrical, physical, or chemical processes), but does not penetrate it. The GAC adsorption capacity can vary considerably by media and contaminant. Adsorbent media must be removed and replaced when it becomes spent, meaning contaminants break through at concentrations above some established criteria. The spent media must be replaced and shipped off-site either for disposal (by landfilling or commercial incineration) or to be regenerated/reactivated for reuse consistent with applicable federal and state regulations.

**State of Development:** GAC is a demonstrated technology and is currently the most common water treatment method used for PFAS. Because of the limited treatment history and available technologies for PFAS, full-scale applications to date have mostly focused on higher priority private and public water supply and residential point-of-use treatment. Currently, only a few operating groundwater pump-and-treat applications use GAC treatment. Much of the published literature on GAC treatment of PFAS involves bench-scale and vendor column studies. Treatability data for full-scale operations involving different technologies, including GAC, have also been compiled and reported for several municipal wastewater treatment plants where PFAS have been detected in the influent.

Many sources in the literature support the use of GAC: Appleman et al. (2013); Szabo et al. (2017); and Woodard, Berry, and Newman (2017); and others cited in this section. These references also include more comprehensive bibliographies if further details are needed on specific topics or studies.

**Effectiveness:** GAC has been shown to reduce select PFAS to very low or nondetectable concentrations, on the order of nanograms per liter (equivalent to parts per trillion), with reported removal efficiencies in various references between 90% and >99%. The lower end of these reported GAC removal efficiencies may be the result of the faster breakthrough times for the short-chain PFAS (Xiao et al. 2017; Dickenson and Higgins 2016). Early municipal treatment plant sampling studies focused mostly on PFOA and PFOS, which are considered long-chain PFAS (defined as six carbon atoms or more) and currently drive most drinking water treatment decisions. Consequently, the shorter breakthrough times for PFAS with five carbon atoms or less were initially missed, and subsequently reported in the literature as lower GAC removal efficiencies.

> Breakthrough and GAC usage should be checked for a variety of PFAS, not just PFOA or PFOS, including various chain-lengths.

Individual PFAS have different GAC usage capacities and corresponding breakthrough times. GAC removal capacity for PFOS is greater than PFOA, but both can be effectively captured. In general, PFAS containing five carbon atoms or less have higher GAC usage and much quicker breakthrough times than PFAS containing six carbon atoms or more with other factors being equal (such as influent concentration). Vendor column studies (Brewer 2017) with equivalent influent concentrations and empty contact bed times have shown that short-chain PFAS breakthrough times are approximately five times quicker than long-chain PFAS. Pilot and full-scale GAC treatment data show similar comparative breakthrough times (Brewer 2017).

In addition to usage capacity, several other factors affect GAC change-out frequency and cost for individual PFAS (for example, influent concentrations). Change-out frequency therefore cannot be predicted solely by the presence of specific short-chain PFAS. When concentrations of short-chain PFAS are much lower than concentrations of long-chain PFAS, GAC is still a cost-effective treatment for PFAS other than PFOA and PFOS. Because of the differences in GAC usage capacities between individual PFAS, treatability studies must evaluate the entire mixture of PFAS present in the influent to the extent practicable. Column studies are the best method to predict GAC performance and change-out frequency.

Column studies show that virgin GAC and thermally reactivated GAC have similar removal rates and breakthrough times (Brewer 2017). Based on vendor feedback (Mimna 2017), commercial thermal reactivation is performed at higher

operating temperatures than steam or nitrogen regeneration systems and is capable of complete desorption and destruction of PFAS from spent GAC (Watanabe et al. 2016; Yamada et al. 2005). Also, vendor testing demonstrates that re-agglomerated bituminous coal provides better removal performance for PFAS than other types of GAC (Brewer 2017; Nowack 2017).

***Sustainability Considerations:*** The carbon footprint for GAC includes energy source and consumption during treatment system operation, as well as manufacturing/disposal of treatment media. Spent single-use media requires incineration, which increase the carbon footprint. Regenerable media presents sustainability benefits because the media is reused; however, in drinking water applications, virgin material achieves greater confidence in treatment. Resources are available for performing a sustainability assessment for sorption remedial design (Amini et al. 2015: Choe et al. 2013, 2015; Dominguez-Ramos et al. 2014; Favara et al. 2016; Maul et al. 2014; Rahman et al. 2014; Ras and von Blottnitz 2012).

## 3.1.2 Biochar

***Technical Description:*** *Biochar* is a hybrid word derived from *biomass* and *charcoal*. Biochar is a carbon-rich, porous solid synthesized from biomass, such as wood or manure, through a high-temperature low-oxygen process called "pyrolysis" (Ahmad et al. 2014). Key factors controlling the properties of biochar (for example, pore size, chemical composition, and hydrophobicity) include the temperature of pyrolysis and biomass feedstock.

***Treatment Mechanism:*** The properties of biochar are comparable to those of GAC for sorptive purposes. Like GAC, biochar can adsorb organic contaminants.

***State of Development:*** Biochar is considered a partially demonstrated technology. Various laboratory experiments have evaluated the efficacy of biochar compared to other media, but no full-scale treatment systems are in place for the removal of PFAS. This work demonstrates that biochar is potentially viable for treatment of PFAS, but additional research is needed to fully establish viability and costs.

***Effectiveness:*** Xiao et al. (2017) compared one GAC and two commercially available biochars for treating an aqueous film-forming foam (AFFF)-impacted water supply. Based on batch studies, they concluded that biochars with large surface areas could be an alternative to GAC, although variability in biochar properties relative to GAC may affect reliability. While biochar removal is effective in ultrapure water, when used to treat river water (with more complicated water chemistry), biochar is ineffective compared to ion exchange and GAC and exhibited significantly slower adsorption kinetics (Rahman 2014).

***Sustainability Considerations:*** The carbon footprint of this technology includes energy source and consumption during treatment system operation, as well as manufacturing/disposal of treatment media. The use of waste material as a starting feedstock results in a lower overall carbon footprint, though reactivation of biochar is not currently feasible and energy-intensive incineration or landfilling are required, which offsets some of the sustainability benefits.

## 3.1.3 Ion Exchange

***Technology Description:*** Ion exchange (IX) uses synthetic, polymeric media to remove PFAS from water. IX media are employed similarly to GAC and can be used in combination with GAC.

Both regenerable and nonregenerable IX media are available. Nonregenerable IX is a single-use, disposable medium. Regenerable IX theoretically can be used indefinitely, however, insufficient operational data are available to understand its long-term durability. IX regeneration is a chemical process; the only demonstrated successful regeneration solution is a solvent-brine solution (Amec Foster Wheeler 2017). The regenerant solution can be distilled for reuse. The distillate residue is a concentrated PFAS waste that can be managed by off-site treatment (for example, incineration or possibly chemical oxidation).

***Treatment Mechanism:*** IX is the process by which ions of one substance are replaced by similarly charged ions of another substance. The term denotes purification, separation, and decontamination of aqueous and other ion-containing solutions with solid polymeric or mineralic ion exchangers. Many organic contaminants are ionic and can be removed through specialized ion exchange media. The media are often derived from organic polymers or plastic, and thus ion exchange media are referred to as "resins." Regeneration of ion exchange resins is accomplished with a chemical flush, typically a highly acidic or basic solution, brine solution, or solvent-brine solution, rendering the resin reusable.

To date, IX has used positively charged, anion exchange media to remove negatively charged PFAS molecules, via binding of the carboxylic and sulfonic acid "heads" of perfluoroalkyl acids (PFAAs). Such IX media are manufactured to

be more selective for PFAS than for typical competing mineral anions such as sulfate and nitrate. The fluorinated carbon chain of the PFAS molecule can also adsorb to IX media. This dual-mechanism, ion exchange plus adsorption, can result in higher removal compared to adsorption alone (Yu et al. 2009).

*State of Development:* IX is a fully demonstrated technology. Column tests comparing both regenerable and single-use ion exchange media have shown IX to be effective for the removal of several PFAS (Woodard, Berry, and Newman 2017; Conte et al. 2015). Full-scale IX systems are currently in operation in Australia at Australian Defense sites, and a full-scale system was installed in the United States in 2017. The U.S. Department of Defense (DOD) recently funded a SERDP project, ER18-C2-1306: "Combined In Situ/Ex Situ Treatment Train for Remediation of Per- and Polyfluoroalkyl Substance (PFAS) Contaminated Groundwater" to optimize regenerable IX and on-site destruction with plasma under a number of laboratory conditions (SERDP-ESTCP 2017).

*Effectiveness:* IX is a demonstrated effective technology for removal of anionic PFAS. It has higher adsorption capacity for some PFAS and significantly faster reaction kinetics compared to GAC (Conte et al. 2015). The combination of these properties means an equivalent treatment system for IX is smaller and thus uses less media. Like GAC, usage capacities and corresponding breakthrough times vary depending on PFAS functional groups and chain length. Short chain PFAS may break through faster under certain influent conditions. However, certain single-use IX media have been identified that may have higher usage capacities for short-chain PFAS. An IX treatment system can also include multiple vessels in a lead-lag configuration, consisting of both single-use and regenerable IX media. This design optimizes removal properties and operating costs for a mixture of short and long-chain length PFAS.

*Sustainability Considerations:* The carbon footprint for IX includes energy source and consumption during treatment system operation, as well as manufacturing/disposal of treatment media. Spent single-use IX media requires incineration or other treatment for disposal, resulting in an increased carbon footprint. Regenerable IX media offers sustainability benefits because the media can be reused, but the process for regenerating requires energy and creates a concentrated waste stream which must be managed. Disposal or treatment of the regenerant stream can be problematic and expensive. Regeneration solutions may present exchange system and treated water corrosion issues if media are not rinsed thoroughly prior to being placed back in service.

## 3.2 Precipitation/Flocculation/Coagulation

*Technology Description:* 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 metals plates inserted into the water (electrocoagulation).

*Technology Mechanism:* Coagulants assist in forming 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, filtration, or a combination of both processes. The solid material containing the PFAS requires disposal.

*State of Development:* Current literature only documents bench-scale study results on treating PFAS via precipitation, flocculation, or coagulation and 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 and Alden 2017).

Unconventional precipitation (for example, electrocoagulation or advanced chemical precipitants) has shown more potential for direct PFAS treatment, but little data is available.

*Effectiveness:* Electrocoagulation reactors, which range from basic to sophisticated designs, are highly efficient, compact, relatively low-cost, and completely automatable (Baudequin et al. 2011; Lin et al. 2015a). 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. 2015a).

One commercially available proprietary chemical product has been shown in tests to reduce PFAS in groundwater containing AFFF (Birk and Alden 2017; CH2M 2017). This research also shows that conventional (ferric salt) and proprietary chemicals in combination are more effective than either alone. Current data have been developed at elevated

concentrations, but removal for lower (µg/L) concentrations has also been shown (CH2M 2017; Birk 2015). No available data show precipitation effectiveness at very low (ng/L) concentration ranges.

Conventional PFAS precipitation induced by coagulation and flocculation has shown limited applicability for complete treatment of PFAS. Therefore, conventional chemical precipitation could be considered mainly as a pretreatment technology to sorb or precipitate PFAS prior to final filtration or destruction. Also, if used to remove conventional parameters such as solids or natural organic material (NOM), pretreatment would allow PFAS removal technologies to achieve the desired treatment goals in a more cost-effective and technically feasible manner.

***Sustainability Considerations:*** The carbon footprint of this technology includes energy source and consumption during treatment system operation, as well as manufacturing of treatment media. Additionally, extracted solids containing PFAS require final disposal or destruction.

## 3.3 Redox Manipulation

***Technology Description:*** Redox manipulation is the process of changing the oxidation-reduction potential of water through addition of oxidizing or reducing amendments, or by adding energy to a system to create oxidizing or reducing free radicals. These changes affect the mobility or structure (transformation or destruction) of the PFAS. PFCAs are generally more amenable to redox manipulation than perfluoroalkane sulfonic acids (PFSAs). Redox manipulation may be effective at treating many co-contaminants and may also alter organic matter, which can affect PFAS mobility. These system changes may allow subsequent treatment steps to manage target PFAS more effectively.

***Treatment Mechanisms:*** Redox manipulation mechanisms may include both redox transformation (oxidative, reductive, and nucleophilic processes) of PFAS and changes in redox conditions in the impacted media (for example, groundwater), resulting in changes in the mobility and sorption of PFAS (McKenzie et al. 2015; Arvaniti et al. 2015). Redox transformation involves the transfer of electrons between reactants. In oxidative processes, electrons are transferred to the reactive species (the oxidant) from the target (PFAS), whereas in reductive processes the opposite occurs. In nucleophilic processes, a reactant (the nucleophile) bonds with the PFAS compound and displaces an atom or group of atoms from the PFAS molecule.

Susceptibility to redox transformation depends on reaction conditions and the reactive species involved. For some specific technologies, more than one transformation mechanism or reactive species may be involved. For example, plasma, sonolytic, and photolytic technologies may combine physical (high-temperature pyrolysis) and free radical attack processes. PFAS carbon chains do not easily transform, because their carbon-carbon bonds are shielded in part by the tightly bound fluorine atoms that surround the carbon chain (Kissa 2001). The carboxylic or sulfonic group "heads" of PFAS are commonly more susceptible to redox transformation than carbon chain "tails," resulting in partial transformation of the parent compound but not in cleavage of the aliphatic chain (Houtz and Sedlak 2012; Anumol et al. 2016). The tail and head structure are illustrated for PFOS and PFOA in the following figure.
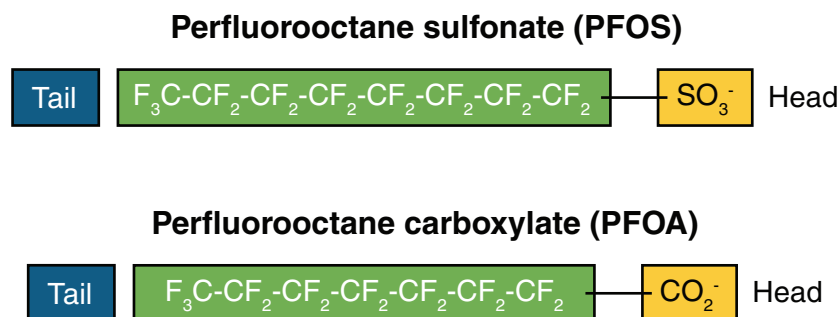
### Perfluorooctane sulfonate (PFOS)

| Tail | $F_3C$-$CF_2$-$CF_2$-$CF_2$-$CF_2$-$CF_2$-$CF_2$-$CF_2$ | $SO_3^-$ | Head |

### Perfluorooctane carboxylate (PFOA)

| Tail | $F_3C$-$CF_2$-$CF_2$-$CF_2$-$CF_2$-$CF_2$-$CF_2$ | $CO_2^-$ | Head |

**Figure 1. The tail and head structure of PFOS and PFOA molecules.**

Reactions of zero valent metals with PFAS, generally considered a reductive process, may also affect mobility and sorption of PFAS in addition to (or rather than) PFAS transformation (Arvaniti et al. 2015). Complete mineralization/ defluorination of PFAS via zero valent metal reactions has not been demonstrated to date; however, research in this area is ongoing.

Combined redox and nucleophilic attack almost completely mineralize PFOA (Niu et al. 2012; Mitchell et al. 2014). A reactant formed in several redox manipulation approaches, the solvated electron (free electron in solution), shows promise for PFAS destruction (Park et al. 2009; Gu et al. 2016; Li et al. 2012; Stratton et al. 2017; Blotevogel, Giraud, and Borch 2018).

***State of Development:*** Redox technologies have not been widely applied beyond laboratory bench-scale tests because of concerns that partial transformation (as opposed to complete destruction) will produce more mobile or toxic products. Therefore, redox technologies are considered a partially developed technology, with both successes and challenges. For example, chemical oxidation affects PFAA transport, but the direction (increased or decreased transport) and magnitude depend on reaction conditions (McKenzie et al. 2015). Apparent in situ destruction of PFAAs in groundwater at a fire training site has also been achieved using a combined ozone/persulfate approach (Eberle, Ball, and Boving 2017). The main difficulty in using redox-based technologies is achieving extremely low (ng/L) PFAS cleanup objectives, particularly for in situ remedies. Additionally, reactive species (for example, oxidizing radicals) interact with other compounds present in soil and groundwater that are more susceptible to oxidation and are at relatively higher concentrations than the target PFAS.

Despite these challenges, several options show promise for ex situ treatment, including electrochemical (Schaefer et al. 2015; Urtiaga et al. 2015), sonolytic (Vecitis et al. 2008; Rodriguez-Freire et al. 2015), plasma (Stratton et al. 2017), and reductive (Arvaniti et al. 2015) technologies. These approaches have successfully degraded an array of high-concentration PFAS at the laboratory scale. However, none of these technologies are sufficiently mature yet to assess PFAS treatment costs and overall effectiveness with confidence.

***Effectiveness:*** A wide range of PFAS treatment methods based upon oxidation-reduction chemistries have been evaluated. These studies demonstrate the following:

- PFAS exhibit a wide range of reactivity toward destructive processes, based upon characteristics including chain length, nature of alkyl groups, and branched versus linear isomers.

- Treatment of PFAS at AFFF sites depends on the composition and production processes of the given AFFF formulation used at the site.

- Except for limited field pilot testing of one ozone and one persulfate-based chemical oxidation technology, none of the technologies summarized in Table 2 have matured beyond laboratory-scale studies.

- While promising, the relatively few field pilot applications have not yet been closely analyzed or duplicated in highly controlled and monitored studies.

Partial transformation can affect other physical and chemical characteristics of PFAS (see Section 1.2). For instance, persulfate-based transformation of PFAS may be incomplete (Houtz and Sedlak 2012) or negligible (McKenzie et al. 2015, 2016), whereas in other cases efficient transformation is reported (Hori et al. 2008; Lee et al. 2009; Liu et al. 2012; Park et al. 2016; Yin et al. 2016). Redox processes in the subsurface can generate unwanted byproducts (for instance, nitrate and bromate from chemical oxidation) depending on site and reaction conditions (Siegrist, Crimi, and Simpkin 2011). Site-specific treatability tests are recommended.

***Sustainability Considerations:*** The carbon footprint for this technology includes energy source and consumption during treatment system operation, manufacturing of amendment materials, and manufacturing and installation of injection points (if implemented in situ). Electrochemical treatment options also require handling of hazardous investigation derived waste, which is a sustainability consideration.

## 3.4 Membrane Filtration

Membrane filtration refers to a variety of separation technologies based on the nominal size of the membrane pores. Types of membranes include reverse osmosis (RO), nanofiltration (NF), microfiltration (MF), and ultrafiltration (UF). Low pressure membranes such as MF and UF cannot reject PFAS since their pore sizes are larger than the effective diameter of the PFAS molecules (about 1 nm) (Tsai et al. 2010; Rahman et al. 2014). For that reason, MF and UF are not discussed here. Although bench-scale studies indicate that the membrane molecular weight cut-off (MWCO) of NF/RO is probably the most important factor for removal of PFAS for these technologies, other factors, such as ionic charge, may also influence performance.

Two terms, "salt passage" and "salt rejection," generally describe how membrane systems perform. Salt passage is the percentage of dissolved constituents (contaminants) in the feedwater allowed to pass through the membrane. The opposite of salt passage, salt rejection, is the percentage of feed water that does not pass through the membrane. In

general, NF membranes have lower rejection rates (95%) than RO (> 99%), because NF membranes have larger pores (Rahman et al. 2014 provides an excellent review of many of the relevant studies). As with all other treatment options, bench-scale and pilot-scale testing are required to understand the field applicability and establish essential detailed design criteria such as pretreatment needs and cost effectiveness.

## 3.4.1 Reverse Osmosis

*Technology 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 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.

> Reverse osmosis is most useful as one element within a treatment train, where the reject water is further treated or captured.

*Treatment Mechanism:* RO separates 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 and particles present.

*State of Development:* RO has been studied in bench-scale studies and pilot plants for wastewater and drinking water PFAS applications and is considered a partially developed technology. Conventional and advanced treatments have been studied in several pilot plants and drinking water treatment plants, demonstrating both treatments operating simultaneously as well as the effectiveness of traditional drinking and wastewater treatment methods alongside PFAS-specific technologies.

*Effectiveness:* Influent pretreatment is critical for RO membranes because of their spiral-wound design. Membranes are highly susceptible to fouling (loss of production capacity) because some accumulated material cannot be removed from the membrane surface.

RO removal of PFAS from various waters has been studied (for example, semiconductor wastewater, drinking water, surface water, and reclaimed water), combined with NF in some cases. PFOS removal > 99% was achieved using four different types of membranes over a wide range of feed concentrations, from 0.5 to 1500 mg/L (Tang et al. 2006). Another study tested five RO and three NF membranes at feed concentrations of 10 mg/L PFOS over four days (Tang et al. 2007). The PFOS rejection and permeate flux performances were > 99% for RO and 90 to 99% for NF. 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-Brugger et al. 2008; Tang et al. 2006). Conventional and advanced treatment efficiencies to remove PFOA and PFOS from surface water of the Llobregat River in northeast Spain were also studied. Results were compared in several pilot plants, and in a drinking water treatment plant that operates with UF and RO treatment alongside traditional treatment processes (Flores et al. 2013).

Another study examined the fate of PFSAs and PFCAs in two water reclamation plants that further treat water from wastewater treatment plants in Australia (Thompson et al. 2011). Plant A used adsorption and filtration methods alongside ozonation, while 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 perfluorononanoic acid (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).

*Sustainability Considerations:* The carbon footprint for this technology includes energy source and consumption during treatment system operation, as well as manufacturing/disposal of treatment media. RO requires power for high-pressure pumps and the management of concentrate, which can be energy intensive. The contaminant-rich brine rejected by RO must be disposed of appropriately. The removal of nontarget minerals from the treated water may increase its corrosivity, and posttreatment corrosion control measures are needed in most cases. Resources are available for performing a sustainability assessment for membrane filtration remedial design (Ras and von Blottnitz 2012).

### 3.4.2 Nanofiltration

*Technology Description:* 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 provides high water flux at low operating pressure (Izadpanah and Javidnia 2012). Like RO, NF is easy to operate and reliable for the removal of chemicals.

*Technology Mechanism:* Nanometer-sized membrane pores are used to separate compounds in a process similar to RO, but NF does not remove smaller ions such as chloride and sodium.

*State of Development:* NF is considered a partially developed technology because available data on the removal of PFAS are limited to laboratory-scale tests performed on flat sheet membrane coupons.

*Effectiveness:* No studies have reported either pilot or full-scale performance of NF membranes. Therefore, variations in performance due to fouling, flux, and concentration distributions in standard spiral-wound membrane configurations have not been characterized.

NF membranes tested include the Dow 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 g/mol to 713 g/mol (Steinle-Darling and Reinhard 2008; Appleman et al. 2013). However, lower rejections were observed for perfluoropentanoate (PFPeA) and perfluorooctane sulfonamide (FOSA)—about 70 and 90%, respectively (Steinle-Darling and Reinhard 2008). Recovery and salt passage information was not reported in these studies. Scaling up these results is challenging because rejection is affected by recovery, which can vary from one application to another.

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). PFOS salt passage also was correlated to sodium chloride salt passage, a common specification for membrane manufacturers (Tang et al. 2007). Salt passage incorporates both rejection and membrane recovery, therefore is a more useful parameter for predicting full-scale performance than rejection.

Pilot and full-scale testing of the selected NF membrane for PFAS removal is a crucial step when considering this treatment process. Choosing membranes with MWCO smaller than the targeted PFAS is also a key design consideration.

Appropriate disposal or treatment of the membrane concentrate stream is another design factor, especially when using high-pressure membranes for inland communities. Furthermore, NF membrane fouling mechanisms are poorly understood and further research is needed to develop cost-effective cleaning methods to restore membrane performance (Al-Amoudi and Lovitt 2007). As with other forms of filtration, pretreatment strategies to avoid fouling and membrane fabrication drive performance results.

*Sustainability Considerations:* The carbon footprint for this technology includes energy source and consumption during treatment system operation, as well as manufacturing/disposal of treatment media. NF requires power for pumps (generally less than RO), and the management of concentrate, which can be energy intensive.

## 4 References and Acronyms

The references cited in this fact sheet, and the other ITRC PFAS fact sheets, are included in one combined list that is available on the ITRC web site. The combined acronyms list is also available on the ITRC web site.
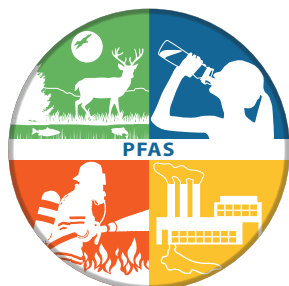
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