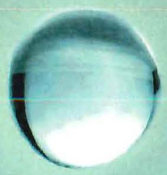
Environmental and Occupational Health Series

Perfluoroalkyl Substances in the Environment

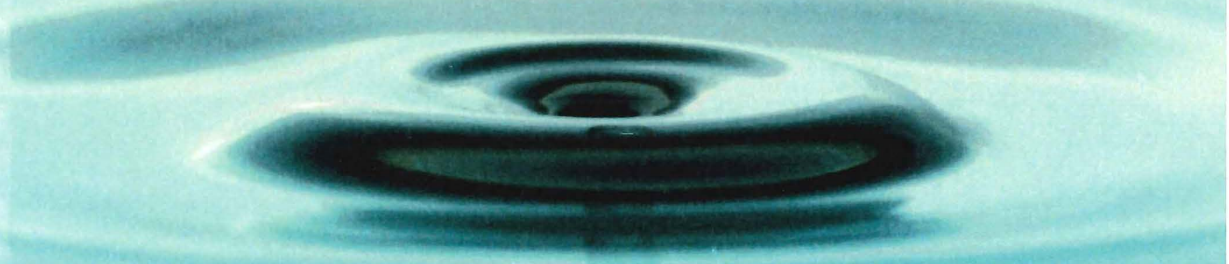
Theory, Practice, and Innovation



Edited by
David M. Kempisty
Yun Xing · LeeAnn Racz







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Foreword

Addressing the issues that poly- and perfluoroalkyl substances (PFAS) raise will be an enduring challenge for our generation of environmental engineers and chemists. Other classes of trace organic chemicals, such as pharmaceuticals and personal care products, may raise concerns wherever and whenever wastewater impacts our aquatic environment; however, to quote Calvin Coolidge, "Nothing in this world can take the place of persistence." In this manner, PFAS seem to have cornered the market.

It is not just the extreme persistence of their multiple carbon-fluorine bonds that have captured our attention. The unique surfactant behavior of many PFAS, particularly those associated with the use of aqueous film-forming foams (AFFFs), which are the focus of this book, is leading to many complications as we consider the environmental fate and transport of these otherwise relatively mobile substances. Moreover, as much as one might want to simplify the PFAS world into just perfluorooctanoate (PFOA) and perfluorooctane sulfonate (PFOS), the chemistry, and everything that goes along with it, is much more complex than I think many of us imagined when we first started to study these chemicals. It is not just about the anions—there are neutrals and cations too! Indeed, developing multiple lines of analytical evidence to demonstrate that one has accurately accounted for the diverse chemistry of PFAS present at AFFF-impacted sites is a current focus of many research groups. Though I am a reluctant analytical chemist, I seem to be more often suggesting that we simply embrace the complexity of the PFAS chemistry (as best we can) in the environment if we want any hope of making sense of the complicated web of precursors and products.

Of course, it is not just the chemistry of the PFAS themselves and what happens to them in the environment that is so complex: the multitude of uses of PFAS has also led to considerable confusion, or at least complexity, related to sources of exposure. Folks can get confused pretty quickly when you explain that the chemicals that they have used to keep stains off of their carpets and clothing are kissing cousins of those that were used to put out fuel fires and are now contaminating their drinking water supply. Never mind the fact that we are really only starting to scratch the surface with respect to understanding their toxicity. Nevertheless, the exposures that are happening and have happened are real, and the public is left wanting at least an explanation, if not a solution, to this complicated problem.

This leads me to why *this* book and why *now*. On the whole, this collection of information is just what is needed at this point in time. In November 2016 the US Environmental Protection Agency issued its long-anticipated health advisories for PFOS and PFOA in US drinking water supplies. Since then, there has been an onslaught of media coverage of the issue, with local press outlets reporting on every new groundwater plume. As a result, many nonacademicians are having to quickly come up to speed on a variety of topics and issues specific to PFAS. For those who have not been directly engaged with the scientific discussions on PFAS for the past 15 years, this could seem a very daunting task. What this book provides is

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information not just on the complicated chemistry and nomenclature, but also on the toxicology, regulatory approaches, analytical chemistry, and perhaps most importantly, the diverse ways in which environmental engineers are trying to remediate PFAS. Though it is downright impossible to capture every PFAS issue, particularly in this rapidly expanding research environment, Drs. Kempisty, Racz, and Xing have included a broad array of perspectives and cover an even broader array of PFAS topics. At the very minimum, this book will serve as an excellent gateway to the wild world of PFAS. Whether you are a federal, state, or local government official being thrust into the PFAS world, a student wanting to learn what all the fuss is about, or simply a member of the public trying to understand just why these chemicals are so difficult to treat, I would encourage you to engage with this book as much as you can. Take notes. Look up references. Follow your passion.

Good luck!

Christopher Higgins
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13 Reactivation of Spent Activated Carbon Used for PFAS Adsorption

John Matthis and Stephanie Carr

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13.1 INTRODUCTION

The reactivation of activated carbon is a well-established, high-temperature process for the thermal destruction of adsorbed chemicals, after which the reactivated carbon can be reused. The desorbed chemical constituents are thermally destroyed in the process, and the reactivation of spent carbon containing perfluorooctane sulfonate (PFOS), perfluorooctanoic acid (PFOA), and other poly- and perfluorinated

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alkyl substances (PFAS) has been practiced for more than 10 years. Thus, to understand the reactivation of spent activated carbon with PFAS, one must understand the process of reactivation.

Granular activated carbon (GAC) is a technology commonly used to remove organic species (volatile organic compound [VOC], total organic carbon [TOC], petroleum hydrocarbons, and PFAS) from a variety of water sources (groundwater, surface water, and wastewater). Activated carbon's service life is dependent on the capacity for components that require removal by a specific application and the treatment objective of the system. Once activated carbon's capacity becomes exhausted or is no longer meeting the required treatment objective of the system, the carbon is said to be "spent" or "exhausted." At this time, the spent carbon must be removed from the adsorption vessel and be replaced with a fresh carbon so that the system can continue to meet its treatment objective.

Once the spent carbon is removed from the vessel, there are three options that are typically available for dealing with the spent carbon: (1) disposal via landfill, (2) disposal via an incinerator (for destruction of the carbon and adsorbates or PFAS), or (3) reactivation of the spent carbon for reuse. Disposal options 1 and 2 can incur long-term liability or high costs. Thus, reactivation is an attractive option when it can be performed.

The term *reactivation* commonly refers to the use of a high-temperature thermal treatment process (approximately 1800°F) to completely remove all adsorbates on the spent carbon and either desorb, devolatilize, dissociate, or char the adsorbate in place in the carbon structure itself. The desorbed chemical constituents (whether desorbed completely or in pieces due to the dissociation of the chemical bonds) are thermally destroyed in the reactivation process, by which the spent activated carbon enters a furnace or kiln where temperatures are increased to approximately 1800°F. In addition to the adsorbed species being removed or destroyed in the reactivation process, there are also losses to the carbon structure (carbon atoms are removed) in this process or during the gasification steps. The removal of adsorbed species results in gaining back adsorptive capacity of the material; however, the loss of carbon structure/atoms results in a carbon pore structure that is different from the virgin carbon.

The term *regeneration*, which may also be familiar to the reader, is the restoration of a portion (not all) of the adsorptive capacity so that the carbon product can be used in another adsorption cycle. Methods include a low-temperature thermal (<400°F) procedure (using steam, air, nitrogen, or hot gas) or chemical extraction or solvent stripping (such as a pH swing to desorb some of the adsorbate from the spent carbon). It can be performed on site *in situ*. The additional adsorption cycles will have less adsorption capacity than fresh carbon. Regenerated carbon maintains the original carbon skeleton structure and can contain some to most of the original adsorbates. High-temperature thermal reactivation is the preferred method for reuse of activated carbon, since with efficient reactivation, most of the adsorptive capacity can be restored.

Carbon reactivation is usually performed at a centralized reactivation facility (some applications, such as sugar decolorization, may generate significant amounts of spent carbon to economically warrant an on-site carbon reactivation facility, but that is not usually the case with water treatment applications). This off-site reactivation facility can be (1) a facility that handles both industrial and potable spent carbons, permitted for both hazardous and nonhazardous spent carbon, or (2) a reactivation

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facility dedicated to custom-food-grade or drinking water spent carbon whereby the incoming spent carbon is segregated by customer, reactivated, and returned to the same customer or application.

In off-site carbon reactivation, the spent carbon is properly transported to a reactivation facility once the necessary waste profile and representative spent carbon sample have been tested or profiled and approved by the reactivation facility. The carbon is then reactivated for reuse by others (can be referred to as "pooled reactivation") or by the same customer (typically referred to as "custom reactivation").

Thermal reactivation is an attractive option from an environmental and cost standpoint. It uses fewer resources to reactivate a spent carbon than activate virgin carbon from a raw material source, reduces one's carbon footprint (produces only 20% of the greenhouse gases compared with virgin activated carbon production), minimizes waste, and can reduce operating costs through the continued use of a reactivated carbon versus a virgin activated carbon.

Commercial carbon reactivation services have been offered and conducted for more than 40 years for a wide variety of applications and adsorbates. Reactivation of spent carbons containing adsorbed PFAS (specifically PFOA or PFOS) has been performed commercially for more than 10 years.

13.2 BASICS OF REACTIVATION AND A CARBON REACTIVATION SYSTEM

As mentioned above, reactivation uses a high-temperature thermal process whereby adsorbed organic compounds (adsorbates) are destroyed and the GAC's adsorptive capacity is restored. Types of thermal reactivation hardware include multiple hearth furnace, rotary kiln (direct fired and indirectly fired), infrared belt furnace, and fluidized bed furnaces. A general overview of a carbon reactivation system is shown in Figure 13.1.

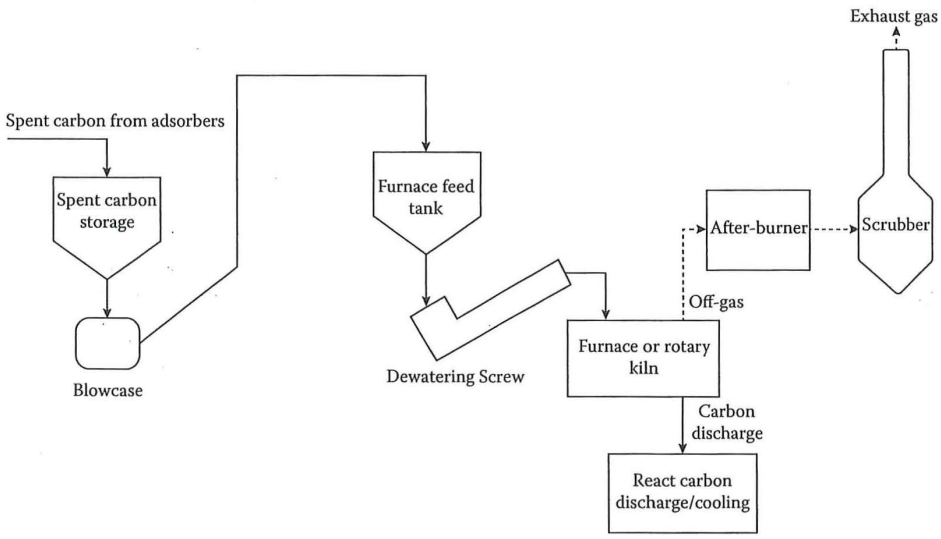


FIGURE 13.1 Generic layout for the typical reactivation process.

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A reactivation system will typically require spent carbon storage; a transport mechanism to a furnace feed tank and/or dewatering screw; the multiple hearth furnace or kiln; an afterburner; a furnace or kiln off-gas treatment, such as a chemical scrubber and/or particulate capture (baghouse); cooling of the reactivated carbon discharge; final product or carbon screening; and reactivated carbon storage. Pumps and/or blowcases will also be needed to convey the various carbon or carbon–water slurries throughout the process.

There are two primary types of reactivation furnaces that are commercially employed as the mainstay of a reactivation system: a multiple hearth furnace or a rotary kiln. More will be discussed about these two types of furnaces in the next section.

13.3 THE CHEMISTRY BEHIND CARBON REACTIVATION

During the reactivation process, the spent carbon will not only have the adsorbates removed and destroyed, but also, some of the carbon structure will be altered, changing some of the material properties compared with the original carbon. It is important to realize that the spent carbon quality (adsorbates, inorganics, and metals present on the spent carbon), as well as the original carbon's base structure, will determine the quality and properties of the reactivated carbon.

The chemistry of carbon reactivation and what happens to the adsorbates and carbon structure during each phase are discussed next. This would apply to any spent carbon containing any type of adsorbate: hydrocarbons, volatile organics, and chlorinated, brominated, or fluorinated compounds.

The four general steps in carbon reactivation (Figure 13.2) are

1. Low-temperature pretreatment: Drying of carbon to remove the water remaining in the carbon pores (212°F)
2. Physical processes and reactions: Thermal devolatilization and desorption of weakly held adsorbates (212°F–1000°F)
3. High-temperature carbon condensation reactions: High-temperature pyrolysis or calcination, in which adsorbates that are not removed in step 2 (thermal devolatilization and desorption) are converted to char (1000°F–1450°F)
4. High-temperature carbon gas or solid reactions: Chemical reactions for carbon gasification with water vapor, carbon dioxide, or oxygen to gasify (partially remove) char formed in the step 3 and regain some adsorptive capacity (1450°F–1800°F)

During a reactivation cycle, the carbon skeleton and adsorption pore volume are partially displaced by char and reduced. However, the sum of the transport and adsorption pore structure remains unchanged in terms of percentage of total granule, measured on a volume basis, during reactivation cycles. This is discussed in greater detail in later segments.

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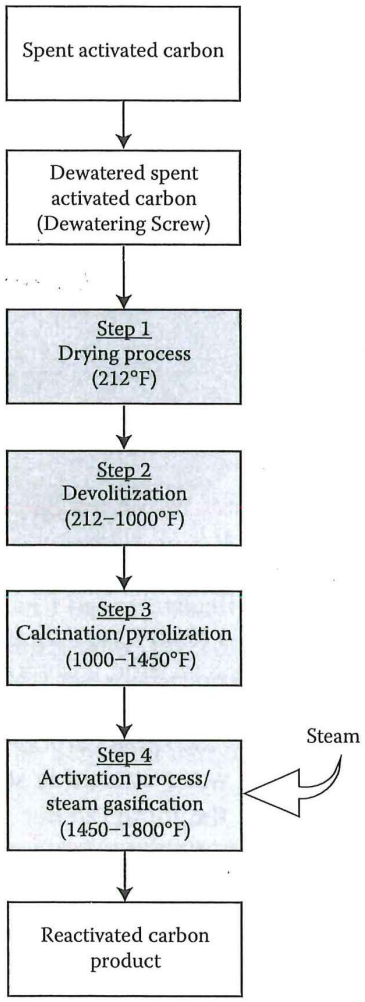


FIGURE 13.2 Steps of reactivating a spent carbon. The gray boxes indicate the steps taking place inside of a furnace.

13.3.1 Drying of Spent Carbon

One commonly used rule of thumb is referred to as the "40/40/20 rule," where 40% of a carbon bed is intergranular voids, 40% is intragranular pores (adsorptive and transport pores), and 20% is the carbon skeleton, by volume. Figure 13.3 illustrates the 40/40/20 rule for a carbon bed, as well as the breakdown of the types of pores (adsorption and transport) and the carbon skeleton for an individual carbon granule. When spent carbon is fed into a reactivation furnace, it is classified as either "wet" or "dewatered." In the case where the carbon is fed wet, it is fed as a carbon–water slurry and the water content is roughly 80% by volume (40% water in the intergranular voids and 40% intragranular pores). In this scenario, a dewatering screw is used prior to the reactivation furnace or kiln to remove the free water present in the intergranular

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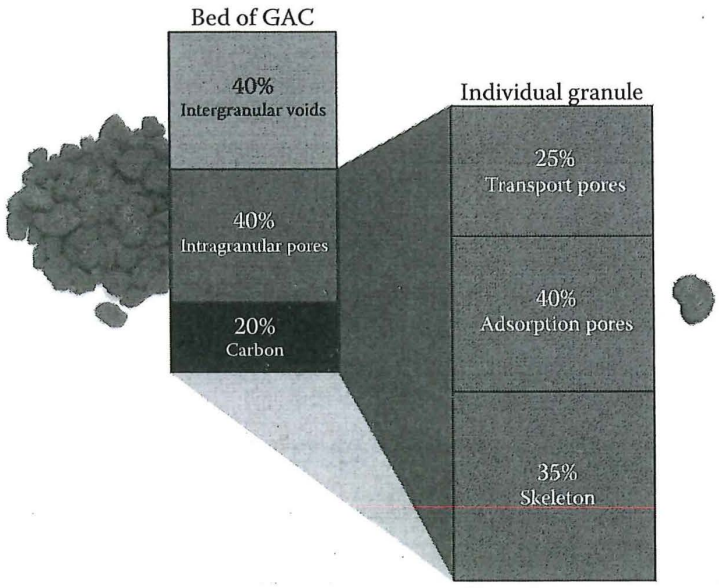


FIGURE 13.3 Graphical depiction of the 40/40/20 rule for a GAC bed (left) and the individual carbon granule breakdown for a carbon skeleton, adsorption pores, and transport pores.

voids (roughly 40% by volume). Once the spent carbon has been dewatered, the carbon undergoes a drying stage as the water content is still roughly 40% by volume, and there is still water remaining in the intragranular pores. To remove this water content, the first one-third to one-half of a react furnace is typically used for drying the carbon, and is the first step in reactivation, as shown in Figure 13.2. Temperatures during the drying stage in the furnace reach 100°C (212°F), simultaneously evaporating moisture and removing the more volatile organics from the granular carbon.

13.3.2 Devolatilization of Spent Carbon

The devolatilization process is desorption of volatile organics that were present as adsorbates on the spent carbon. This is accomplished, in order of preference, by (1) vaporizing low boiling or thermally stable adsorbates, (2) thermally breaking chemical bonds and desorbing smaller molecules, or (3) pyrolizing adsorbates that were not devolatilized by the previous two mechanisms.

The devolatilization process is a function of the individual adsorbates' stabilities and boiling points. Because the adsorption forces of activated carbon act like a pressure cooker, this step typically requires temperatures 400°F above the boiling point of an adsorbate to achieve desorption. When the species has a low boiling point or high stability, species will desorb from the pores completely (species such as alkanes [<C10], aromatics [<C4 side chains], and aliphatic alcohols [<C10]). When the species are high boiling or thermally unstable adsorbates, a different mechanism of desorption will occur whereby the adsorbate bonds break and the resulting fragments desorb (typically observed at temperatures <1000°F). Examples of these types of species are alkanes (>C10), aromatics (>C4 side chains), aliphatic alcohols (>C10), and organic halides.

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13.3.3 Pyrolyzation of Spent Carbon

The pyrolyzation process is the thermal destruction of adsorbates. What does not desorb during devolatilization forms char in the adsorbing regions of the carbon structure. Char formation means a loss of adsorption volume; it does not possess any adsorption properties. Char can also be further condensed through thermal calcinations to form a purer and denser form of carbon and restore some adsorptive properties. Whether a species is desorbed, devolatilized, or charred will be adsorbate specific.

13.3.4 Carbon or Steam Gasification

At 1450°F–1800°F, the char is burned along with a small amount of the original carbon. Both the char and the graphitic plates within the activated carbon granule are able to undergo gasification reactions with water vapor, carbon dioxide, and oxygen present in the kiln or furnace atmosphere. It is important to note that the gasification reactions will increase the adsorption pore volume of the activated carbon product, and the pore structure will be intrinsically different and typically less than the adsorption pore volume of the product pre-reactivation.

Figures 13.4 and 13.5 show water–carbon dioxide–oxygen gasification reactions that occur with the carbon plates and structure whereby a carbon atom is removed from the carbon platelet. The activated carbon structure is composed of randomly

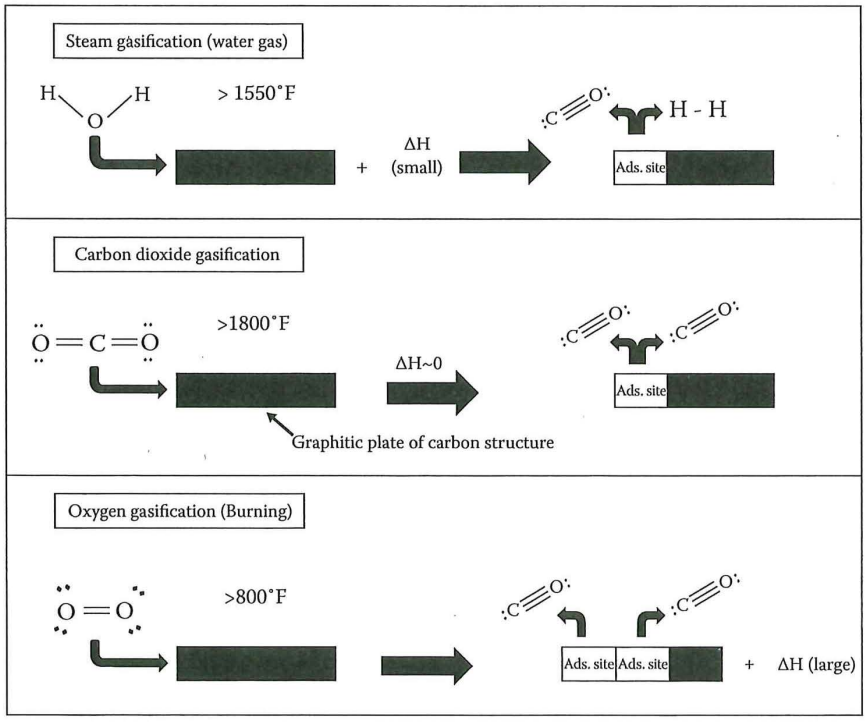


FIGURE 13.4 The three gasification reactions during the reactivation process that can occur with both the carbon structure and the char that is formed in the pores. Ads. = adsorption.

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Solid/Gas Reactions	
$C(s) + H_2O_{(g)} \rightarrow CO_{(g)} + H_{2(g)}$	Endothermic
$C(s) + CO_{2(g)} \rightarrow 2\,CO_{(g)}$	Endothermic (3× slower than H_2O)
$C(s) + \frac{1}{2}\,O_{2(g)} \rightarrow CO_{2(g)}$	Exothermic
$C(s) + O_{2(g)} \rightarrow CO_{2(g)}$	Exothermic
Gas/Gas Reactions	
$CO_{(g)} + \frac{1}{2}\,O_{2(g)} \rightarrow CO_{2(g)}$	Exothermic
$H_{2(g)} + \frac{1}{2}\,O_{2(g)} \rightarrow H_2O_{(g)}$	Exothermic

FIGURE 13.5 The gasification reactions and their enthalpy values (ΔH), where exothermic reactions are $\Delta H < 0$ and endothermic values are $\Delta H > 0$.

arranged (amorphous) graphitic plates, commonly referred to as "platelets." The removal of the carbon atom from the platelet leaves a "spot" that is then available for an adsorption site. While the gasification of the carbon structure and platelets can increase adsorption pore volume, it should be balanced and minimized as much as possible as losses to the carbon skeleton can reduce the hardness and abrasion of the product (discussed in future sections), as well as decrease the number of reactivation cycles a product can undergo. Thus, the atmospheric conditions of the furnace should be carefully controlled.

As mentioned above, whatever is not devolatilized or desorbed out of the carbon structure is converted to char in the adsorption pores. Since char has no adsorption characteristics, its presence reduces the adsorption pore volume for a reactivated material. In order to restore some of the adsorptive pore volume lost to char formation, the same three gasification reactions (water vapor, carbon dioxide, and oxygen) discussed in Figure 13.4 for the carbon platelet gasification also occur with the char. It is important to reemphasize that the gasification reactions, while restoring some adsorptive capacity by reducing the char, also react with the original carbon structure at the edges of the graphitic plates and dislocations from the carbon plates. Figure 13.6 shows the order of attack on the carbon structure from these gasification reactions.

In summary, reactivation is a process that restores a spent or used activated carbon product's adsorptive capacity so that the product can be reused. This is accomplished by the thermal devolatilization and desorption of weakly held adsorbates and pieces of contaminants whose bonds are broken and desorbed at elevated temperatures. This devolatilization restores a fraction of the adsorptive pore volume of the original activated carbon product. The adsorbates that are not removed are converted to char within the adsorptive pore space, which has no adsorptive capacity. To restore a larger percentage of adsorptive pore volume, gasification reactions are performed that remove the char that has formed in these pores. These gasification reactions must be balanced carefully, as they will also react with the carbon structure.

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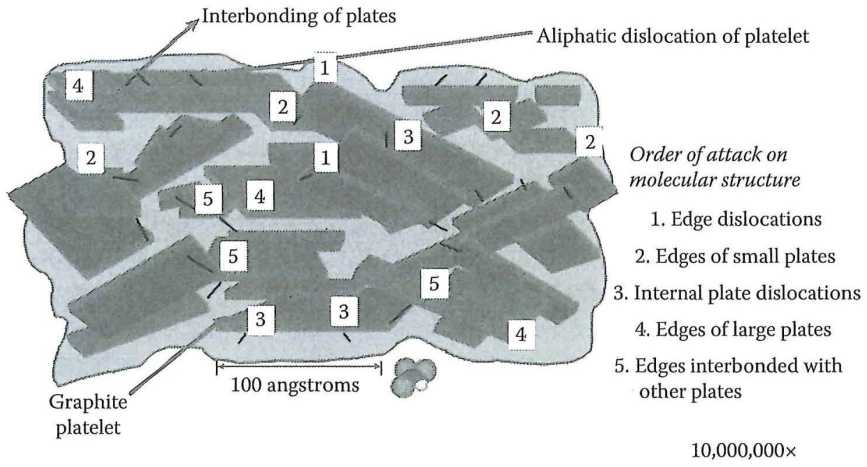


FIGURE 13.6 Order of carbon atom removal on graphite plate, creating greater adsorption capacity during gasification.

13.4 SOME RULES OF CARBON REACTIVATION THAT SHOULD BE CONSIDERED WHEN EVALUATING A SPENT CARBON AND ITS POTENTIAL FOR REACTIVATION

Rule 1: The characteristics of a spent carbon predetermine the best available reactivated carbon product that can be achieved. A poor spent activated carbon structure and ash and char levels will limit the best obtainable reactivated product.

Ash is defined as the noncombustible mineral matter that is contained in activated carbon and is the residue that remains after the combustion of a carbonaceous material. The measurement of ash is performed under specified conditions and is normally defined on a weight percent basis.

Char is defined as the resulting residue of organic matter of adsorbates that are not devolatilized or vaporized from the surface of activated carbon at high temperatures.

Rule 2: High-ash (such as calcium and other inorganics and metals) adsorbates on spent carbons make high-ash reactivated carbons or cause other ash-related problems (e.g., leaching of inorganic species).

Rule 3: The spent carbon cannot be reactivated if it cannot be fed to the furnace.

Rule 4: Balance char buildup with acceptable performance decay. Minimize carbon graphite plate gasification, as a shortening or loss of graphite plates will result in a loss of adsorptive capacity.

Rule 5: Only gasify the carbon plate structure when justified by actual performance decay in an application. Do not gasify the plate structure just to achieve an arbitrary activity specification.

Rule 6: Treat reactivated carbons as differentiated products. A reactivated carbon with virgin density and activity is not equal to a virgin carbon structure. The pore structure has been altered in the reactivation process due to the formation of char and gasification reactions as addressed above.

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13.5 REACTIVATION EQUIPMENT AND FURNACES

The reactivation process equipment will need to include auxiliary equipment in addition to the reactivation furnace or kiln. At the onset, spent carbon is transferred from an adsorber or a delivery container (bulk truckload or supersaks if spent carbon is sent to an off-site regional reactivation facility by the customer) to a storage tank or elevated furnace feed tank. If dewatering is required, the spent carbon is then metered into a furnace feed dewatering screw, an inclined screw conveyor that serves the dual purpose of draining slurry water from the carbon and providing a water seal for the top of the furnace. Drained but still wet (40% by volume, 50% by weight moisture), the spent carbon flows into the furnace and proceeds downward through the hearths, seeing increasingly higher-temperature reactivation zones in the furnace.

Six to nine hearths are used in carbon reactivation furnaces that consist of a cylindrical refractory-lined steel shell containing the hearths, one above the other, and a central rotating shaft that drives rabble arms across the hearths (Figure 13.7a and b). Carbon entering the top hearth is raked toward the center and down a central hole to the center of the next hearth, from where the rabble teeth move it outward again in a spiral path toward the rim. The flow pattern is repeated through subsequent pairs of

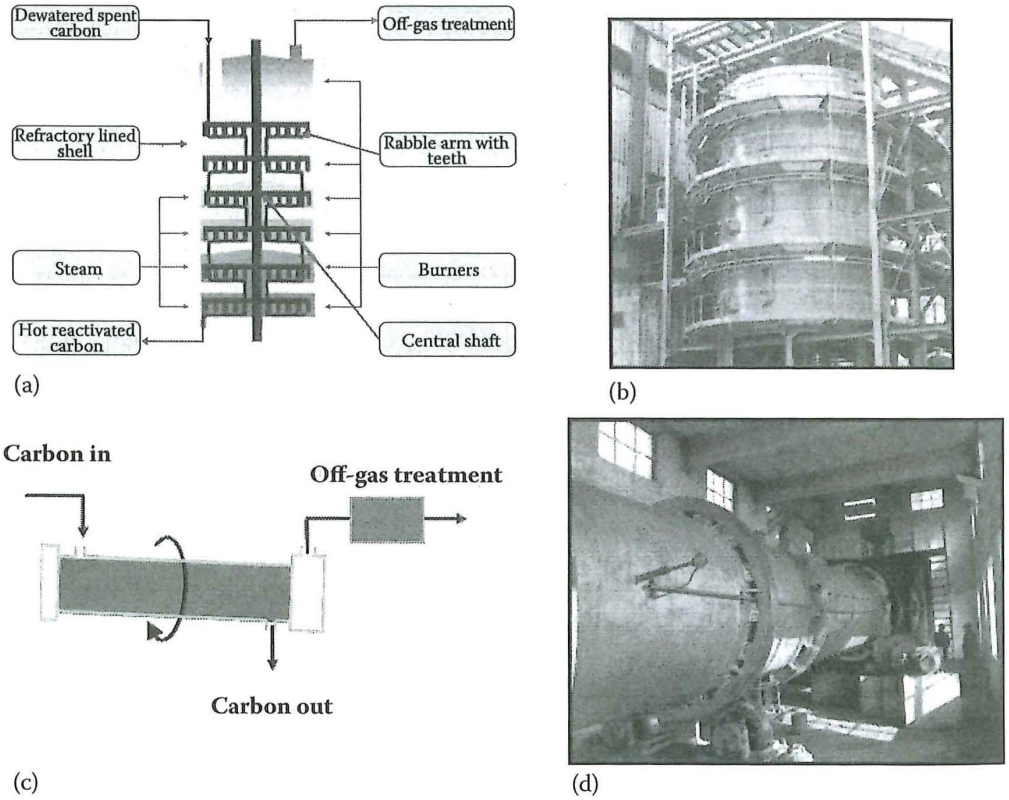


FIGURE 13.7 Illustrations and photographs of both styles of furnaces: (a and b) multiple hearth and (c and d) rotary kiln.

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hearths, until the reactivated carbon is discharged from the bottom hearth. Burners using natural gas or fuel oil are mounted on the shell so as to direct their flames tangentially into the space above the hearths. Steam for controlling the reactivation stage is added through ports above the bottom several hearths.

A rotary kiln is a refractory-lined steel cylinder closed at the ends by stationary hoods and mounted so as to slope downward from inlet to outlet (Figure 13.7c and d). This type of kiln passes carbon granules either cocurrent with or countercurrent to combustion gases and steam. The kiln rotates with wet spent carbon entering onto flights through a feed screw or chute. The reactivated carbon discharges from the lower end of the kiln. The atmosphere inside the kiln is controlled by burners plus steam addition. Similar treatment of the off-gases is used for reactivation furnaces and kilns.

Reactivated carbon exits the furnace and is dried through one of two methods: (1) entering a water quench tank or (2) being cooled by contact with air. A water quench tank is typically used by on-site reactivation facilities, as the reactivated carbon can be transferred as a water and carbon slurry from the kiln or furnace. This method also has the added benefits of removing the fines present via the quench tank overflow water and provides a bottom seal for the furnace. Dry cooling, or cooling the carbon with air, is typically used at off-site reactivation centers, as the carbon can be rescreened and packaged into bags or supersaks. This cooling method is typically used by off-site reactivation centers where the carbon is being shipped to other locations since wet carbon will weigh roughly twice as much as dry carbon (see Figure 13.3).

Reactivation furnaces or kilns should be maintained under negative pressure, ensuring that there will be no leaks to the outside environment. In most reactivation facilities, an afterburner (destroys any unburned organics), chemical scrubber (removal of acid gases), and baghouse are also installed for destroying organics and removing residual particles from the furnace off-gases. The reactivation facility should be permitted and required to meet certain local, state, and federal regulations and requirements.

Afterburners and thermal oxidizers combust desorbed organic compounds. Dry scrubbers and spray dryer units are used to remove acid gases from the furnace or kiln off-gas stream. A baghouse (dust collector) will remove particulate matter from the afterburner and spray dryer as well as furnace dust. For some operations, a wet venturi scrubber is used for particulate control.

Any wastewater or solid waste generated in the process may require treatment and discharge and/or waste disposal in accordance with the classification of the waste and plant discharge permits.

13.6 POOLED VERSUS CUSTOM REACTIVATION OPTIONS

There are three typical reactivation scenarios for spent carbons. Regional or off-site carbon supplier–owned reactivation facilities are used for pooled reactivation or custom or segregated reactivation (Figures 13.8 and 13.9). Customers may also use on-site reactivation facilities.

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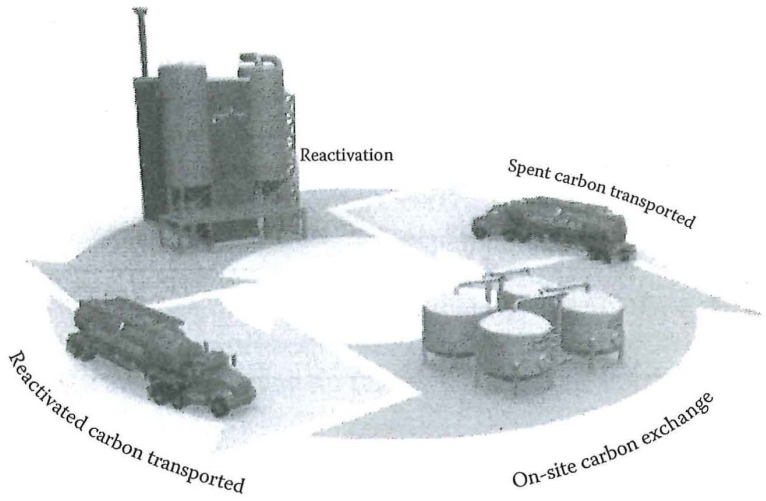


FIGURE 13.8 Example of a custom reactivation cycle.

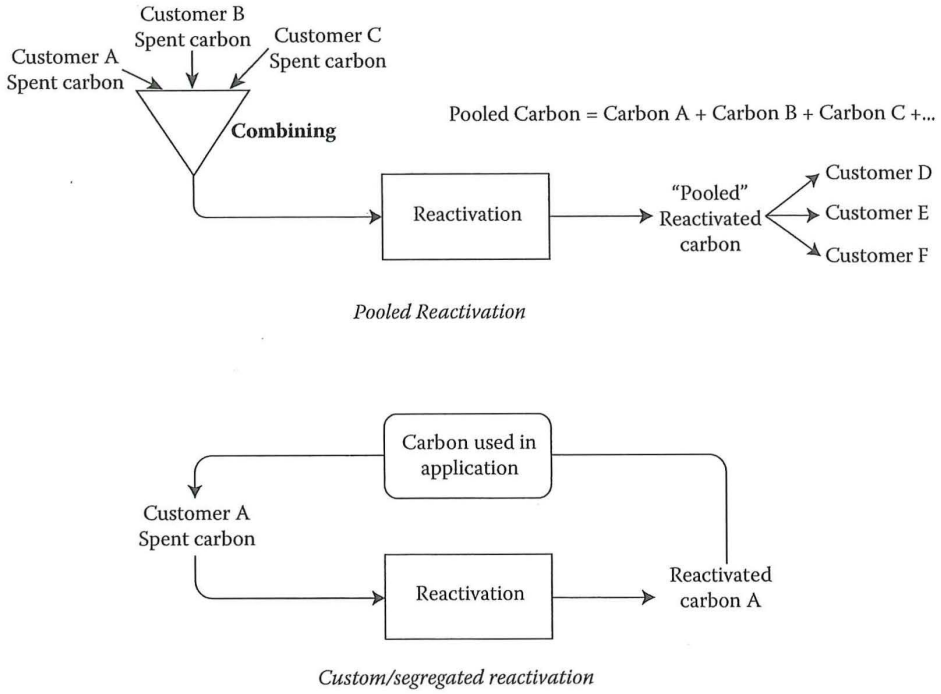


FIGURE 13.9 Visual representation of pooled reactivation versus custom reactivation.

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13.6.1 Regional or Off-Site Carbon Supplier–Owned Reactivation Facility for Pooled Reactivation

More prevalent for spent carbon from water treatment applications is the use of an off-site reactivation facility that services many types of applications, sites, and customers. These reactivation centers are available worldwide and typically produce an industrial-grade reactivated carbon. Pooled reactivated carbons are approved spent carbons from many applications (potable, food grade, industrial process, remediation, etc.) and are all received at one reactivation facility and combined into a singular "pool" of carbon. It should be noted that this pool is an assortment of carbons from a wide range of applications, typically with separate pools for liquid phase and vapor phase carbons. In addition, note that a non-food-grade or industrial reactivation facility can also be a Resource Conservation and Recovery Act (RCRA)–approved facility. The pool of spent carbons is fed to a reactivation furnace or kiln. This yields a reactivated grade of carbon that can be used for many nonpotable or non-food-grade applications.

These sites are usually considered "industrial reactivation sites," meaning that the reactivated carbons will be used for industrial or non-food-grade applications. These reactivation centers, if RCRA hazardous permitted, can then handle both RCRA hazardous and non-RCRA-classified spent carbons from any application. The spent carbons received are combined, fed through a reactivation furnace or kiln, and produce a consistent quality and "age" of reactivated carbon product. This industrial reactivated carbon can then be used by appropriate customers or applications. Since the spent carbons received may be from previous react-grade carbon or from virgin carbons that have been used once by a customer, and some reactivated carbons shipped from the reactivation pool do not get returned for reactivation, the overall life cycle or age of the reactivated carbon pool remains relatively constant.

A particular customer or application can be supplied any type carbon that is required (virgin or reactivated) and still return their spent carbon for reactivation pending reactivation approval.

Since vapor phase (commonly 3 or 4 mm pellets, 4 × 6 and 4 × 10 mesh sizes) activated carbon and liquid or water phase (commonly 8 × 30 and 12 × 40 mesh sizes) activated carbons are different particle size ranges, typically there would be separate vapor phase and liquid phase reactivated carbon product pools. Both coal-based and coconut-based activated carbons can be reactivated in similar manners and reused successfully. They may be reactivated in the same pool or be provided as separate reactivation products, depending on the supplier.

13.6.2 Regional Carbon Supplier–Owned Reactivation Facility for Custom or Segregated Reactivation

There is also a need in the food and drinking water market segments for reactivation of a specific customer's spent carbon and the return of their same reactivated carbon for reuse in the same application. The amount of spent carbon generated may not justify on-site reactivation, or the customer may not desire to run a carbon reactivation facility, making an off-site custom or segregated food-grade or potable reactivation

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process a favorable option. Custom food-grade or potable water carbon reactivation is conducted at a dedicated food-grade facility where the process should be tailored to meet the requirements of the American Water Works Association and National Sanitary Foundation (NSF)/ANSI Standard 61. The customer's spent carbon will be segregated and traceable from the time it leaves the specific customer's location, through the receiving, storage, and reactivation at the reactivation facility, and until it is delivered back to the same customer or site (Figure 13.8).

13.6.3 Customer On-Site Reactivation Facility

If an application will exhaust a sufficient amount of carbon per day (10,000 lb spent carbon per day as an estimated minimum), logistics and costs may justify an on-site reactivation facility. This will involve spent and react carbon handling systems, a reactivation furnace or kiln, off-gas treatment permits, and manpower to operate and oversee the reactivation operation. On-site reactivation is not typically used in water treatment applications and is more common in sugar or sweetener GAC applications.

The reactivation process equipment will be essentially the same for both pooled reactivation and custom reactivation. Depending on the nature of the spent carbon and how much adsorbate it contains, as well as the species, furnace or kiln operating conditions may be different, but the overall flow diagram given in Figure 13.1 applies to both pooled and custom reactivation.

13.7 ACTIVATED CARBON TESTS USED FOR MONITORING AND CONTROLLING REACTIVATION PRODUCT QUALITY

To ensure the quality and consistency of a virgin or reactivated carbon, physical and adsorptive properties are specified. Certain industry standard test methods or ASTM methods are used for this purpose. Although the carbon reactivation process will result in a reactivated carbon that has a different structure than virgin carbon, the desired end goal is to produce a carbon of sufficient adsorptive quality to make reactivation cost-effective.

There are three industry-wide parameters typically used and accepted as reactivated carbon specifications:

1. An adsorption capacity or activity parameter (usually iodine number or I_2#)
2. Apparent density (AD)
3. A screen or mesh size (typically an over and under mesh size, maximum percentage value)

Iodine number (ASTM D4607): The iodine number is a measurement of the amount of iodine (concentration of 0.02 N) adsorbed by 1 g of carbon. The iodine number is reported as milligrams of iodine per gram of activated carbon. Iodine is very strongly adsorbed and will occupy all available adsorption sites over every adsorption energy level. It is understood as an indicator of total pore volume. In a given application, the adsorbate of interest (e.g., PFAS) may only be able to adsorb in a portion of these sites.

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Apparent density (ASTM D2854): AD is a physical property defined as the mass per unit volume of a granular material under specified conditions and dense packing. The AD includes the carbon skeleton volume plus the pore and void volumes. The units are typically grams of activated carbon per cubic centimeter.

Mesh size (ASTM D2852): The measurement of the particle size of GAC determined by the US Sieve Series. This is generally represented by a two-sieve size designation (e.g., 8 × 30 or 12 × 40), representing particles passing through the first sieve size but being retained by the second sieve size. The particle size distribution within a mesh series is typically given in the specification of a particular carbon.

When a carbon has been saturated with adsorbates (spent), this will be reflected in an increase in the AD of the carbon. Ideally, in a carbon reactivation process the goal is to remove the adsorbates and restore the carbon to a usable form. Thus, the AD of a reactivated product should be similar to the AD of the carbon that was initially in the vessel (virgin or previously reactivated product). In addition to a quality specification for the reactivated product, the AD is a simple and quick in-house test method to monitor the reactivation process and adjust reactivation furnace or kiln conditions as needed. Targeting a reactivated carbon's AD to be close to the virgin or original carbon's AD will ensure that the adsorbates are removed while minimizing char formation and loss of carbon adsorptive structure in the reactivation process. If the AD of the reactivated carbon is too high, it can indicate that (1) the spent carbon adsorbate loading has changed in nature or increased and the current furnace conditions are no longer adequate, or (2) the adsorbed species are not being adequately removed by the current furnace conditions (i.e., furnace temperatures, atmosphere of steam and/or O_2 or air, and residence time). If the AD is too low, that can indicate overactivation and loss of activated carbon structure along with the adsorbate. This can lead to poor adsorption capacity or performance as well as a loss of too much carbon skeleton. Such a loss can result in fewer reactivation cycles before the carbon granular "falls apart" from losing enough skeleton.

Although the I_2# is a measurement of total adsorption volume over all sizes of adsorption pores, it is an industry standard test and is typically used for the measurement of spent and reactivated carbon. A reactivated carbon product would ideally have an I_2# that was near the virgin or fresh carbon specification. In reality, perhaps an I_2# 100–200 mg/g less than the corresponding virgin or fresh carbon value is more realistic. The I_2# of the reactivated carbon will depend on the reactivation conditions as well as the spent carbon's I_2# value. Typically, an increase of more than 300 I_2# points from the spent carbon I_2# value is not advisable, as this often indicate overreactivation and a significant loss of carbon skeleton structure.

During the reactivation process, there can be physical carbon attrition due to transport, the dewatering screw, gasification, or the particle's life cycle (the point where a carbon granule disintegrates). This can result in fines that are not removed in the overall process. Therefore, a reactivated carbon that is indirectly cooled is usually screened after it exits the reactivation furnace or kiln. It will typically be screened to match the over- and underspecifications of the virgin or fresh carbon used. As an example, if a virgin or fresh carbon specification had 5.0 weight percent maximum on 12 US mesh and 4.0 weight percent maximum smaller than 40 US mesh, the reactivated carbon for this product on a custom reactivation basis would be screened and have similar mesh size specifications.

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13.8 EFFECTIVENESS OF REACTIVATION IN THE DESTRUCTION OF PFAS COMPOUNDS

As discussed in this chapter, the goal of reactivation is to restore the adsorptive capacity of GAC utilizing a high temperature thermal process that devolatilizes, dissociates, and/or chars adsorbed material in the carbon pores. This process destroys the adsorbed compounds, eliminates liability, and allows the activated carbon to be reused in appropriate applications. This process is different from regeneration, where adsorbates are partially removed and the adsorption pore volume is restored to a fraction of the original levels. In applications where destruction of adsorbates is required, regeneration processes are not acceptable. While both terms are often used interchangeably, it is critical to differentiate these processes.

In order to demonstrate the effectiveness of reactivation in the destruction of adsorbed material, such as PFAS compounds, Calgon Carbon, a subsidiary of Kuraray Co., Ltd., conducted leachability studies on reactivated reagglomerated bituminous coal-based GAC (FILTRASORB) previously used in a PFAS removal application. The carbon used in this trial treated approximately 310 million gallons of drinking water with influent PFAS concentrations ranging from 0.5 to 1 ppb (μg/L). This spent carbon was reactivated in a full-scale custom reactivation facility operated by Calgon Carbon Corporation and the reactivation conditions were as outlined in the above reactivation section.

The spent carbon was tested and approved for reactivation via Calgon Carbon's Carbon Acceptance program. This determined that the spent samples were able to be safely and effectively reactivated, as described in Section 13.10.

In order to determine if there were leachable PFAS compounds, the reactivated carbon underwent the NSF42 leaching protocol, a well-accepted and robust method for determining extractable material from activated carbon. The reactivated carbon sample was loaded into a column, was backwashed with approximately 8 bed volumes of NSF42 leaching protocol water (50 ppm total dissolved solids [TDSs], 0.5 ppm Cl^-, and pH 6.75), was allowed to sit for 24 hours in 1 BV of water, and then sampled. These steps were repeated two additional times and the three leachate samples were composited for analysis. All samples were analyzed per the EPA 537 method and the results of the leaching test are reported in Table 13.1. These results are shown in Table 13.1. Calgon Carbon Corporation also attempted to utilize a thermal destruction technique on the reactivated carbon to examine fluoride present before and after reactivation, but, because the detection limit of this technique is so high, the data generated was inconclusive and not meaningful. The fluoride present on the spent carbon was at the detection limit prior to reactivation and therefore not included in Table 13.1.

13.9 PROPERTIES OF ACTIVATED CARBON THAT CAN CHANGE WITH REACTIVATION

We have mentioned previously that the reactivation process removes not only adsorbates from the spent carbon but also some carbon atoms or carbon structure, creating a slightly different activated carbon product with restored adsorptive capacity.

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TABLE 13.1
EPA Method 537 Results on Leachate from an NSF42 Extraction on a Reactivated GAC Used in a PFAS Application

		PFAS Customer-Plant React
PFBA	ppt	1.9
PFPeA	ppt	<0.43
PFHxA	ppt	<0.51
PFHpA	ppt	<0.22
PFOA	ppt	<0.75
PFNA	ppt	<0.24
PFDA	ppt	<0.27
PFUnA	ppt	<0.97
PFDoA	ppt	<.049
PFTriDA	ppt	<1.1
PFTeA	ppt	<0.26
PFBS	ppt	<.18
PFHxS	ppt	0.23[ab]
PFHpS	ppt	<0.17
PFOS	ppt	<0.48
PFDS	ppt	<0.28

Note: All leachate from the reactivated reagglomerated bituminous carbon was at or below the quantifiable limit of EPA 537 method, indicating that reactivation was effective in destroying the adsorbed PFAS compounds.

[a] Compound was found in blank.

[b] Result is less than the RL but greater than or equal to the MDL and the concentration is an approximate value.

In addition to the I_2#, AD, and mesh size, some other properties that can be altered in a reactivation cycle are

1. The mean particle diameter (MPD): Even with screening to meet the under and over mesh size of the original carbon, a reactivated carbon can have 99%–95% of the original carbon's MPD.
2. Particle size distribution: Reactivated carbon will be slightly wider.
3. Particle shape: Reactivated carbon will have fewer sharp edges as a result of physical attrition.
4. With each reactivation cycle for a given carbon granule, the volume percent char and percent transport pores of that particle will increase as the volume percent adsorption pores and carbon skeleton decrease. As shown in Table 13.2, the volume percentage of transport pores will increase with the

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TABLE 13.2
Volume Percent of Activated Carbon Granule as a Function of the Reactivation Cycle

Component	Virgin	First Cycle	Second Cycle	Fifth Cycle
1. Transport pores	22%	23%	24%	30%
2. Adsorption pores	36%	35%	34%	28%
3. Carbon skeleton	34%	30%	25%	14%
4. Ash	8%	8%	8%	8%
5. Char	0%	4%	9%	20%
Total	**100%**	**100%**	**100%**	**100%**
Sum of adsorption pores + transport pores	58%	58%	58%	58%
Sum of carbon skeleton (graphitic plates) + char formed	34%	34%	34%	34%

number of reactivation cycles, while the volume percentage of adsorption pores will decrease. The sum of transport pores and adsorption pores will remain unchanged since the gasification reactions convert adsorption areas to transport structure as the graphitic plates within the carbon structure are shortened slightly each reactivation cycle.

If a carbon reactivation is performed properly, the react carbon will have good reactivation results. Characteristics of good results include

1. Slight increase in ash content
2. I_2# within 100–200 mg/g of the original carbon
3. AD of the reactivated carbon relatively similar to that of the original carbon
4. Screens under and over the specified mesh size relatively similar to those of the original carbon used

If a carbon reactivation is performed poorly, the react carbon will be of lower quality and lead to poor adsorption performance or pressure drop problems (too many fines) as characterized by the following:

1. Hardness and abrasion will drop. The hardness number (ASTM D3802) is a measurement of the resistance of a granular carbon to the degradation action of steel balls in a Ro-Tap machine. This number is calculated by using the weight of granular carbon retained on a particular sieve after the carbon has been in vigorous contact with the steel balls. The abrasion number (AWWA-B604) is obtained from a test performed on a particulate material to define the resistance of the particles to degrade on handling. It is calculated by contacting a sample with steel balls in a Ro-Tap machine and determining the ratio of the final to the original MPD.
2. AD (g/cc) will be too low or be too high.

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3. I_2# will be too low or too high.
4. Too many fines will result in pressure drop problems.

In a pooled reactivated product, there is a continuous infusion of spent carbons that result from one adsorption cycle of virgin carbon, as well as spent carbon of previously reactivated carbon. With some particles being lost or degraded structurally after a finite number of react cycles, the overall quality of a reactivated pool reaches equilibrium and remains essentially constant. In custom reactivation, there is typically the addition of some amount of virgin carbon to a specific custom reactivated product to make up for reactivation volume or mass losses and/or to bring the react quality back to some predetermined specification.

Since there can be overall physical carbon losses of typically 5%–10% per reactivation cycle, custom reactivation will require, at a minimum, virgin carbon makeup addition to compensate for these physical losses to supply the customer the same weight or volume of reactivated carbon back for their use. Virgin makeup also maintains the overall quality through multiple reactivation cycles and typically is the same carbon type as initially used in the application system. A higher amount of virgin carbon makeup may be desired on a case-by-case basis if a higher quality of reactivated–virgin blend (usually reported by I_2#) is required for a given application.

The original carbon base material can influence not only the amount of losses per cycle but also the quality of the reactivated carbon. The density, particle shape, hardness or abrasion number, and manufacturing process of the original carbon are important. Some GACs will reactivate more effectively than others and thus require less virgin makeup. Reagglomerated bituminous coal activated carbons typically require less makeup than direct activated (coal or coconut carbons) or lignite carbons. A reagglomerated bituminous coal activated carbon has superior physical durability than direct activated coal, coconut, or lignite products, which results in less attrition and fewer losses in each reactivation cycle.

13.10 SPENT CARBON PROFILING AND REACTIVATION

Before a specific spent carbon can be reactivated (pooled or custom reactivation) at a reactivation center, there is usually an acceptance procedure that a reactivation provider will require. It typically involves completion of a waste and adsorbate profile document by the customer and testing of a representative spent carbon sample to ensure that the spent carbon can be handled and reactivated safely and yield a reusable product. Once this acceptance procedure is completed, spent carbon from the given application or site can be shipped to the reactivation service provider. Depending on the spent carbon classification (nonhazardous or RCRA hazardous) and whether it will be for potable custom reactivation, the receiving reactivation facility will have the necessary permits and certifications to handle the spent carbon.

In most instances and for most applications, including spent carbons that have adsorbed PFAS, the spent carbon can be approved and reactivated at an appropriate reactivation facility. The classification of the spent carbon (RCRA hazardous or non-RCRA hazardous) is determined by the generator of the spent carbon and should be handled accordingly.

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There can be some instances or applications where the spent carbon quality or characteristics would make it unacceptable for reactivation, such as

1. If certain contaminants are adsorbed and present that are not permitted in a given react facility or under their permits (e.g., polychlorinated biphenyls [PCBs] and dioxins)
2. If the amount of volatile halides (chlorides, fluorides, and bromides) present on the carbon is higher than can be handled by the off-gas treatment system at the reactivation facility
3. If the carbon contains certain metals above a guideline for pool reactivated carbon
4. If the spent carbon is ignitable

Typical modes of spent carbon packaging, depending on its classification, may include bulk dump trucks, bulk pneumatic trailers, roll-off boxes, supersaks, and drums.

13.11 POSSIBLE ISSUES WITH A SPENT CARBON THAT WOULD RESULT IN A POOR CANDIDATE FOR REACTIVATION

There may be cases where spent carbon generated from an application will contain inorganics, metals, solids, or another property that would make it unacceptable as good-quality feed to a reactivation furnace or kiln, or would result in a reactivated carbon quality that is not usable by the same customer (custom reactivation) or by others (pooled reactivation). Some of these spent carbon characteristics that need to be considered and can result in an unacceptable reactivated carbon or damage to the reactivation equipment are

1. High content of calcium and sodium salt species on or in the spent carbon can lead to furnace hearth failure by attacking the brick or linings in the reactivation furnace, in addition to forming slag and linkers (mass of incombustible matter fused together with no adsorption properties) in the furnace or kiln.
2. Metals such as iron and magnesium can agglomerate and harden the carbon and result in a non-free-flowing react product. Metals may also remain on the reactivated carbon for the next adsorption cycle or reuse.
3. Hardness as $CaCO_3$ can agglomerate and harden the carbon, cause processing or mechanical problems in a furnace or kiln, and produce a poor-quality reactivated carbon.
4. Oil and grease (O&G) or excess hydrocarbons, if free or emulsified, can (a) coat the carbon, making it nonwettable and non–free flowing, preventing it from being able to be fed to the react furnace; and (b) result in high adsorbate or hydrocarbon loading, which makes the carbon ignitable.

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13.12 REACTIVATION AS A SUSTAINABLE AND ENVIRONMENTALLY RESPONSIBLE APPROACH

Incineration of any concentrated PFAS waste is required for complete destruction. Spent activated carbon containing adsorbed PFAS compounds can be thermally reactivated, destroying the adsorbed contaminants and allowing the activated carbon to be recycled and reused. When reactivated, carbon can be restored at a lower cost than the manufacture of virgin activated carbon from raw starting materials. Reactivation also avoids the cost and long-term liability associated with disposal and produces only about 20% of the greenhouse gases as does new carbon production.

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14 Ion Exchange for PFAS Removal

Steven Woodard, Michael G. Nickelsen, and Marilyn M. Sinnett

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14.1 PROPERTIES OF ION EXCHANGE RESINS

The predominant carboxylic acid and sulfonic acid poly- and perfluorinated alkyl substances (PFAS) are strong acids and therefore almost completely dissociate at common water pH values (i.e., $4 < pH < 10$). In the anionic form (carboxylate ion or sulfonate ion), PFAS are susceptible to removal with ion exchange (IEX) resins.

14.1.1 Physical Properties

14.1.1.1 Structure

IEX resins consist of a polymer matrix and introduced functional groups that interact with ions of interest. The most common IEX resin matrix is a copolymer made from styrene and divinylbenzene (DVB) (Figure 14.1), although polyacrylic, phenol-formaldehyde, and polyalkylamine matrices are also available for specialty applications. Standard IEX resins are spherical shaped, with bead diameters ranging from 0.3 to 1.2 mm.

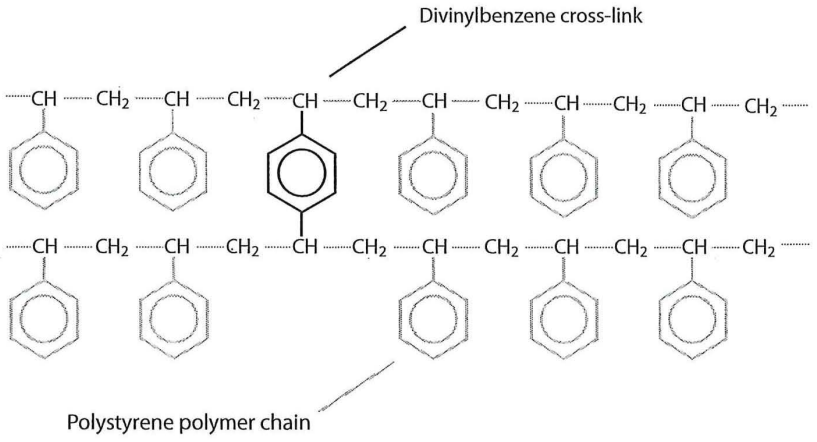


FIGURE 14.1 Structure of styrene–DVB copolymer.

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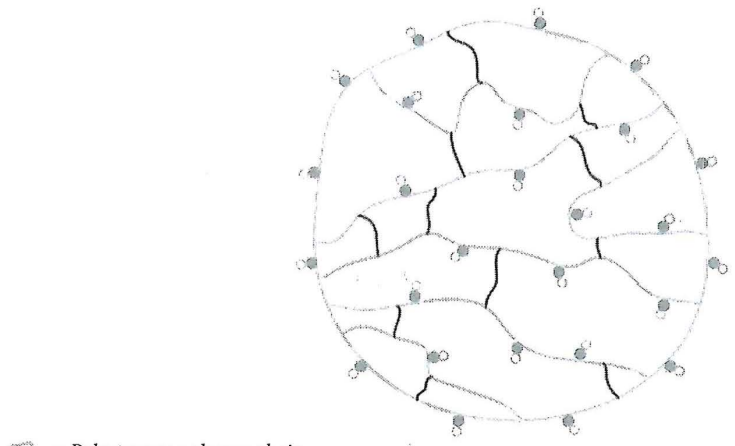


FIGURE 14.2 Structural model of a microporous IEX resin.

IEX resins are classified as either cationic (resins that remove positively charged anions, such as Na^+ and Ca^{2+}) or anionic (resins that remove negatively charged anions, such as SO_4^{2-}, NO_3^-, and PFAS). Cation IEX resins are further subdivided into strongly acidic cation (SAC) (sulfonic acid) and weakly acidic cation (WAC) (carboxylic acid) active functional groups. Anion IEX resins are similarly subdivided into strongly basic anionic (SBA) (quaternary ammonium functional groups) and weakly basic anionic (WBA) (primary, secondary, or tertiary amine groups).

A typical IEX resin bead is a complex three-dimensional structure of cross-linked elastic polystyrene chains with DVB cross-linking of irregular lengths and intervals (Figure 14.2).

The structure and porosity of an IEX resin are determined principally by the conditions of polymerization of the backbone polymer. Porosity determines the size of the molecule or ion that may enter a specific structure and its rate of diffusion and exchange. There also is a strong interrelationship between the equilibrium properties of swelling and ionic selectivity.

For example, in IEX resins with a styrene–DVB copolymer backbone, porosity is inversely related to the DVB cross-linking. The amount of DVB cross-linking in a typical SBA IEX resin ranges from a low of 5% to a high of 12% and can be tailored to optimize the removal of specific molecules or anions. Below 5% DVB, the resin is too soft and susceptible to oxidative attack; above 12%, the resin is too dense (molecules or anions cannot enter the pore structure) and too hard. Beads frequently shatter from osmotic pressures experienced during IEX (swelling and shrinkage).

14.1.1.2 Functional Groups and Exchange Sites

Since most PFAS are strong acids (i.e., very low pKa values) and therefore occur predominantly in anionic form at common water pH values, the most applicable IEXs for their removal are SBA IEX resins. SBA IEX resins are prepared by chloromethylation of the benzene ring of polystyrene, followed by replacement of the chlorine

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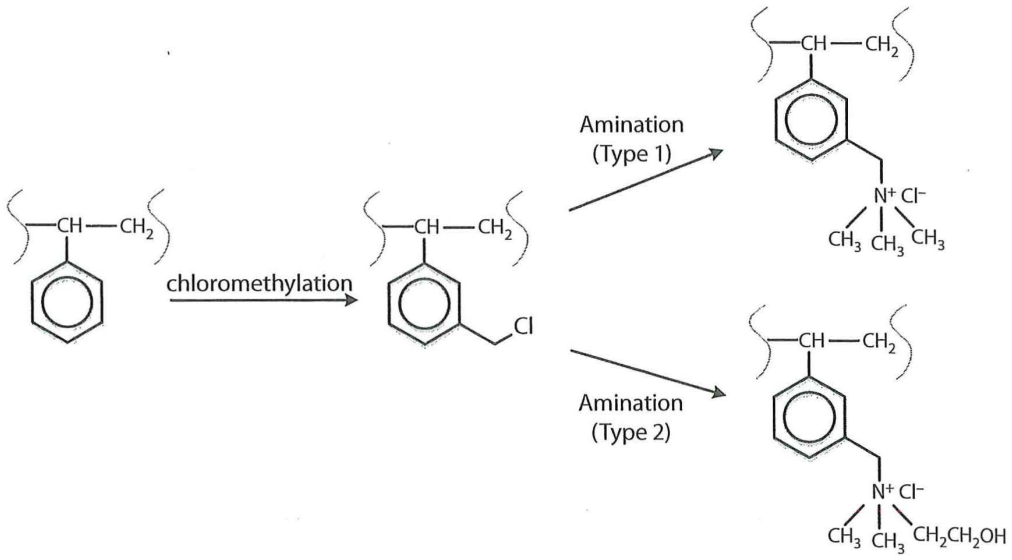


FIGURE 14.3 Functionalization of styrene–DVB copolymer—SBA Type 1 and SBA Type 2 IEX resins.

in the chloromethylated group with a quaternary ammonium group (Figure 14.3). Strong base anion resins are classed as Type 1 and Type 2. The Type 1 functional group is a quaternized trimethylamine and is the most strongly basic functional group available. Type 1 SBA IEX resins have the highest affinity for weak acids. Type 2 functionality is obtained by the reaction of the styrene–DVB copolymer with dimethylethanolamine. This quaternary amine has lower basicity than that of the Type 1 resin, yet it is high enough to remove the weak acid anions for most applications. In general, Type 2 resins have less chemical stability than their Type 1 cousins. Type 1 resins are favored for high-temperature applications (Owens, 1995).

14.1.1.3 Adsorption Sites

Depending on the percentage of DVB cross-linking, porosity structure (micro-, meso-, and macropores), and functional group, the IEX resin can exhibit some adsorptive properties akin to nonfunctionalized styrene–DVB polymeric-based adsorbents. The primary driving forces for adsorption are the hydrophobic (water-disliking) character of the molecule to be adsorbed (sorbate) and/or the high affinity of the sorbate for the resin (sorbent). Non-IEX-based sorption results from the net effect of the combined interactions of these two driving forces. The affinity of the sorbate for the sorbent can result from physical or chemical mechanisms.

Physical mechanisms include dipole–dipole interactions and van der Waals interactions. Dipole moments are caused by a net separation of positive and negative charges derived from the position of atoms and electrons within the molecule. When dipoles from two molecules (e.g., sorbate and sorbent) are near each other, they tend to orient their charges to lower their combined free energy; the negative poles of one molecule tend to approach the positive pole of another, and vice versa. This realignment results in a net attraction between the two molecules.

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When two neutral molecules with no permanent dipoles approach each other, a weak polarization is induced in each because of slight variations in each molecule's charge distribution. The slight variation in charge distribution generates a weak attraction between the two molecules. This attractive phenomenon is known as the van der Waals force. Van der Waals interactions are generally weaker than dipole–dipole interactions.

Chemical mechanisms, or chemisorption, is a type of adsorption involving a chemical reaction between the sorbate and the surface of the sorbent. This strong attraction or reaction creates new chemical bonds. Resins that employ chemisorption for constituent removal are single use and disposable because they are very difficult or impossible to regenerate.

14.1.2 Chemical Properties

14.1.2.1 IEX Capacity

IEX capacity is expressed as either total capacity or operating capacity. Total capacity is based on the total number of fixed sites available for exchange, whereas operating capacity is a measure of the useful capacity observed during site-specific operating conditions (i.e., site water, temperature, flow rate, etc.). Some factors affecting operating capacity will be described in more detail in Section 14.3.

Total capacity is expressed on a dry weight, wet weight, or wet volume basis. Total capacity is a measure of the number of available IEX sites and is typically expressed as equivalents of ionic charge per mass or volume of resin.

Operating capacity is a measure of the useful performance obtained during dynamic loading conditions (flow conditions in a column or vessel containing the IEX resin). Operating capacity is dependent on the total capacity of the resin, the completeness of conversion or regeneration, the complexity or composition of the matrix being treated, the flow rate through the column or vessel, temperature, particle size, and flow distribution through the resin bed (i.e., plug flow or uneven flow distribution).

14.1.2.2 Kinetics

Kinetics are the speed or rate at which IEX or adsorption takes place. The rate of IEX or adsorption is directly related to the diffusion of the sorbate through the film of solution that is in close contact with the resins and diffusion within the resin particle. Film diffusion is the rate-limiting step at low sorbate concentrations, whereas particle diffusion (diffusion through the bulk medium) is the rate-limiting step at high sorbate concentrations. Resin bead particle size is also a rate-determining factor; uniform particle size (i.e., relatively small) yields enhanced kinetic behavior, while nonuniform particle size yields slower kinetic behavior due to the presence of kinetically slower, larger resin beads.

14.1.2.3 Selectivity

For an IEX resin to be effective, there must exist a difference in the affinity for the counterion on the resin in its as-received form (e.g., typically the chloride form for an

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TABLE 14.1
Selectivity Coefficients of Various Anions (Compared with the Hydroxyl Ion) on Functionalized Styrene–DVB Type 1 and Type 2 Anion Exchange Resins

Anion	Type 1	Type 2
OH^-	1.0	1.0
SO_4^{2-}	85	15
ClO_3^-	74	12
NO_3^-	65	8
CN^-	28	3
Cl^-	22	2.3

SBA IEX resin) and the ion to be removed from solution. That is, the resin must have a higher affinity for the ion in solution than the ion already on the resin.

Several resin manufacturers have developed selectivity coefficients of various ions for both cation and anion IEX resins. These selectivity coefficients have been normalized to a value of 1.0 for hydrogen ion (H^+) for cation IEX resins and hydroxide ion (OH^-) for anion IEX resins. Table 14.1 shows examples of selectivity coefficients for Type 1 and Type 2 SBA IEX resins.

14.1.2.4 Swelling

Swelling of IEX resins results from hydration of the fixed IEX group. Resins with a lower percentage of cross-linking experience more swelling from hydration. IEX resin volume also changes when converting from the as-received form, typically the chloride ion form for SBA IEX resins, to the PFAS-exchanged form. Allowance must be made in system design to accommodate resin swelling and shrinkage.

14.1.2.5 Stability

IEX resins are readily and rapidly attacked by strong oxidizing agents, such as nitric acid. More common oxidants, such as peroxide, oxygen, or chlorine, react more slowly, but the rate and severity of oxidation can be induced catalytically by the presence of metal ions, such as iron, copper, titanium, and manganese. Cation IEX resins are principally attacked at the polymer backbone, whereas anion IEX resins are principally attacked at the functional group, both of which can lead to total loss of capacity.

From a thermal stability perspective, cation IEX resins are more stable and can handle temperatures as high as 150°C, whereas anion IEX resins have a temperature limitation of approximately 60°C. Both cation and anion IEX resin stability is influenced by pH; anion IEX resins are more stable at lower pH, whereas cation IEX resins are more stable at elevated pH.

14.2 MECHANISMS OF PFAS REMOVAL USING IEX RESINS

Anion exchange resins are highly effective at removing PFAS from water because of the multiple removal methods involved. The molecular structure of most PFAS

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compounds can be broken into two functional units: the hydrophobic, nonionic "tail," consisting of the fluorinated carbon chain, and the anionic "head," having a negative charge. Figure 14.4 illustrates this structure.

Anion exchange resins are essentially adsorbents with IEX functionality. The resin beads are composed of neutral copolymers (plastics) that have positively charged exchange sites. Figure 14.5 shows the basic structure of an anion exchange resin with its neutral, hydrophobic backbone and one of its positively charged exchange sites. Anion exchange resins tend to be effective at removing PFAS from water because they take advantage of the unique properties of both the resin and the perfluorinated contaminants. The hydrophobic carbon-fluorine tail of the PFAS adsorbs to the hydrophobic backbone on the resin, and the negatively charged head of the contaminant is attracted to the positively charged IEX site on the resin. Depending on the specific properties of both the resin and the PFAS molecule, this dual mechanism of removal can be highly effective, and certain anion exchange resins have very high removal capacity for PFAS (Nickelsen and Woodard, 2017).

While this dual mechanism of PFAS removal can be highly effective at removing PFAS from water, it also makes resin regeneration and reuse challenging. A brine solution can be used to effectively desorb the anionic head of the molecule from the resin IEX site, but the hydrophobic carbon-fluorine tail tends to stay adsorbed to the resin backbone. Similarly, an organic solvent, like methanol or ethanol, can be used to effectively desorb the hydrophobic tail, but then the anionic head of the PFAS stays attached to the resin IEX site. Research to date has demonstrated that effective regeneration techniques must address both mechanisms of attraction. For example, certain surfactants that have both nonionic and anionic properties have shown promise for use in regenerant solutions (Nickelsen and Woodard, 2017). Solutions combining organic solvents and sodium chloride have produced the most successful results to date (Deng et al., 2010; Chularueangaksorn et al., 2013; Nickelsen and Woodard, 2017). Other research has focused on using combinations of ammonium

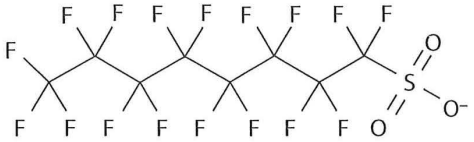


FIGURE 14.4 Structure of PFOS molecule.

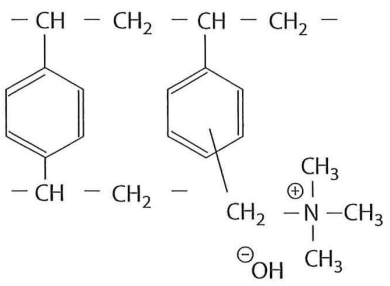


FIGURE 14.5 Molecular structure of a typical anion exchange resin.

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salts, including ammonium hydroxide and ammonium chloride (Conte et al., 2015). Du et al. (2014) disclosed a need to further treat the resulting waste regenerant solution to concentrate the PFAS and minimize the volume of waste. Chapter 21 is a case study that describes isotherm, bench-scale, and pilot-scale work conducted at the former Pease Air Force Base, including the process that was used to narrow the field from eight candidate resins to the single best performer (taking into account both the effectiveness of PFAS removal and the ability of the resin to be regenerated).

It should be noted that although the majority of PFAS compounds have an anionic charge, certain PFAS molecules are cationic and others are zwitterionic, having both a positive and a negative electrical charge. This opens the door for future research in the rapidly changing field of PFAS removal from water. IEX resins hold significant promise given the wide variety of resins, both cationic and anionic in nature.

In summary, the PFAS removal effectiveness of individual resins varies based on multiple factors, which will be explored in more detail in Section 14.3 (Deng et al., 2010; Dudley, 2012; Appleman et al., 2014). For example, the PFAS capacity of some resins is highly dependent on the inorganic content of the water, including both the type and concentration of ions in solution. Other resins are less sensitive to inorganic ions, as these resins have a substantially higher affinity for the PFAS molecules than for the inorganic ions. Given the resin specificity and highly variable nature of PFAS-contaminated water, bench-scale column testing is recommended to determine the most effective resin for a specific application.

14.3 IMPORTANCE OF WATER QUALITY ANALYSIS

For proper sizing of an IEX treatment system, the processing flow rate, quality of water being treated, required quality of treated water, and capital and operation and maintenance (O&M) costs must all be considered. This section focuses on the importance of the quality of the water to be treated, specifically the types and concentrations of nontarget constituents present in the water, as their presence has direct implications on system design and capital and O&M costs.

The capacity of an IEX resin is expressed in equivalents per liter (eq/L) of resin or equivalents per kilogram (eq/kg) of resin, where an equivalent is defined as the number of moles of a given ion in solution multiplied by the valence state of the ion in solution. For example, if 1 mol of nitrate ion and 1 mol of sulfate ion were present in a solution, there would exist 1 eq of nitrate (nitrate ion has a valence state of 1) and 2 eqs of sulfate (sulfate ion has a valence state of 2). Carboxylate and sulfonate PFAS compounds each have an ionic valence state of 1.

The major ions typically found in natural groundwater are shown in Figure 14.6 (Dardel and Arden, 2001). Natural organic matter (NOM) is included under the anion group because NOM is a complex mixture of cross-linked organic polymers containing phenolic and carboxylic acid functional groups, and at typical groundwater pH levels, the carboxylic acid functional groups are ionized to carboxylates.

In addition to the major ions shown in Figure 14.6, additional ions, such as iron (Fe^{2+}/Fe^{3+}), other transition metals, transition metal complexes, and silicon dioxide, can impact the performance of IEX resins. The discussion in this section, however, is limited to how water quality parameters can impact the performance of SBA IEX

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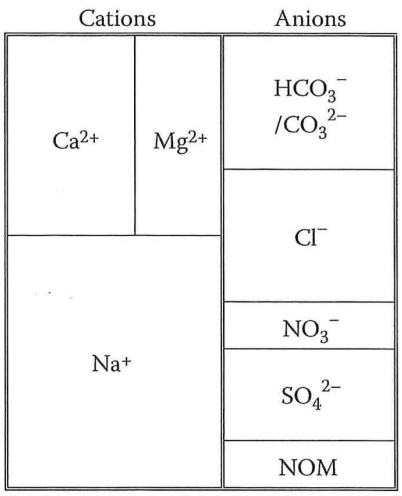


FIGURE 14.6 Composition of water.

resins for the removal of PFAS compounds. It is important to understand the impact of water quality on IEX resin effectiveness and to perform a detailed water characterization prior to design.

14.3.1 Solids

Solids, whether suspended or dissolved, can prevent the efficient exchange of ions by blocking access to IEX sites. Prefiltration of feedwater is often accomplished with small-pore (<10 μm) filtration media, deep-bed sand filtration, or multimedia filtration for the removal of particulate matter. In some cases, pretreatment with a strong acid cation resin for the removal of the cation portion of total dissolved solids (TDS) may be necessary for effective and/or economical PFAS treatment. For some applications, pretreatment with a cation exchange resin will enhance anion exchange resin performance because the cation exchange resin prevents precipitation of insoluble metal hydroxides and shifts NOM to a protonated, nonionic form.

14.3.2 Natural Organic Matter

The heterogeneous mixture of organic compounds in natural waters, more commonly known as NOM, can reduce the number of resin sites available for PFAS removal, either by direct competition for adsorption sites or by pore blockage. In general, NOM is an ill-defined mixture of naturogenic organic compounds arising from plants and animals and their decomposition products. Two major organic constituents of NOM are humic acid (Figure 14.7) and lignin. Both are large organic molecules that contain a relatively complex mixture of phenol and carboxylic acid groups. The presence of phenolate and carboxylate groups means that the mixture behaves functionally as a dibasic or tribasic acid, and at common groundwater pH values, NOM is negatively charged and is therefore readily captured by anion IEX resins. Pretreatment vial physical filtration or pH adjustment (via acid addition or

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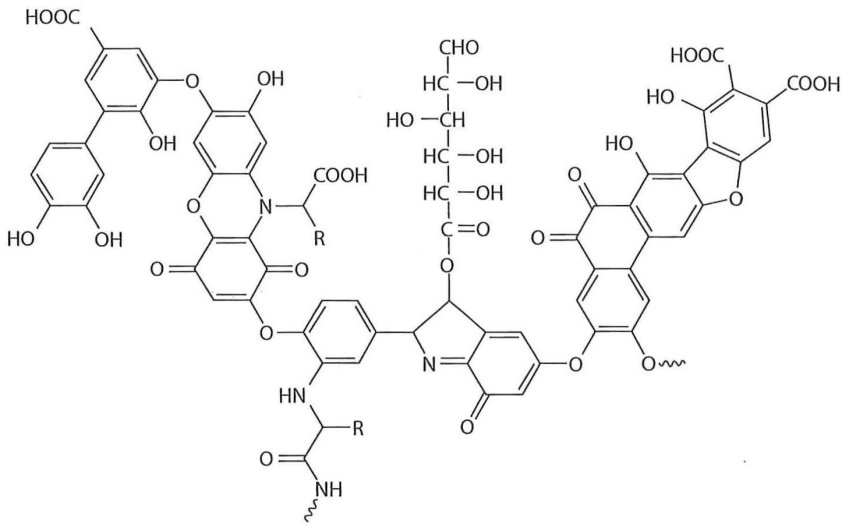


FIGURE 14.7 Generalized structure of humic acid.

use of a cation IEX resin) may be required for effective and/or economical PFAS treatment.

14.3.3 Nitrate, Sulfate, and Other Inorganic Anions: Relative Affinity

The effectiveness of SBA IEX resins is highly dependent on the water quality analysis. Specifically, the constituents to be removed, the treatment objective, and what is present in the water could adversely affect IEX performance. Ion selectivity is the primary driving force governing appropriate resin selection. Selectivity is determined by the ionic charge of the specific ion and the resin type. Typically, IEX resins have a higher selectivity for higher-valence state ions (2^+, 2^-, 3^-, etc.) than for singly charged ions. As discussed in Section 14.1.2.3, the general affinity of an SBA resin for anions in solution follows the general trend shown in Table 14.2.

In waters with moderate to high alkalinity, pH adjustment to acidic levels or use of an SBA IEX resin in the chloride form will minimize the impact of competition from bicarbonate anion (HCO_3^-). However, even if selectivity is low, IEX can

TABLE 14.2
SBA Resin Anion Selectivity

Anion	Affinity
SO_4^{2-}	Higher
NO_3^-	↓
Cl^-	↓
HCO_3^-	↓
$HSiO_3^-$	↓
OH^-	Lower

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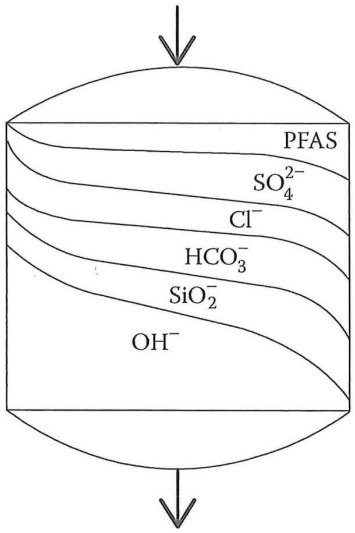


FIGURE 14.8 SBA selectivity profile.

still take place on a mass action basis. That is, if the resin is clean and free from the contaminant of interest, the resin will still remove a modest percentage of that contaminant.

During typical SBA IEX treatment, more attractive ions are removed first (i.e., SO_4^{2-}) and concentrate at the inlet side of the IEX bed. As more ions pass through the bed, ions with less affinity are displaced and gradually move downgradient through the resin bed. This is known as the "chromatography effect" (anions with lower affinity are displaced with ions of higher affinity). Based on observed ion elution profiles, PFAS constituents have a much higher selectivity profile than even sulfate ions on SBA IEX resins (Figure 14.8), because of the combined IEX and adsorption mechanisms described in Section 14.2.

14.3.4 Iron Fouling

Iron fouling is one of the predominant causes of IEX failure. Most waters contain some level of soluble iron in the reduced (Fe^{2+}) state. To minimize the potential for iron fouling, iron must either be kept in the reduced state by preventing aeration of the process water or be removed by precipitation and filtration.

Aeration induces oxidation of ferrous iron (Fe^{2+}) to ferric iron (Fe^{3+}), resulting in precipitation of ferric hydroxide, carbonates, and complexes, which clog resin beads, preventing IEX. If aeration cannot be avoided, another approach is to intentionally oxidize the iron using aeration or by adding a chemical oxidant. This promotes the precipitation of insoluble ferric iron, which is then removed via sedimentation and/or filtration prior to the IEX resin.

14.3.5 pH

In general, anion exchange resin performance increases as pH decreases due to less interference from metal hydroxide precipitates and NOM. Once the pH drops to less

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than 3, however, the efficiency of short-chain PFAS compound removal begins to diminish since these compounds begin to shift from their ionic to neutral, protonated forms. At a pH value less than 1, PFAS removal is significantly impacted and pH adjustment is required.

14.4 IMPORTANT DESIGN PARAMETERS

There are several key parameters to consider when designing an IEX resin treatment system for PFAS removal. These include, but are not limited to, influent equalization, pretreatment, empty bed contact time (EBCT), vessel sizing and geometry, flow distribution through the resin bed, face piping and valves, fixed-bed versus backwashable systems, vessel arrangement, and whether to use single-use or regenerable IEX media. Each of these important parameters is discussed below.

14.4.1 Influent Equalization

Vessel sizing is based mainly on EBCT, so it is important to maintain a relatively steady influent flow rate to the IEX resin system to minimize occurrences of low-level leakage. Groundwater extraction systems often employ multiple extraction wells, and influent flow rates can fluctuate substantially. Equalization is generally recommended to dampen these variations. This topic is covered in more detail in Section 14.6, which discusses major equipment used in the IEX treatment and regeneration processes.

14.4.2 Pretreatment Considerations

Pretreatment for fouling control should be considered for all PFAS IEX resin systems. Important water quality considerations have been covered in Section 14.3, including solids, iron and manganese, NOM, inorganic anions, and pH control. Bench and/or pilot testing is typically recommended to better understand and provide design criteria for pretreatment systems. When fixed-bed IEX vessels are used, suspended solids must be removed upstream of the IEX media to avoid solids accumulation in the IEX vessels. As discussed in Section 14.3.4, when metals (i.e., iron, manganese, etc.) are present in the dissolved form, the treatment train can be designed to keep solids in the dissolved state (i.e., avoid oxidation or aeration) and minimize the need for pretreatment. Sequestering agents and/or pH adjustment may be incorporated to aid in keeping these metals in the dissolved state.

Common pretreatment methods include

- Particulate filtration (multimedia, catalytic media, sand filters, bag filters, cartridge filters)
- Oxidation using aeration and/or chemical agents
- Granular activated carbon (GAC)
- Sequestering agents (examples include Redux 601, a chelating dispersant blend; Redux RDB, a reducing dispersant blend; and CARUSQUEST 101, a phosphonic acid)

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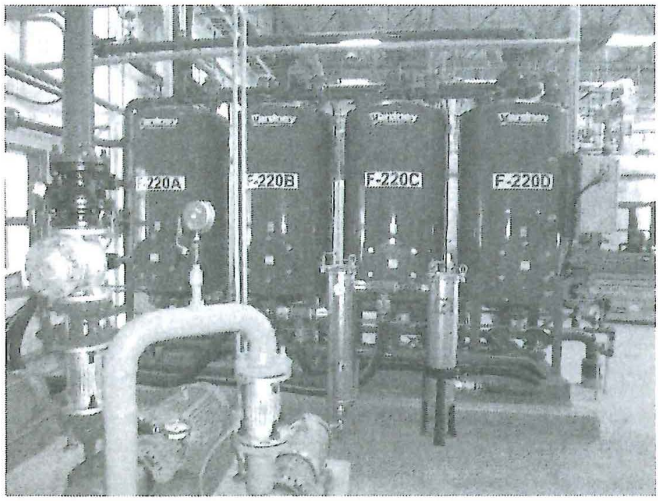


FIGURE 14.9 Catalytic media filtration system for pretreatment.

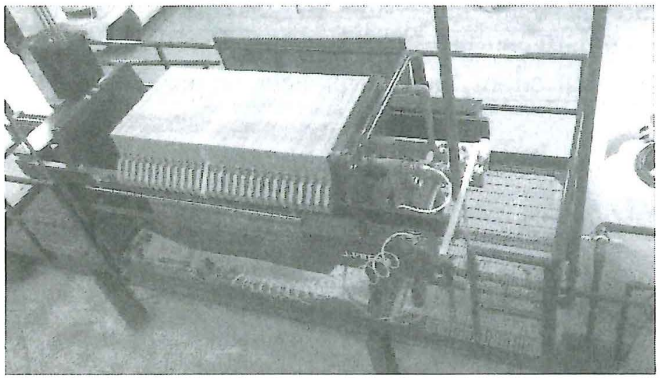


FIGURE 14.10 Plate and frame filter press.

- pH adjustment
- IEX resins for softening, total organic carbon (TOC) removal, and so forth

Backwash, air scour, and solids handling may also be required depending on the selected pretreatment approach. Figure 14.9 shows a four-vessel catalytic media filtration system for removing suspended solids, iron, and manganese. Figure 14.10 shows a plate and frame filter press for dewatering the solids generated by backwashing the pretreatment filters.

14.4.3 Empty Bed Contact Time

IEX resin systems have faster kinetics and higher capacities than GAC systems for PFAS removal. This allows the use of shorter EBCTs. Whereas GAC systems are usually designed in the 10- to 20-minute EBCT range, a resin system can be sized for EBCTs as low as 2 minutes. This provides advantages in terms of footprint and

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capital cost. Final design EBCT selection is based on numerous factors, including footprint, regeneration requirements, capital cost, and O&M costs.

14.4.4 Vessel Sizing and Geometry

IEX contactor vessels are sized based on process flow rate and the minimum EBCT necessary to balance achievement of treatment objectives and O&M costs. Using a height-to-diameter ratio of 1.5 to 2.0 is preferred for resin system vessels when used for adsorption. Lower height-to-diameter ratios can be and often are used for IEX vessels. However, minimum bed depth, velocities, flow distribution, spatial considerations, and material cost must be considered in the design at lower ratios.

Height-to-diameter ratios greater than 2.0 yield better treatment capacity because the hydraulic conditions are closer to plug flow, but higher ratios also cause increased head lead loss. Pump size and energy use increase as differential pressure increases across the resin vessel(s). These issues are discussed in greater detail in Section 14.6.

Cylindrical pressure vessels are normally used to contain the resin. The tanks can be made of steel or fiberglass-reinforced plastic (FRP) construction, and tank operating pressures normally range from 10 to 50 psig. In addition to vessel sizing, the design engineer must consider inlet and outlet connections, resin fill and removal connections, vent connections, and instrumentation ports when selecting the appropriate vessel.

14.4.5 Flow Distribution through the IEX Resin Bed

Treatment vessel internals should be designed to maximize plug flow conditions and minimize short circuiting by distributing process water and regenerant solution uniformly through the resin bed. This is accomplished by the use of flow distributors and collectors. To maximize resin bed capacity, it is critical that the distributors or collectors are properly sized and installed to control flow and flow velocity. Distributor or collector slot width should be small enough to keep resin particles from escaping while providing sufficient open area to handle the design flow range and maintaining enough back pressure to uniformly distribute the flow throughout the entire cross section of the vessel (Owens, 1995).

There are various types of flow distributors, including perforated plates outfitted with screens, filter caps, sintered metal plates, and lateral and/or hub-and-spoke assemblies. Figures 14.11 and 14.12 show examples of a hub-and-spoke design and a lateral-type distributor or collector design, respectively.

14.4.6 Face Piping and Valves

An IEX resin system for PFAS removal typically consists of multiple vessels connected with face piping to allow different directions and volumes of flow, including forward flow (loading cycle), regeneration, and backwash (if applicable). It is desirable to design these systems to maintain forward-flow treatment while one or more vessels is offline for regeneration and/or backwash. The valves that control these various flows can be either manual or automatic, depending on the project needs and

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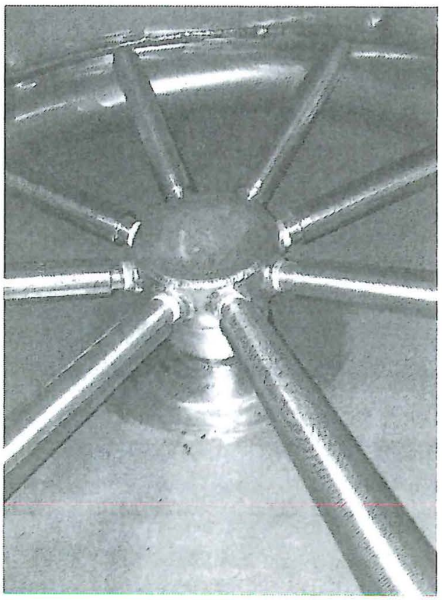


FIGURE 14.11 Hub and spoke distributor or collector.

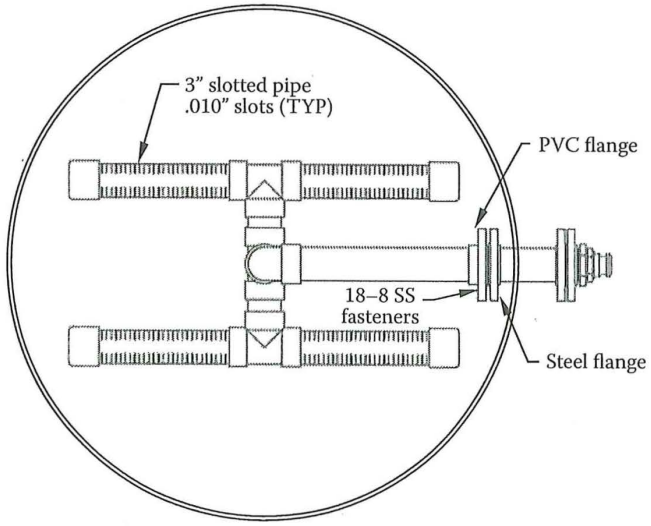


FIGURE 14.12 Lateral-type distributor or collector. (Used with permission from Carbon Service & Equipment.)

system requirements. Valve choice is important to prevent leakage and associated cross-contamination from regenerant or backwash water.

14.4.7 Fixed Bed versus Backwashable

Although the design engineer should strongly consider providing the ability to backwash the resin vessels, there are some notable exceptions. The primary advantage of backwashable beds is the ability to relieve excess pressure drop caused by the

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buildup of solids. The disadvantage is that backwashing disturbs the mass transfer zone, which can cause premature leakage and reduced treatment capacity. Disruption of the mass transfer zone also makes it more difficult to effectively regenerate the resin using countercurrent flow, and therefore requires more regenerant solution to completely desorb the PFAS from the resin bed.

It is generally safer to include backwash capability, but the decision is situation specific, depending on influent water quality, fouling potential, and the effectiveness of pretreatment, including solids filtration and iron and manganese removal. If a backwash system is included, then the design should include

- Added tankage for clean and dirty backwash water
- Pumps, piping, valves, and solids processing
- Freeboard in the vessel to allow for media expansion
- Air scour capability
- Appropriate pipe sizes, including the distributors and collectors, to handle the potentially higher flow rates associated with backwash

Fixed-bed system designs, on the other hand, should provide some freeboard to account for potential resin swelling. Countercurrent operation is preferred for these systems to maintain the highest PFAS concentrations at the influent end of the bed. This helps maintain relatively clean conditions at the discharge end and reduces the potential for "smearing" the mass transfer zone. The overall goal of countercurrent operation is to minimize the volume of regenerant solution required, which helps reduce the volume of waste that must ultimately be disposed and the associated O&M costs.

14.4.8 Lead–Lag Vessel Arrangement

IEX resin treatment systems are typically designed with multiple vessels in series. Vessel arrangements include lead–lag and lead–lag–polish configurations (Figure 14.13).

Having multiple vessels in series accommodates longer loading cycles and more complete resin use before a regeneration cycle must be initiated. The higher capital cost associated with multiple vessels in series is offset, to varying degrees, by the reduced O&M costs and the enhanced ability to maintain compliance (i.e., better

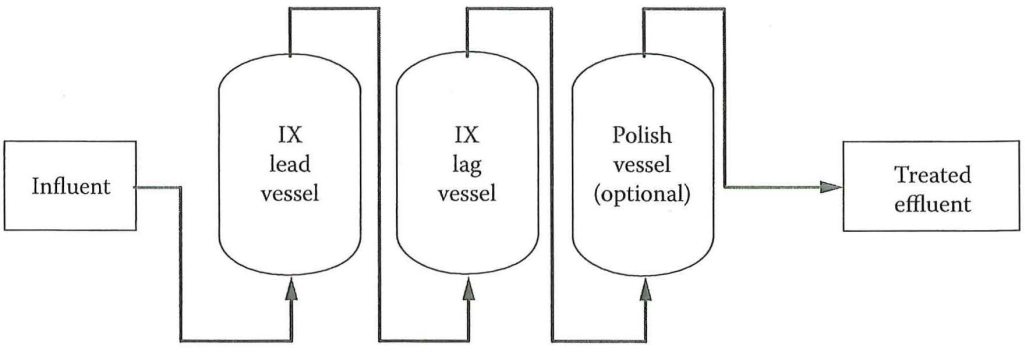


FIGURE 14.13 Typical IEX vessel configuration.

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treatment performance). It also allows continuous operation while one or more vessels are regenerated or backwashed. The decision to add a third (polish) vessel is largely dependent on influent PFAS concentrations and effluent permit limits. Again, the trade-off between capital and O&M costs needs to be considered, as additional vessels increase capital cost and power costs to pump water through the beds, but can reduce the required regeneration frequency.

14.4.9 Single-Use versus Regenerable Systems

The design engineer must decide whether to incorporate a resin regeneration system or simply go with single-use resin. The inclusion of a regeneration system is typically based on payback. If the contaminated groundwater is from a source area, such as a fire training area, then the resin will likely require regeneration with such frequency that the O&M savings would more than offset the additional capital expense. More dilute applications, including plume containment and drinking water treatment, may have low enough PFAS concentrations that a resin regeneration system does not make financial sense. In these cases, the IEX resin systems are still normally more cost-effective than GAC because the resin's treatment capacity is much higher (i.e., smaller vessels and longer time between media change-outs). The resulting waste resin can be either landfilled or thermally destroyed via incineration.

14.5 IEX CYCLES

Regenerable IEX treatment systems are operated using three primary operating cycles: loading, regeneration, and rinse. When using a single-use IEX media, the regeneration cycle is replaced with media change-out. This chapter describes the loading cycles for regenerable IEX media.

14.5.1 Loading Cycle

In the loading cycle, contaminated water is pumped through the IEX media vessels, typically in a lead–lag or lead–lag–polish configuration, with treated water exiting the bed. The loading cycle is the longest stage in the typical IEX cycle, normally consisting of 80%–95% of the overall cycle duration, with the regeneration and rinse cycles comprising the remaining 5%–20%. This breakdown differs somewhat when treating PFAS, since the influent concentrations are normally much lower (i.e., ppb and ppt levels instead of ppm) and the resins have a higher selectivity for PFAS than for inorganic ions. The PFAS loading cycles are typically in the 90%–99% range, with the regeneration and rinse cycles comprising the remaining 1%–10%. The lead vessel is subject to the highest contaminant loading during the loading cycle, which concludes when a regeneration trigger is reached. The trigger can be a predetermined amount of time, contaminant breakthrough, differential pressure, or a combination of these factors. The regeneration trigger is influenced by several factors, including (1) the contaminant breakthrough curve, (2) vessel configuration, (3) effluent limitations, (4) differential pressure, and (5) owner or operator preference. These factors are expanded on in Table 14.3.

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TABLE 14.3
Factors Influencing IEX Regeneration or Change-Out

Factor	Description/Considerations
Contaminant breakthrough curve	The contaminant breakthrough curve will be developed during bench and/or pilot testing. In general, the steeper the breakthrough curve, the lower the allowable breakthrough percentage prior to triggering a regeneration.
Vessel configuration	Adding a polish vessel (lead–lag–polish) provides a safety factor that can allow for an increased or extended regeneration trigger with reduced risk of effluent breakthrough.
Effluent limitations	If contaminant effluent limits are near the analytical detection limit, regeneration may be triggered by timing before any breakthrough is observed at the lead bed effluent.
Differential pressure	If excessive differential pressure is observed, a regeneration or backwash may be triggered prior to achieving contaminant breakthrough.
Owner preference and risk tolerance	This may take into account any factor, or combination of factors, listed above. For example, operators with variable influent concentrations or dynamic contaminant loading scenarios that result in less predictable breakthrough times may elect regeneration at predefined times, regardless of effluent breakthrough.

Data collected during bench and/or pilot testing will provide guidelines for loading cycle duration for full-scale systems. Once the full-scale system is operational, these parameters are refined during start-up and the initial operating period, for optimal system efficiency and risk minimization.

14.5.2 Regeneration Cycle

When a regeneration is initiated, the lead vessel is taken offline and the lag vessel becomes the new lead. The vessel designated for regeneration (either in place or off-site) is typically drained prior to starting the regeneration to minimize dilution of the regenerant. The water drained from the regeneration vessel can be recycled to the system influent and metered into the forward-flow stream. Next, regenerant is pumped through the vessel, typically in a countercurrent arrangement (discussed further in Section 14.4). A block flow diagram for one patent-pending IEX regeneration process is shown in Figure 14.14.

Empirical data suggest that a constant, low, single-pass flow-through of regenerant solution achieves optimal regeneration results. The optimum regenerant solution, concentration, flow rate, and volume used during regeneration to desorb PFAS from the IEX media and restore capacity are best approximated through bench testing, followed by optimization work at full scale. After the desired amount of regenerant has passed through the media, the remaining regenerant left over in the vessel is then drained to recapture the maximum amount of regenerant and minimize the amount of regenerant lost during the rinse cycle. Spent regenerant is collected in a tank or drum(s) and stored for additional processing to recycle the regenerant. Simple distillation, adsorption, IEX, filtration, and/or membrane processes can be used to effectively recover and reuse a substantial portion (greater than 98%) of the regenerant. The resulting PFAS

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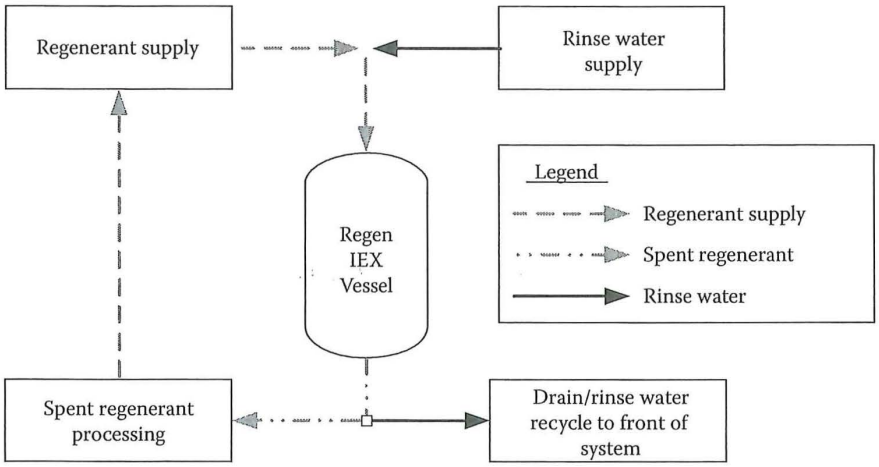


FIGURE 14.14 IEX regeneration block flow diagram.

waste stream can be converted to solid waste through a process called superloading, which minimizes the volume of waste to be landfilled or incinerated. This results in significant overall process savings, helping to make regenerable IEX resin systems an attractive, affordable, and sustainable alternative to GAC for PFAS removal.

14.5.3 Rinse Cycle

After the regenerant has been drained from the vessel, the IEX resin is flushed with clean water until the rinse water exiting the bed is below target concentrations (typically below effluent discharge limitations). The volume of rinse water required is best determined through testing during system start-up. Processed rinse water can either be collected in a holding tank or metered directly into the influent flow stream. The rinse water will initially contain a small amount of residual regenerant, more concentrated at the beginning of the rinse cycle and increasingly diluted throughout the rinse cycle. Testing must be performed during system start-up to understand the concentrations of regenerant and PFAS in the rinse water since rinse water will be a component of the overall system mass balance. Incorporating a rinse water holding tank provides the advantage of equalizing the rinse water, thereby eliminating a potential spike of spent regenerant concentration in the influent flow stream.

At the conclusion of the rinse cycle, the regenerated vessel is placed back into service in the lag vessel position. Having multiple vessels provides the opportunity to maintain forward flow while one vessel is offline for regeneration. This is an advantage compared with systems where the forward flow is interrupted for multiple hours while media change-out takes place.

14.5.4 Recovery and Reuse

Solvent-based spent regenerant can be recycled for reuse in the next regeneration by using a patent-pending distillation and superloading process (Nickelsen and Woodard, 2017). First, the spent regenerant is transferred to a solvent recovery unit. Solvent is recovered

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by the distillation process, given its low boiling point relative to water, and transferred to the regenerant supply tank for reuse in the next regeneration cycle. The leftover still bottoms (i.e., brine and concentrated PFAS) from the distiller are either further concentrated by evaporation or pumped through superloader vessels, transferring the bulk of the PFAS onto the superloaded media. Superloading is the process by which a relatively small volume of highly concentrated PFAS solution is passed slowly through a relatively small volume of media (either GAC or IEX resin). The long EBCT approaches equilibrium (isotherm) conditions, thereby maximizing PFAS mass transfer onto the media and minimizing the amount of solid waste requiring disposal or incineration.

14.6 EQUIPMENT

IEX resin treatment for PFAS removal can involve either single-use or regenerable resin systems. The type of resin system selected depends on multiple factors, including influent PFAS concentrations, treatment system objectives, characteristics of the water treated, and presence of co-contaminants. Figure 14.15 shows a generic process flow diagram of a groundwater pump-and-treat system using regenerable IEX treatment.

Some guidance and considerations for the treatment system components are provided in this section, which is broken into two parts: primary treatment equipment and regeneration system equipment.

In general, the primary treatment components include

- Extraction well pumps
- Influent equalization tank
- System feed pump(s)
- Pretreatment equipment
- IEX contactor vessels

Regeneration equipment for IEX media regenerated using a solvent–brine mixture typically includes the following

- Regenerant supply tank
- Spent regenerant tank
- Solvent recovery unit (distiller)
- Cooling equipment (chiller, fan cooler, or cooling tower)
- Still-bottoms tank
- Superloader contactor vessels
- Pumps and instrumentation

14.6.1 Primary Treatment Equipment

14.6.1.1 Extraction Well Pumps

Extraction well pumps are typically controlled based on flow rate or water level in the extraction well. Extracted groundwater is either pumped to an equalization tank or sent directly to the groundwater treatment system. If an equalization tank is not used, steady, consistent flow is recommended for consistent treatment performance.

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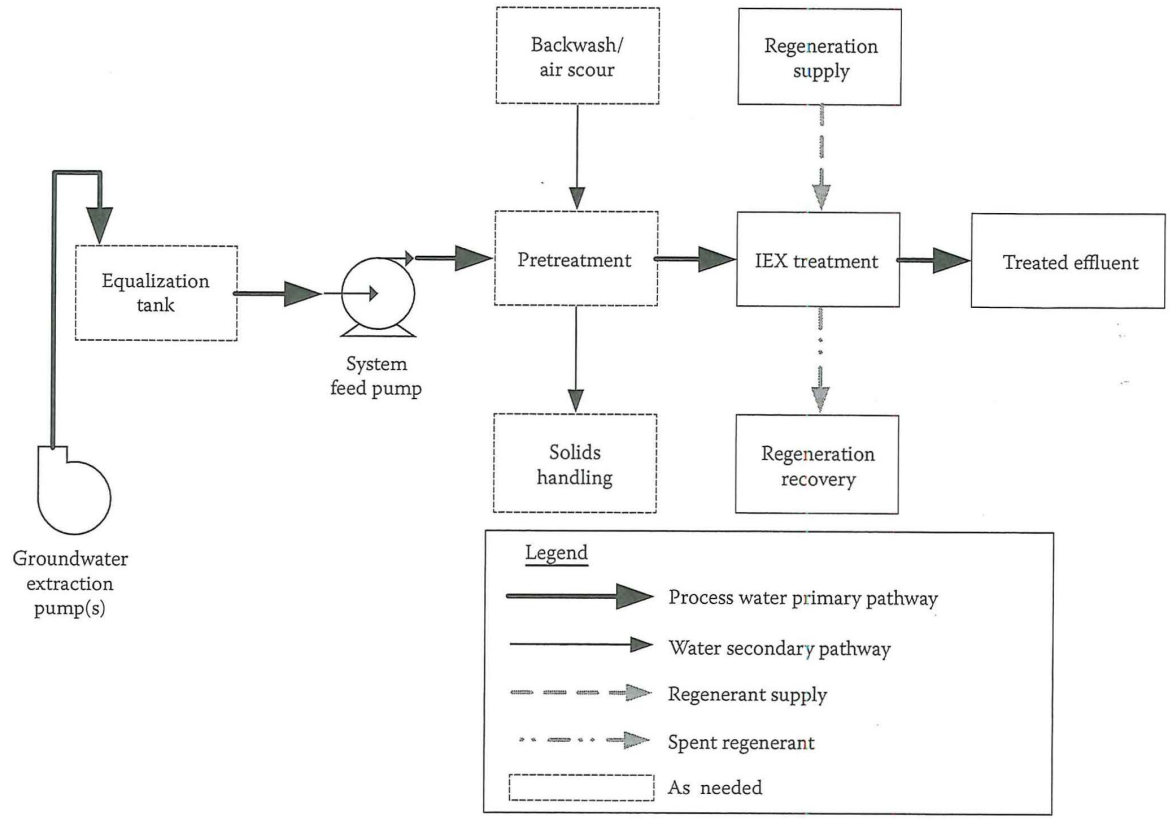


FIGURE 14.15 Typical pump-and-treat system using IEX.

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Therefore, when equalization tanks are not used, extraction pumps with variable-frequency drives (VFDs) are recommended to maintain steady flow.

14.6.1.2 Equalization Tank

An equalization tank provides a collection and equalization point for extracted groundwater. If iron is present in the reduced state, the design engineer may choose to consider bypassing the equalization tank to avoid aeration and subsequent oxidation or precipitation. Keeping the iron in its reduced, soluble ferrous form and taking advantage of the zero-headspace IEX vessels will potentially reduce pretreatment equipment and solid waste generation, as discussed in Sections 14.3.4 and 14.4.2. If the extraction well pumps are configured for on–off operation (e.g., on at high level, off at low level) or surge flow (i.e., air-driven pumps), an equalization tank helps to balance flow and avoid surging through the contactor vessels.

Equalization tanks are typically plastic or steel. When steel tanks are used, consideration is given to the corrosiveness of the groundwater being treated.

14.6.1.3 System Feed Pumps

System feed pumps are selected to provide steady, continuous flow at the desired rate with sufficient discharge head to move the feedwater through the treatment system. A VFD is recommended to control pump speed based on the water level in the equalization tank to provide steady flow and minimize cycling and surging. The design engineer should consider overall system losses (including pretreatment equipment, IEX vessels, effluent discharge, and interconnecting pipe and fittings), as well as allowable differential pressure buildup across pretreatment and IEX equipment. Duplex system feed pumps are typically used to provide redundancy and minimize downtime.

14.6.1.4 Pretreatment Equipment

The design engineer must understand the site-specific constituents in groundwater and corresponding effluent limitations prior to selecting a pretreatment approach. In addition, bench and/or pilot testing is recommended to confirm that pretreatment is sufficiently protective of the IEX media. Typical constituents that may foul or limit the capacity of an IEX bed include suspended solids, iron, manganese, nitrate, and high concentrations of NOM as indicated by TOC levels. Pretreatment to control and/or remove these constituents was discussed in more detail in Section 14.4.2.

14.6.1.5 IEX Contactor Vessels

IEX contactor vessels are sized to achieve target contaminant reduction and adequate EBCT. EBCTs for IEX treatment system vessels are typically lower than those using GAC, resulting in a smaller system footprint, as discussed in Section 14.4.3. Materials of construction for contactor vessels are selected for compatibility with groundwater and regenerant and compliance with applicable regulations. Vessels are designed to be fully draining to maximize effectiveness of media regeneration. Using greater height-to-diameter ratios offers treatment advantages, as discussed in Section 14.4; however, this must be balanced with differential pressure (head loss), material cost, and practical spatial considerations. Figure 14.16 shows a three-vessel IEX resin treatment system with associated face piping and valves.

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If differential pressure increases across IEX contactor vessels due to solids buildup and is not restored after regeneration, treatment with a reducing agent or Iron-Out® may be considered. However, a better approach is to improve pretreatment to minimize suspended solids reaching the IEX contactor vessels.

IEX systems can be installed in shipping containers to provide a compact, mobile, efficient, cost-effective PFAS treatment solution. Figure 14.17 is a photo of the outside of a shipping container housing a treatment system, and Figure 14.18 shows a plan view representation of IEX resin vessels inside the box.

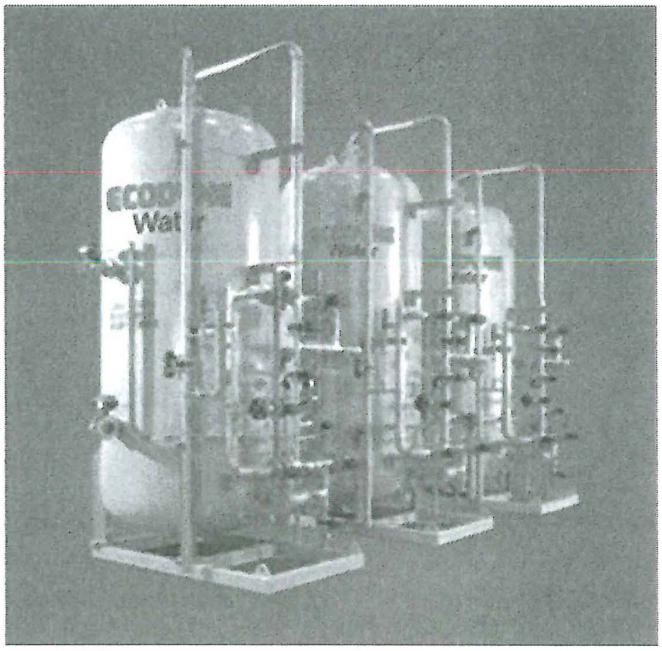


FIGURE 14.16 Three-vessel IEX resin treatment system.

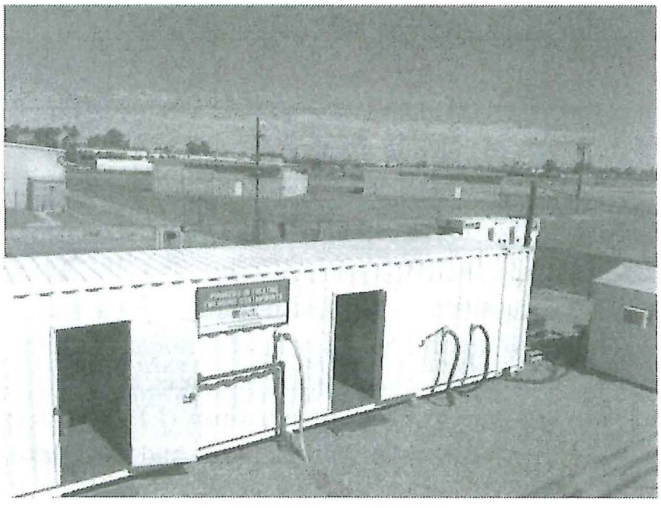


FIGURE 14.17 Shipping container housing groundwater treatment system.

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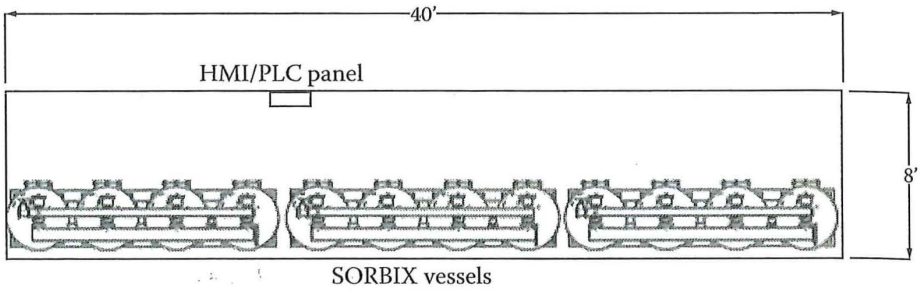


FIGURE 14.18 Plan view of IEX resin vessels inside storage container. HMI = Human–Machine Interface; PLC = programmable logic controller.

14.6.2 Regeneration Equipment

Depending on the influent PFAS concentrations and life cycle cost analysis, it may be desirable to install a resin regeneration system. Regeneration systems can be in place or at a centralized regeneration facility where vessels are transported to the facility for regeneration and then returned to service. Regeneration systems provide the capability to periodically desorb PFAS compounds from the IEX resin, facilitating reuse of the resin without removing it from the vessels. Equipment considerations for regeneration system components are provided in this section. When using flammable liquid for regenerant, additional regulations apply, including NFPA 30: "Flammable and Combustible Liquids Code." A code review and area classification should be performed in the early stages of design.

14.6.2.1 Supply and Spent Regenerant Tanks

Supply and spent regenerant solution (regenerant) holding tanks are sized to contain an adequate volume of regenerant to sufficiently restore the IEX media capacity, plus freeboard and safety factor. Bench or pilot testing may be used to verify this volume. Regenerant tank materials of construction are selected for compatibility with all components of the regenerant blend and compliance with regulations. One effective, patent-pending regenerant blend includes flammable liquids and brine. Therefore, tanks must meet applicable codes for storage of flammable liquids, and consideration must be given to materials of construction to minimize corrosion.

14.6.2.2 Pumps and Instrumentation

Regenerant transfer pumps should be self-priming and are selected for material compatibility and area classification. Instrumentation is used in the regeneration cycle for safety and process control and may include some or all the following: flow meters, pressure and temperature gauges or transmitters, conductivity sensors, level transmitters and switches, and lower explosive limit (LEL) sensors or controllers. Instruments are selected for compatibility with fluids and area classification.

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14.6.2.3 Regenerant Recovery Equipment

It is often economically and environmentally favorable to recover and reuse regenerant solution, especially since the process is relatively straightforward. Spent regenerant, stored in the spent regenerant tank, is recovered in stages and returned to the regenerant supply tank. Regenerant recovery equipment is sized to ensure that all stages of the recovery process can be completed prior to the next regeneration. For example, if regenerations are expected to occur on a monthly basis, the regenerant recovery process must be completed in less than a month.

14.6.2.4 Solvent Recovery Unit (Distiller)

When solvents are used to regenerate the IEX resin, the first stage of regenerant recovery is solvent recovery, which is typically achieved through distillation. A typical distiller is shown in Figure 14.19.

The distillers are sized such that the total volume of spent regenerant is processed in the first part of the regeneration cycle, allowing adequate time for still-bottoms recovery. The distiller produces two effluent streams: distillate (i.e., recovered solvent) and still bottoms. The vast majority of contaminants are concentrated in the still bottoms.

14.6.2.5 Still-Bottoms Handling

Still bottoms generated from the distillation process are collected in a holding tank and are typically processed through superloader vessels prior to being transferred to the regenerant supply tank. The still-bottoms holding tank is sized to contain the total volume of still bottoms for a regeneration cycle plus margin and freeboard. Materials of construction of the still-bottoms holding tank are selected for compatibility with still-bottoms constituents and temperature considerations.

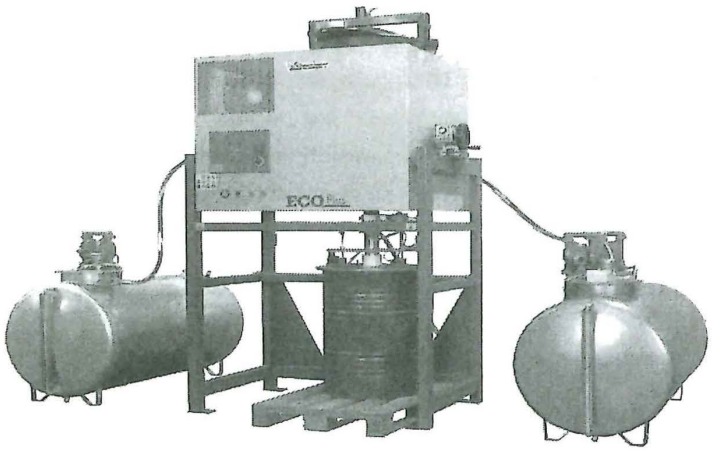


FIGURE 14.19 Typical distiller (center) shown with supply stocking tank (left), still-bottoms drum (bottom center), and distillate stocking tank (right). (Photo courtesy of NexGenEnviro Systems, Inc.)

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Still bottoms are pumped from the still-bottoms holding tank through superloaders at a slow, steady flow rate to maximize superloader performance. Superloading is the final step in the three-step PFAS ultraconcentration process: IEX, distillation, and superloading. Millions of gallons of contaminated groundwater can be concentrated into less than 100 gallons (13 cubic feet) of solid waste.

14.7 SUMMARY

Certain anion exchange resins have properties that lend themselves well to high-capacity removal of PFAS from water. These resins are essentially adsorbents with IEX functionality and take advantage of the unique properties of both the resin and the perfluorinated contaminants: the hydrophobic carbon-fluorine tail of the PFAS adsorbs to the hydrophobic backbone on the resin, and the negatively charged head of the contaminant is attracted to the positively charged exchange site on the resin. This dual-removal mechanism provides higher capacities and faster removal kinetics than GAC, resulting in a treatment system with a smaller footprint and lower life cycle costs. A pilot-scale case study highlighting these advantages is provided in Chapter 21.

Another significant advantage of IEX resin is its ability to be regenerated in vessel. Proprietary regeneration methods have been developed that are capable of restoring resin capacity to near-virgin conditions, making resin a more sustainable treatment solution than GAC. Distillation is used to recover and reuse the majority of regenerant solution, and the concentrated PFAS in the still bottoms can be further concentrated into a solid waste using superloading.

In addition to being more sustainable than GAC, IEX resin systems have the potential to share a central resin regeneration system. For example, multiple groundwater treatment systems are often required to address the PFAS contamination at a single military installation. Using IEX resin treatment provides the opportunity to use one central regeneration facility to serve these multiple treatment systems by simply transporting resin vessels to and from the central regeneration system. IEX resin systems, including the regeneration components, also tend to be compact, relatively lightweight systems that can be installed inside shipping containers. The result is a compact, rapidly deployable, mobile, cost-effective PFAS treatment process.

Although the majority of PFAS compounds have an anionic charge, certain PFAS molecules are cationic, and others are zwitterionic, having both a positive and a negative electrical charge. This opens the door for future research in the rapidly changing field of PFAS removal from water. IEX resins hold significant promise, given the wide variety of resins, both cationic and anionic, in nature. The use of IEX resins for PFAS removal is a rapidly developing field as new resins and regeneration methods are being developed to address the expanding market for PFAS remediation.

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REFERENCES

Appleman, T.D., C.P. Higgins, O. Quinones, B.J. Vanderford, C. Kolstad, J.C. Zeigler-Holady, and E.R.V. Dickenson. Treatment of poly- and perfluoroalkly substances in U.S. full-scale treatment systems. *Water Research* 51, 246–255 (2014).

Chularueangaksorn, P., S. Tanaka, S. Fujii, and C. Kunacheva. Regeneration and reusability of anion exchange resin used in perfluorooctane sulfonate removal by batch experiments. *Journal of Applied Polymer Science* 10(1002), 884–890 (2013).

Conte, L., L. Falletti, A. Zaggia, and M. Milan. Polyfluorinated organic micropollutants removal from water by ion exchange and adsorption. *Chemical Engineering Transactions*, 43 (2015).

Dardel, F. De, and T.V. Arden. Ion exchangers. In *Ullmann's Encyclopedia of Industrial Chemistry*. 6th ed. Weinheim: Wiley-VCH Verlag GmbH (2001).

Deng, S., Y. Yu, J. Huang, and G. Yu. Removal of perfluorooctane sulfonate from wastewater by anion exchange resins: Effects of resin properties and solution chemistry. *Water Research* 44, 5188–5195 (2010).

Du, Z., S. Deng, Y. Bei, Q. Huang, B. Wang, J. Huang, and G. Yu. Adsorption behavior and mechanism of perfluorinated compounds on various adsorbents—A review. *Journal of Hazardous Materials* 274, 443–454 (2014).

Dudley, L.M.B. Removal of perfluorinated compounds by powdered activated carbon, superfine powdered activated carbon, and anion exchange resins. Master's thesis, North Carolina State University (2012).

Nickelsen, M., and Woodard, S. A Sustainable System and Method for Removing and Concentrating Per- and Polyfluoroalkyl Substances (PFAS) from Water. U.S. Patent Application Serial No. 15/477,350, April 2017.

Owens, D.L. *Practical Principles of Ion Exchange Water Treatment*. Littleton, CO: Tall Oaks Publishing (1995).

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