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PFAS Removal by Ion Exchange Resins: Background and Knowledge Gaps with Respect to the Hanford Site

July 2025

Alex J Kugler
Sarah A Saslow
Carolyn I Pearce
Christian D Johnson
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U.S. DEPARTMENT OF ENERGY

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Summary

Per- and polyfluoroalkyl substances (PFAS) have been a growing concern for the past two decades, with the U.S. Department of Defense and U.S. Environmental Protection Agency investing millions of dollars in research into remediation and cleanup technologies. Due to the environmental persistence, toxicity, and biological uptake of PFAS, and ongoing changes in both federal and state regulatory space, understanding the fate and transport of PFAS compounds has become increasingly important to the U.S. Department of Energy (DOE). At the Hanford Site, DOE is investigating historical use of PFAS and will be characterizing the site for PFAS. Thus, PFAS have not yet been identified as a contaminant concern in Hanford regulatory documents. Based on historical records that mention the discharge of aqueous film-forming foam containing PFAS as well as onsite fire stations (a risk factor for PFAS contamination), environmental releases of PFAS may have occurred, though that does not mean there is longstanding contamination.

Pump-and-treat (P&T) remediation is the remedy selected for multiple groundwater contaminant plumes at Hanford. These P&T systems use ion exchange (IX) as a component of aboveground treatment, with the specific resins depending on the target contaminants. These IX resins may be able to remove PFAS from groundwater, but investigation is needed to understand affinity/selectivity and removal capacity given the groundwater composition and operating conditions.

This report describes the background on PFAS uses and chemistry, then reviews IX resin applications for PFAS, identifying knowledge gaps. Recommendations are provided regarding research needed to address knowledge gaps and acquire information needed to propose IX as a future PFAS remediation technology at Hanford (should PFAS contamination be identified for remediation) and other DOE sites.

Generally, PFAS compounds are fluorinated substances that contain at least one fully fluorinated methyl or methylene carbon – with a few noted exceptions, any chemical with at least one perfluorinated methyl group ($–CF_3$) or one perfluorinated methylene group ($–CF_2–$) is a PFAS. These chemical compounds are characterized as non-biodegradable, non-reactive, non-photolytic, and hydrolysis resistant. This makes them highly recalcitrant in the environment; however, polyfluoroalkyl materials are less recalcitrant as the carbon chains contain carbon–hydrogen bonds, which are more easily broken than carbon–fluorine bonds. The backbone carbon structures are commonly punctuated with a head group; the most well-known of them are perfluorooctanesulfonic acid and perfluorooctanoic acid, which possess a sulfonate and a carboxylate group, respectively. IX resins are marketed for the removal of PFAS from water systems and industrial water; however, the mechanism of removal is not as well understood for PFAS as it is for anion or cation removal. A better understanding of this mechanism would enable the development of IX resins with improved specificity for PFAS removal. Commercial off the shelf resins have been shown effective for PFAS remediation in simple systems with minimal complexity; however, sites managed by the DOE Office of Environmental Management are often highly complex systems which require additional testing. Four knowledge gaps were identified: (i) the influence of dissolved ions on the effectiveness of IX resin for PFAS removal, (ii) the influence of additional primary contaminants of concern or secondary contaminants of concern on the effectiveness of PFAS removal via IX resin, (iii) the mechanisms of PFAS removal from water, and (iv) practical solutions to IX resin regeneration and waste disposal.

Understanding the extent to which the knowledge gaps identified may impact potential remediation strategies for PFAS at Hanford (as well as other sites which make use of ion exchange resins) can be preliminarily explored using laboratory batch and column experiments designed to evaluate the effects of comingled contaminants and uptake mechanisms for removal of PFAS (i.e., perfluorooctanoic acid, perfluorooctanesulfonic acid, etc.) by IX resins. A greater understanding of PFAS/IX resin interactions and the effects of comingled contaminants will enable stakeholders to make more informed decisions (e.g., treatment options or resin selection). The data collected from the suggested batch and column experiments would help determine the site-specific and area-relevant conditions for IX PFAS treatment operations. Ultimately, these experiments would test a range of commercially available IX resins for PFAS removal and explore whether IX would be an effective treatment method should PFAS be found in the groundwater at Hanford.

Acknowledgments

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Acronyms and Abbreviations

CEC	Contaminant of emerging concern
C–F	carbon fluorine bond
$–CF_2–$	difluoromethyl group; perfluorinated methylene
$–CF_3$	trifluoromethyl group; perfluorinated methyl
C–H	carbon hydrogen bond
DOE	U.S. Department of Energy
EPA	U.S. Environmental Protection Agency
HFPO-DA	hexafluoropropylene oxide dimer acid
IX	ion exchange
MCL	Maximum Contaminant Level
MCLG	Maximum Contaminant Level Goal
MD	molecular dynamics
P&T	pump and treat
PCOC	primary contaminant of concern
PFAS	per- and polyfluoroalkyl substances
PFBS	perfluorobutane sulfonate
PFHxS	perfluorohexanesulfonic acid
PFNA	perfluorononanoic acid
PFOA	perfluorooctanoic acid
PFOS	perfluorooctanesulfonic acid
PTFE	polytetrafluorethylene
SCOC	secondary contaminant of concern

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1.0 Introduction

This report introduces per- and polyfluoroalkyl substances (PFAS), ion exchange (IX) resins, and the complex interplay between the two. It also outlines the current knowledge gaps that may impact ongoing and future use of IX resins for groundwater remediation across the U.S. Department of Energy (DOE) complex. Section 1.0 provides an overview of (i) groundwater remediation and current regulatory standards with respect to PFAS, (ii) PFAS chemistry, (iii) IX resins, (iv) PFAS-IX resin interactions, (v) IX resin use at the Hanford Site, and (vi) the current DOE roadmap for PFAS and the potential implications for the Hanford Site. Section 3.0 discusses the knowledge gaps that persist for IX resin and PFAS interactions. Opportunities for future work to support decision-making are proposed in Section 4.0, and general conclusions are presented in Section 5.0.

1.1 Quality Assurance

This work was performed in accordance with the Pacific Northwest National Laboratory Nuclear Quality Assurance Program (NQAP). The NQAP complies with the DOE Order 414.1D, *Quality Assurance*. The NQAP uses NQA-1-2012, *Quality Assurance Requirements for Nuclear Facility Application*, as its consensus standard and NQA-1-2012, Subpart 4.2.1, as the basis for its graded approach to quality.

This work emphasized acquiring new theoretical or experimental knowledge. The information associated with this report should not be used as design input or operating parameters without additional qualification.

1.2 Groundwater Contamination

Treatment technologies for groundwater contamination have improved significantly over the past several decades (Chen et al. 2019), and advances in analytical equipment and industrial production have led to the detection and creation of new and previously unknown groundwater contaminants (Kadadou et al. 2024). *Contaminants of emerging concern* (CECs) is a term applied to chemicals found in natural systems that do not have a regulatory standard due to the inability to detect the presence of the contaminants or because the chemical compounds have been recently developed and determined to have harmful effects on aquatic life or water quality (Glassmeyer et al. 2023). CECs include persistent organic pollutants such as polybrominated diphenyl ethers and perfluorinated organic acids, pharmaceutical and personal care products, veterinary medicines, endocrine disrupting chemicals, and nanomaterials.

A major category of CECs is PFAS. PFAS are a wide range of synthetic chemicals including 14,735 distinct compounds as of April 2024 (Williams et al. 2017). PFAS are ubiquitous throughout the environment as they have been used in many industries since their initial development in the late 1930s (Lyons 2007). The widespread contamination, recalcitrant nature, and complex chemistry of these compounds have led to considerable notoriety in recent years and lawsuits against prominent manufacturers of these compounds (Brennan et al. 2021). Six compounds of the more than 14,000 PFAS identified are of the most immediate concern due to upcoming regulations proposed by the U.S. Environmental Protection Agency (EPA). On April 10, 2024, EPA announced the final National Primary Drinking Water Regulation (NPDWR) for six PFAS[1] (Table 1),

- Perfluorooctanoic acid (PFOA)
- Perfluorooctanesulfonic acid (PFOS)

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[1] At the time of writing, there are legal challenges to the EPA limit filed in the U.S. Court of Appeals for the District of Columbia Circuit.

- Perfluorohexanesulfonic acid (PFNA)
- Perfluorohexanesulfonic acid (PFHxS)
- Perfluorobutane sulfonate (PFBS, as a mixture with other PFAS)
- Hexafluoropropylene oxide dimer acid (HFPO-DA; commonly referred to by the trade name Gex-X)

These compounds fall within one of two classes of PFAS: perfluoroalkyl carboxylic acids and the perfluoroalkyl sulfonic acids. While the list of known PFAS continues to grow and there is no authoritative way to categorize the compounds, many institutions, including DOE and the U.S. Department of Defense, use a categorization approach similar to that shown in Figure 1 (Dixit et al. 2021). The finalized NPDWR established legally enforceable levels, called Maximum Contaminant Levels (MCLs), for six PFAS compounds in drinking water. Of the six, PFOA, PFOS, PFHxS, PFNA, and HFPO-DA are considered contaminants with individual MCLs. Additionally, PFAS mixtures containing at least two or more of PFHxS, PFNA, HFPO-DA, and/or PFBS are required to use a Hazard Index MCL to account for the combined and co-occurring levels of these PFAS in drinking water. EPA also finalized health-based, non-enforceable Maximum Contaminant Level Goals (MCLGs) for these PFAS. Table 1 presents the MCLs and MCLGs.

Table 1. List of compounds finalized by the EPA with Maximum Contaminant Levels and Maximum Contaminant Level Goals.

Compound	Final MCLG	Final MCL (enforceable levels)
PFOA	Zero	4.0 parts per trillion (ppt orng/L)
PFOS	Zero	4.0 ppt
PFHxS	10 ppt	10 ppt
PFNA	10 ppt	10 ppt
HFPO-DA	10 ppt	10 ppt
Mixtures containing two or more of PFHxS, PFNA, HFPO-DA, and PFBS	1 (unitless)	1 (unitless)

These compounds are generally considered to have the potential for negative impacts on human health, with the most widely studied of the compounds (PFOA and PFOS) showing significant absorption after ingestion, and distribution from blood to organ tissue (e.g., liver, kidney, lung, heart, and brain) often increases the risk of developing cancer (Pérez et al. 2013; Fenton et al. 2021; Greaves et al. 2013; Chambers et al. 2021). This has led the EPA to establish MCLs that are most relevant to surface and drinking water, but it is important to understand the significant impact that regulatory limits can have on stewardship of water resources.

Initial monitoring of public water systems for the PFAS listed in Table 1 must be complete by 2027, followed by ongoing compliance monitoring (EPA 2023). This information must also be available to the public by 2027. By 2029, public water systems must implement solutions to ensure public drinking water systems are at or below these limits, and if they are unable to do so, they must provide public notice of the violation akin to other contaminant violations (EPA 2023). The increased interest in PFAS has led to a dramatic increase in research and an expanded understanding of fluorine chemistry and the mechanics that control their use and function.

1.3 Per- and Polyfluoroalkyl Substances

Per- and polyfluoroalkyl substances, or PFAS, is a broad term used to encompass a wide range of fluorinated compounds or substances, sometimes referred to as fluorochemicals or fluorinated chemicals. Generally, PFAS compounds represent an organic or inorganic compound that contains at least one fluorine atom where a hydrogen atom could be. The Organization for Economic Co-operation and Development offers a more specific definition: "PFASs are defined as fluorinated substances that contain at least one fully fluorinated methyl or methylene carbon atom (without any H/Cl/Br/I atoms attached to it), i.e., with a few noted exceptions, any chemical with at least a perfluorinated methyl group or ($–CF_3$) a perfluorinated methylene group ($–CF_2–$) is a PFAS" (OECD 2021).

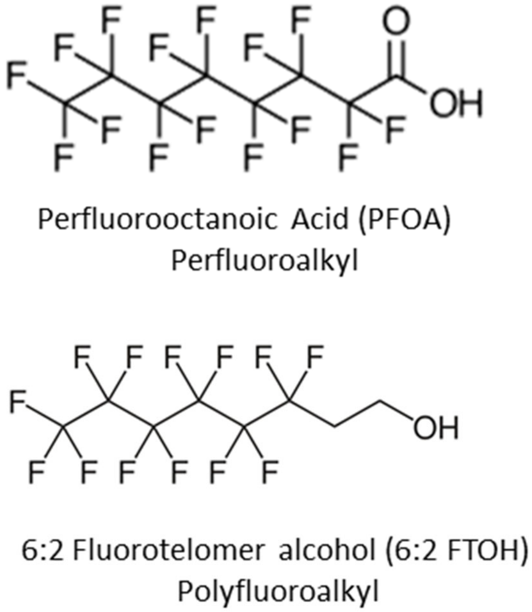

Figure 1. Chemical structures of two PFAS compounds: perfluorooctanoic acid, a perfluoroalkyl compound (top); and 6:2 fluorotelomer alcohol, a polyfluoroalkyl compound (bottom).

With more than 14,000 different chemicals considered PFAS, it can be difficult to discuss them without grouping similar compounds. There are several taxonomies used to further distinguish between groups of compounds. The broadest means is to categorize the PFAS as either perfluorinated, polyfluorinated, or fluorinate polymers. Perfluorinated chemicals have fully fluorinated carbon chains, whereas polyfluorinated chemicals have at least one carbon that is not fully fluorinated, as shown in Figure 1. Polymeric PFAS are macromolecules such as perfluoropolyether, fluorinate polymers, and fluoropolymers, which are made of many monomers; for example, polytetrafluorethylene or PTFE is a very common PFAS polymer. Fluoropolymers are not currently identified as CECs by the EPA and do not enter water systems as soluble contaminants. As such, they are not discussed further in this report. Dixit et al. (2021) has a simple taxonomy tree, which has been reproduced here as Figure 2.

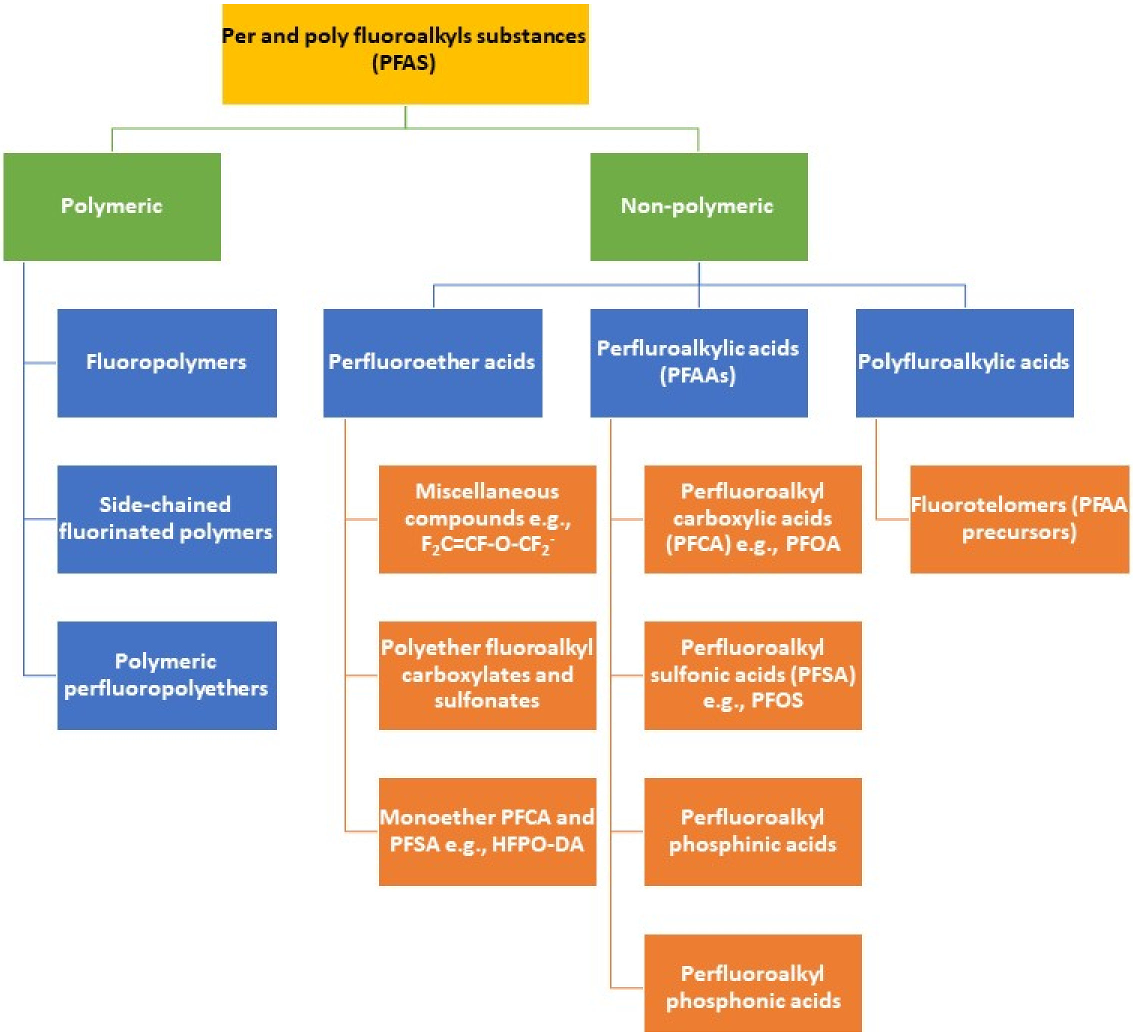

Figure 2. Per- and polyfluoroalkyl classification taxonomy separating PFAS into polymeric and non-polymeric and further categorizing based on the chemical structure of the compounds (adapted from Dixit et al. (2021)).

PFAS compounds are recalcitrant and difficult to destroy. Several technologies have been suggested for the destruction of PFAS compounds, including sonolysis (use of ultrasonic waves to destroy a molecule), electrochemical oxidation, photocatalysis, plasma, and thermal degradation. However, many of these technologies cannot be deployed for remediation due to the dilute concentrations found in contaminated ground or surface water (Kugler et al. 2021)(). PFAS are persistent contaminants for a variety of purposes, the most significant being the stability of the C–F bond, which provides PFAS with thermal and chemical stability.

PFAS are also often lipophilic and hydrophobic, which increases their enduring nature (Hekster et al. 2003)). Generally speaking, the more lipophilic a molecule, the more permeable across a biological membrane, which is governed by a biological construct called the Overton rule (Al-Awqati 1999). The hydrophobic interactions of the PFAS C–F tail and sediments has been identified as the primary contributor to sorption in subsurface sediments and soils (Milinovic et al. 2015). These interactions often overpower any electrostatic interactions in the soil unless the PFAS compounds exhibit cationic or zwitterionic mechanisms; however, this does not apply to any of the PFAS mentioned in Table 1 (McGarr et al. 2023). The high electronegativity of fluorine makes the bond difficult to degrade as it is resilient to most oxidative or reductive processes(Kugler et al. 2021). While the fluorine can provide hydrophobicity for insoluble compounds, several of the most concerning PFAS are protonated acids, which, when fully dissociated, are solubilized in their anionic form. Chain length and functional groups also significantly affect the chemistry of the compounds, and a full review is beyond the scope of this report. Several documents referenced herein provide a more detailed explanation of PFAS chemistry (Buck et al. 2011; Hekster et al. 2003; Ahrens and Bundschuh 2014; Fenton et al. 2021; Domingo and Nadal 2019).

The unique and complex chemistries of PFAS make it challenging to develop appropriate remediation technologies, which continues to be an active area of research. With the EPA finally setting limits on PFAS in drinking water, the complexity of aqueous and subsurface environments will continue to be a challenge where PFAS persist in dilute concentrations that exceed the actionable MCL.

1.4 Ion Exchange Resin

IX-based materials are commonly used for *ex situ* treatment of ground (Charbeneau 1981), surface (Jiang et al. 2021), drinking (Vaaramaa and Lehto 2003), and industrial waters (Dąbrowski et al. 2004). IX is a reversible reaction where solubilized ions are exchanged from solution with other ions of the same or similar electrical charge occupying exchange sites on the solid. Various materials are capable of IX reactions, including smectites (García-Romero et al. 2021), zeolites (Townsend and Coker 2001), and IX resins (Alexandratos 2009).

IX resins are crosslinked insoluble polymers that serve as a structure to a ligand. The ligand acts as an exchange site, electrostatically binding various ions to the resins, which can then be transferred to the aqueous phase as different compounds preferentially adsorb to the same sites. Some resins are designed with a suite of targeted compounds, and some are designed to specifically target specific contaminants. The use of covalent ligands can further increase the selectivity of IX resin beyond just the charge and size of the ion in question (Saslow et al. 2023a). Most IX resins are synthesized in one of two ways: (i) post-functionalization, which occurs after polymerization; or (ii) incorporation of a functionalized monomer during polymerization.

Resins have other characteristics that should be examined when determining which is best for a system, including capacity, swelling, selectivity, stability, and pore size (Harland 1994). IX is driven by a range of physiochemical parameters, such as the ionic strength of the solution, the affinity of the ions in solution for the resin exchange site (as determined by charge state, hydration energy, size, and other characteristics), the pH and redox potential of the solution, and any additional compounds in the solution that may interfere with the targeted IX process.

Figure 3 depicts the process of contaminant removal from water. Contaminated water flows through a column packed with a resin bed. This parent ion on the resin (e.g., chloride in Figure 3) will exchange with the targeted contaminant for which the resin is designed to have a higher affinity or selectivity relative to the parent ion. The "clean" water will flow out the resin bed and can then be further treated (e.g., not 100% removal, or presence of additional contaminants) or reinjected into the (sub)surface as necessary. This method is widely used for various technologies, including the pump-and-treat (P&T) facilities on the Hanford Site (Byrnes 2013; DOE 2023).

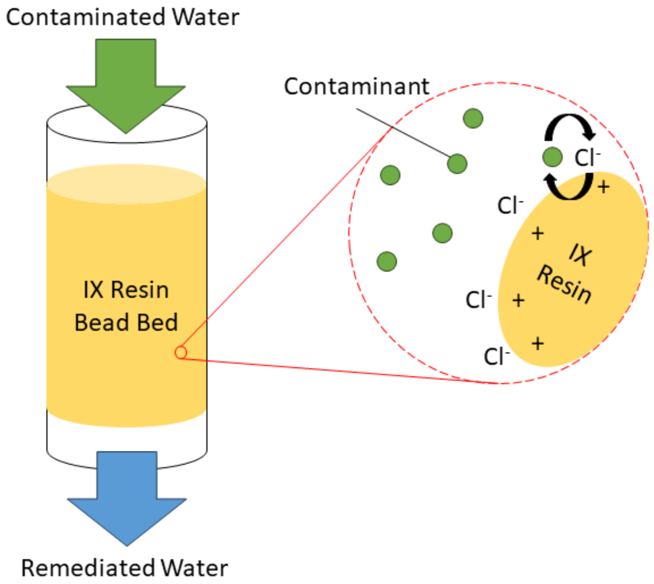

Figure 3. Process of contaminant removal from water. Contaminated water (green) is pumped through a column or tank filled with IX resin beads. Active sites on the example resin, in this case positive sites loaded with chloride, then exchange the chloride for the aqueous contaminant (green circles), allowing the water to flow through the bed of resin beads, effectively removing the contaminants from solution.

IX resin is widely used in both commercial and residential water treatment, and anion IX resins have shown promise for the widespread removal of PFAS from water (Boyer et al. 2021; Woodard et al. 2017). IX as a potential resin for PFAS remediation has grown in popularity in the last decade, as reflected in the increase in scientific literature (Boyer et al. 2021; Woodard et al. 2017; Gao et al. 2017; Park et al. 2020). Commercially marketed IX resins for PFAS offer high removal capacities – sometimes higher than 99% for aqueous removal of PFAS when tested as a single contaminant in deionized water or drinking water analogs (Rahman et al. 2022). Several companies such as Purolite, DuPont, and Calgon Carbon Corporation manufacture PFAS-specific resins. Examples include Purolite A592E (macroporous) and Purofine PFA694E (gel), Amberlite PSR2 Plus (DuPont Water Solutions), CalRes 2301 (Calgon Carbon Corporation), Sorbix PURE LC (ECT2 Inc.), and Resin Tech SIR-110-HP (ResinTech Inc.), as summarized in Table 2. Many IX resins listed in the table are polystyrenic resins that have been crosslinked with divinylbenzene and further complexed.

Table 2. Commercially available IX resins marketed for PFAS removal.

Manufacturer	Name	Polymer(s)	Functional Group	Ionic Form	Exchange Capacity[(a)]
Purolite	A592E	Gel polystyrene with divinylbenzene	Complex amino	Cl^-	0.6 eq/L
Purolite	PFA694E	Gel polystyrene with divinylbenzene	Complex amino	Cl^- or OH^-	1.3 eq/L
Dupont	Amberlite PSR2 Plus	Gel polystyrene with divinylbenzene	Tributyl amine	Cl^-	≥ 0.7 eq/L
Calgon Carbon Corporation	CalRes 2301	Gel polystyrene with divinylbenzene	Tributylamine	N/A[1]	0.5 eq/L
ECT2 Inc.	Sorbix PURE LC	Gel polystyrene with divinylbenzene	N^+	Cl^-	N/A[(b)]
Resin Tech	SIR-110-HP	Styrenic gel	Tributylamine	Cl^-	0.8 eq/L

(a) Exchange capacity may vary by analyte of interest; for example, 0.6 eq/L would exchange 0.6 moles per unit charge (i.e., one IX site occupied by Cl^- or NO_3^-, two IX sites occupied by SO_4^{2-}, etc.)
(b) No information provided by manufacturer.

Many mechanisms are at play during the uptake of PFAS into capture materials; however, those of primary significance to the IX process are electrostatic and hydrophobic effects (Dixit et al. 2021; Lei et al. 2023). Electrostatic effects include a wide range of particle interactions, including Coulombs law, ionic bonding, dipole-dipole moments, hydrogen bonding, and Van der Waals forces. Hydrophobic effects include the influence nonpolar molecules (or parts of molecules in the case of various PFAS), which can lead to aggregation of molecules to minimize surface area exposed to the polar solvent (i.e., water). Anionic PFAS removal can be directly influenced by the protonation of the IX resin. Similarly, the hydrophobic effects result from PFAS migration to the non-polar hydrophobic surfaces provided by the resin. However, it is important to note that the complex interactions and mechanisms between each IX resin and PFAS are poorly understood and are an area of ongoing research. Due to these unknown effects, as well as the complexities of groundwater with respect to additional contaminants and ions in solution making it difficult to predict or model the effectiveness or efficiency of P&T activities, these knowledge gaps must be examined prior to any decision-making.

1.5 Hanford Pump-and-Treat Using Ion Exchange

During its primary years of operation, the Hanford Site experienced releases of various chemical and radioactive wastes that contaminated soil and groundwater throughout the site (DOE 2023). Various technologies have been used for remediation at the Hanford Site, including permeable reactive barriers, dig and dump, and the successful P&T technologies that have treated over 2 billion gallons of water a year (DOE 2023). The Hanford Site operates six groundwater P&T facilities, including one located in the 200 Area, which is one of the four original areas at Hanford included in the EPA National Priorities List. The 200 Area is further divided into the 200 East and 200 West areas to better address cleanup concerns. The 200 West P&T facility, for example, treats ground and perched water that has been contaminated with various inorganic (i.e., uranium, technetium, hexavalent chromium) and organic (trichloroethene and carbon tetrachloride) contaminants (EPA 1995). The primary groundwater P&T areas are 200-W, 100-HX, 100-DX, 100-KW, 100-KX, and 100-KR4.

The P&T facilities at Hanford use various IX resins to remove contaminants. For example, Purolite A530E/A532E resin has been used regularly to target the removal of technetium; however, analysis has shown that this resin has also removed and retained radioiodine, cobalt, and untargeted groundwater constituent ions such as calcium, iron, silicon, and sulfate (Campbell et al. 2018), SIR-700 (ResinTech

Inc.) is currently used in the four P&T facilities in 100 Area and has been proposed for use in the 200 West Area for the removal of Cr (Saslow et al. 2023a). Purolite A532E has been shown to remove several common PFAS from water (Zaggia et al. 2016), which may have implications for efficiency if PFAS is comingled into a P&T system that uses A532E to target specific contaminants. To date, there have been limited or no studies on the effectiveness of SIR-700 for PFAS sorption; however, there are similarities in functional groups in the SIR-700 and Purolite PFA684E. This suggests SIR-700 may remove PFAS; however, its potential capacity is uncertain, as are the interactions with the other contaminants found throughout the 200 West Area.

1.6 DOE PFAS Roadmap

The *PFAS Strategic Roadmap: DOE Commitments to Action 2022-2025* establishes and details the goals, objectives, and steps being taken to address PFAS contamination at DOE sites (DOE 2022b). The roadmap includes plans for increasing research on current and past uses and releases of PFAS to the environment, investigating PFAS concentrations in DOE affected drinking water and environmental sites, preventing additional releases, and engaging stakeholders to further inform ongoing PFAS strategies. The *Initial Assessment of Per- and Polyfluoroalkyl Substances at Department of Energy Sites* specifies that Hanford possesses some PFAS, but less than 100 total pounds of any product(s) known to contain at least one PFAS at this time (DOE 2022a).

No PFAS were detected in the Hanford 400 Area groundwater in December 2019, which is the only active water system on the site using groundwater sources; however, that does not account for other areas where PFAS may be present (DOE 2022a) . The site used a fire training facility, fire department, and Aqueous Film Forming Foam (AFFF)-based fire suppression systems that used Ansul and ANSULITE AFFF, which are known to contain PFAS. While AFFF is no longer used, an internal memo was drafted in 1996 authorizing the discharge of wastewater from a fire foam test using ANSULITE 3% AFFF to the 200 Area Treated Effluent Disposal Facility (DOE 2022a).[1] Additionally, because Hanford is a legacy site of the Manhattan Project and Cold War era, discharges of enrichment liquid waste that may have contained PFAS chemicals cannot be ruled out.

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[1] The nature and extent of PFAS contamination in soil and groundwater on the Hanford Site is currently unknown. At the time of this writing, Hanford Site contractors are developing a characterization and monitoring plan to better identify PFAS contamination on the site. The need for PFAS removal from groundwater is being considered here as a forward-looking and parallel evaluation. Treatment may be unnecessary.

2.0 Knowledge Gaps

Understanding the most significant knowledge gaps is essential to prioritizing research goals. As the previous section describes, there is a large library of research literature on PFAS and the environmental fate and transport of various compounds. However, there are fundamental gaps in the understanding of how applied environmental remediation involving IX resin is affected by additional contaminants, as well as other site-specific conditions. Four major knowledge gaps are described below: (i) the potential competitive influence of dissolved ions present in contaminated groundwater on the effectiveness of PFAS removal via IX resin, (ii) the influence of additional primary contaminants of concern (PCOCs) or secondary contaminants of concern (SCOCs) on the effectiveness of PFAS removal via IX resin), (iii) the mechanisms of PFAS removal from contaminated water, and (iv) practical solutions to IX resin regeneration and waste disposal.

2.1 Influence of Dissolved Ions on the Effectiveness of PFAS Removal via IX Resin

Various other technologies have demonstrated reduced efficiency or effectiveness as the result of additional ions in solution (Kugler et al. 2021; Palma et al. 2022), and previous studies have examined the effects of competing ions on the performance of resins used at the Hanford Site in depth (Saslow et al. 2023a; Saslow et al. 2023b, 2023c). IX resins are capable of capturing other organic and inorganic species, such as sulfate, phosphate, and nitrate, in addition to the contaminant ions they are designed to target (Saslow et al. 2023a; Saslow et al. 2023b, 2023c). Generally, the competitiveness of the inorganic ions is directly related to various properties such as charge state, charge density, relative concentration, and hydration energy (Dixit et al. 2018). Organic materials such as humic or fulvic acids have also been shown to impact the effectiveness of IX resin (Qi et al. 2022). However, these organics are not a primary concern at the Hanford Site because the organic content of the groundwater is low (Ames and Serne 1991).

These competitive constituents in ground and surface water necessitate a better understanding of the interactions between co-contaminants and ions within natural waters to determine which IX resins are most effective under the conditions at a particular site. While there are resins marketed for the removal of PFAS from environmental waters, it is important to elucidate the effects of contaminants of concern that are also present with the PFAS to maximize efficiency and understand which resin should be used based on the complex water chemistry and any additional site-specific contamination. The variable groundwater of the Hanford Site, coupled with the longstanding complexity of additional comingled contaminants, requires study regardless of the treatment technology selected. Also note that this preferential sorption potential may also work in the opposite fashion.

Understanding the influence of dissolved ions on the effectiveness of PFAS removal is critical for developing a strategy for efficient removal and compliance with MCLs. Dissolved ions compete with the targets of interest for IX resins and may hamper their effectiveness based on the concentration of the present ions. In addition to ions, the complicated effects of dissolved organic matter have also recently been studied. Qi et al. (2022) demonstrated that dissolved organic matter increases the desorption of PFAS in plant root soil; however, the effects were dependent on the types and functional groups associated with the organic matter, demonstrating the complex effects that groundwater chemistry can have on the sorption process. This is important not only for site-specific groundwater ions, but for other ions that likely were not originally examined by resin manufacturers, which includes various contaminants found throughout the Hanford Site. By examining the effects of those additional ions, the most cost-effective and efficient IX resin can be selected.

2.2 Influence of Additional PCOCs or SCOCs on the Effectiveness of PFAS Removal via IX Resin

Groundwater chemistry is diverse and can significantly impact the effectiveness of IX and other remediation techniques (Deutsch and Siegel 2020). In addition, diverse microbial populations are known to catalyze critical *in situ* biogeochemical reactions, which are directly correlated to the groundwater chemistry. This complex interaction, while not relevant to the direct function of IX resin, can influence the groundwater chemistry in unexpected ways as nutrients flux over time and with natural or anthropogenic inputs (Maroubo et al. 2021). These factors are greatly enhanced by the addition of PCOCs and SCOCs, which (i) can serve as electron donors, acceptors, or carbon sources for microbial populations; (ii) further complicate the groundwater by changing characteristics such as ionic strength, pH, or organic content; and (iii) have ions that compete for sorption sites on sediments, IX resins, and other technologies (Deutsch and Siegel 2020).

Like the effects of groundwater ions (see above), the effect of comingled contaminants, inorganic and organic, may be pivotal to the IX rates and capacities for PFAS. It has been shown that nitrates can significantly impact both the sorption and degradation of PFAS and other compounds when present in high concentrations associated with contamination (Kugler et al. 2021; Gu et al. 2017; Gu et al. 2004). Another recent study indicated that the presence of hexavalent chromium (Cr(VI) has the potential to increase the migration potential of PFOS in soil and groundwater (Huang et al. 2022). This is of significance for the Hanford Site specifically as Cr(IV) is the PCOC in the 100 Areas and is also present in the 200 West Area, which could cause increased migration of PFOS throughout the site.

Understanding the complex interactions not only of groundwater constituents but of COCs and PCOCs in a system is fundamental to accurately understanding the efficiency and effectiveness of IX resin. This effect would also be true of areas contaminated with PFAS in which secondary contaminants interfere with targeted removal. While PFAS contamination is often an order of magnitude lower than many common contaminants (with MCLs in the ppt level), it is likely that other contaminants could outcompete for removal by IX if the resin used was not highly specific for PFAS removal. These unique sets of chemistry interact with each other in unique ways and can change the conditions under which the IX resins interact with the contaminants, making it necessary to study their effects in as close to real conditions as possible.

2.3 Mechanisms of PFAS Removal from Contaminated Water

While the need for remediation technologies and practical applications for PFAS removal has grown in the past two decades, there have been limited advancements in understanding how IX resin and PFAS interact on a chemical level. Various intermolecular forces have been suggested as the driving factors; however, the inconclusive nature of the data suggests that it is a multivariable effect (including those discussed herein and the differences between each PFAS such as chain length, bonding, and head group) that should be validated for a specific situation or environment prior to adopting the technology.

As discussed above, the polymer resin is covalently bonded with a functional group. It has been established those hydrophobic interactions involving van der Waals (London Dispersion Forces and dipole-dipole forces) play a role in the process; however, the significance of this interaction is not well understood (Maimaiti et al. 2018; Zaggia et al. 2016; Franke et al. 2019; Fang et al. 2021). It has also been suggested that electron donor–acceptor interactions may play a role in the retention of PFAS (Gagliano et al. 2020). Studies of chain length have been inconclusive, as different studies have suggested that anion exchange is more effective for long, short, or intermediate chain length PFAS depending on the study (Parker et al. 2022).

Understanding the mechanisms of PFAS removal by IX would enable the development of IX resins that are optimized for PFAS removal or hybrid resins that can remove PFAS in addition to other PCOCs. Understanding which mechanisms are most effective under each site-specific condition can also make it simpler to determine which resins would be most effective under similar conditions, which could be expanded across the Hanford Site or extended to other sites as well.

2.4 IX Resin Regeneration and Waste Disposal

The treatment, regeneration, or disposal of spent IX resin is a necessary end of process decision that is fundamental to the life cycle of remediation. IX resin regeneration after PFAS removal is also an area of active research; however, these resins were tested exclusively in the presence of PFAS without any added potential for remobilization of comingled contaminants such as hexavalent chromium or technetium (Liu and Sun 2021; Tamanna et al. 2023). While resin regeneration is an option if exposed to PFAS, this is unlikely to be an option at Hanford due to the complex intermingling of contaminants on the site.

Other traditional spent resin disposal technologies should be explored to ensure that PFAS will not affect encapsulation technologies. Cement, asphalt, and plastic are common forms of solidification, which are then transported to disposal facilities (Wang and Wan 2015). However, their effectiveness may be negatively impacted by the presence of PFAS, as many of the compounds listed in Table 1 are surfactants which can negatively impact the grout performance. The potential for other PCOCs and SCOCs to be present will also impact the end-of-life process for the resins. Incineration is also widely used for the final disposition of resins impacted by both radioactive contaminants and PFAS; however, the burning of PFAS produces highly corrosive hydrofluoric acid, and the incorporation of radioactive material into the ash remaining from the incineration of the resins may lead to unexpected reactions that would also require further study – though it is also possible that the process would volatilize similarly to the off-gassing caused during vitrification.

3.0 Addressing Knowledge Gaps and Uncertainties

The previous sections outline the emerging concerns surrounding PFAS groundwater contamination and the potential to use IX resin as a remediation technology. Prior to any remedial decision or design and implementation of IX treatment of PFAS at the Hanford Site, experimental work would be needed to address the knowledge gaps (Section 2.0), evaluate the performance of commercial resins, and determine important operational specifications under field-relevant conditions. Experimental and theoretical work that would further support the decision-making process is outlined below and summarized in Figure 4.

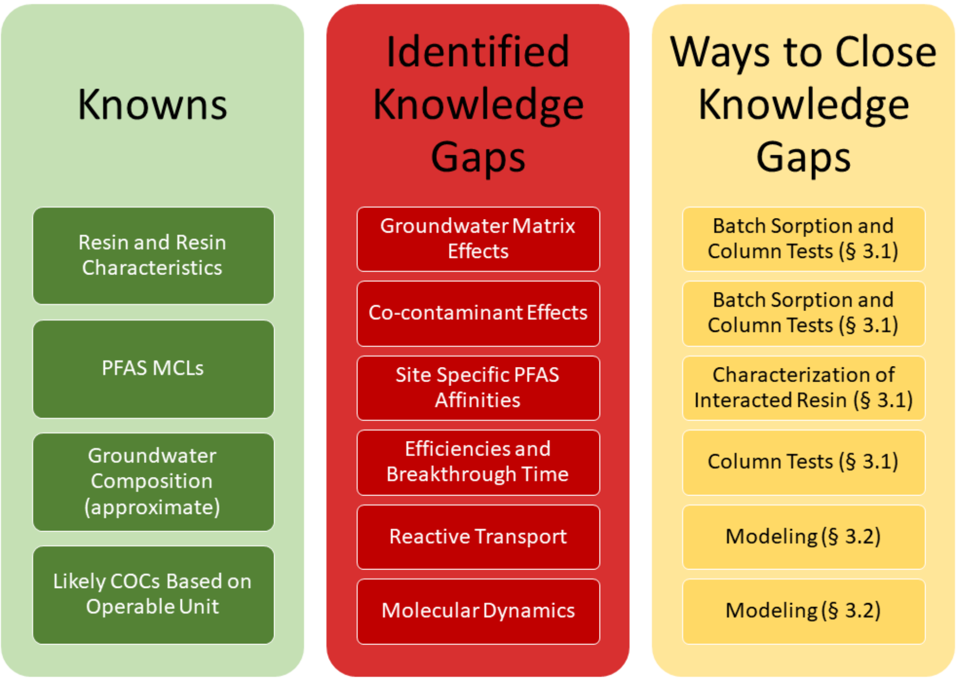

Figure 4. Summary of information known (green), knowledge gaps identified (red), and how the uncertainties can be addressed (yellow). The resin characteristics listed as known are supplied by the manufacturer; more testing may be required to obtain additional specific information.

3.1 Experimental

Batch sorption experiments are used to determine the kinetics of a reaction and investigate variables such as concentration, time, solid to liquid ratio, and competitive ion concentration. The advantage of initial batch experimentation is that it can be done at a small laboratory scale with limited space and resources. Adsorption isotherms are an empirical relationship used to quantify the amount of solute (i.e., PFOA) adsorbed by the substrate of interest (i.e., IX resin). This can then be extrapolated to the amount of solute adsorbed by a unit weight of resin and the amount of adsorbate remaining in a test at equilibrium. Batch experiments are carried out at small scale (i.e., 200 mL solution: 1 g resin) and without flow. While these experiments are not wholly representative of field conditions, they are less labor intensive than more field-representative tests (e.g., 1-D flow column experiments) and can be completed relatively quickly and have been used previously to investigate resin usage at P&T facilities.

Batch experiments are conducted with a known ratio of solid to solution and spiked with known concentrations of the analyte of interest (i.e., PFAS). The results provide kinetic information when intermittent sampling is performed, and values for the adsorption isotherm are at equilibrium with respect to PFAS concentration. This information would ultimately be used to calculate the amount of resin necessary for PFAS removal from a given system. The impact of other ions on resin performance would be evaluated through additional experiments carried out in synthetic groundwater and with comingled contaminants, as opposed to the more commonly used deionized water. The results could be used to down-select the commercial resin candidates to a subset that may be best suited for use should PFAS remediation be required going forward, as resin which do not perform well in batch will not perform well in column testing.

Following batch experiments, column or flow-through experiments are often carried out to determine how flow conditions will affect the retention and sorption of the compounds of interest. These experiments build on the static batch experiments by including the effects of fluid dynamics. This additional variable is used to determine loading capacity when flow is applied, lag time, and breakthrough for each selected resin. These tests, done in synthetic groundwater with comingled contaminants, would determine which reins could be best used in a P&T facility either as part of a treatment train or as a standalone skid unit.

While batch and column tests are primarily used to understand the sorption and remediation potential of the resins, they also enable investigation of the phenomena that are not yet well understood with respect to the sorption of PFAS to resin. Using advanced spectroscopic techniques (e.g., Fourier transform infrared spectroscopy or nuclear magnetic resonance), it may be possible to further understand the interactions with PFAS and resin, which would allow for a more fundamental understanding of the chemistry of these materials and enable the development or selection of resins that would work better for PFAS removal. This information would lead to an understanding of the uptake potential and kinetics of IX resin with respect to PFAS as well as other contaminants, which would directly address the knowledge gaps discussed in Sections 2.1 and 2.2, while spectroscopic analyses would aid in understanding the complex interactions with the IX resin, which would help increase understanding from a mechanistic view as described in Section 2.3.

3.2 Modeling

Based on the laboratory study results recommended above, a reactive transport model could be developed to predict resin performance at full-scale under site-specific flow conditions, which would be scaled based on the needs of the system. Reactive transport models focus on the physical mass transport using linear distribution coefficients or linear decay terms, advective-dispersion, which can then be modified with necessary retardation factors of the operable units. Geochemical thermodynamic descriptions are also regarded to examine reaction paths, alternations, and changes in reactivity. Model predictions could then be tested in pilot-scale remediations to determine the effectiveness of the resin at scale prior to field implementation. Given the ever increasing number of PFAS, it is impractical to run pilot-scale studies for each, and each source on the Hanford Site has varying chemistry that would also require testing, for which it may prove advantageous to collaborate with manufacturers to compare efficiencies and model predictions. Also, pilot scale studies are limited to the design and intake at the time of the analysis. Models are best used to complement carefully designed laboratory experiments that produce the necessary data that can be fitted with, as an example, a regressive loop to determine effectiveness for IX resins that are basic models that can be expanded on.

Additional modeling could be done in conjunction with other efforts to increase the understanding of PFAS contamination if found on the site. Due to the unique complexities of the Hanford Site, modeling of plume interactions may also be required. For example, the interaction of PFAS with light non-aqueous phase liquids has proven to be a multiscale phenomenon. The difference between the surface and bulk diffusion of thin films results in spatial and temporal changes of the surface tensions and hence the specific surface area solutocapillary effect, which may be relevant to proposed or ongoing treatment (Sookhak Lari et al. 2024). Groundwater and plume map modeling, for example, as done in SOCRATES

(Suite Of Comprehensive Rapid Analysis Tools for Environmental Sites) (Johnson et al. 2023), would allow for tracking the contaminants and for communicating with stakeholders and academic communities if deemed necessary by stakeholders.

Intermediate-scale IX resin performance modeling and groundwater plume migration modeling are best used for specific IX remediation technologies under environmental conditions specific to the contaminated site. More generally, molecular-scale modeling could be used to better understand the chemical interaction between different PFAS compounds and IX resins with different polymeric backbones and functional groups. This mechanistic understanding would provide a theoretical means to down-select to the best resins that are currently commercially available and would inform development of resins that are more selective for PFAS removal, or hybrid resins that could remove PFAS in addition to PCOCs.

Molecular dynamics (MD) simulations are a powerful tool for examining molecular interactions. A key component in MD simulation is the representation of molecular mechanics such as electrostatic (Coulombic) interactions, the preferred length of each covalent bond, and other interatomic interactions. Quantum mechanical methods provide more accurate results; however, they are computationally expensive and only examine time scales on the order of several picoseconds, involving relatively few atoms (Sookhak Lari et al. 2024). Additional molecular simulation methods include density functional theory, hybrid quantum and classical MD, *ab initio* MD, and coarse-grained MD (Hollingsworth and Dror 2018; Hospital et al. 2015).

Length and scale of the interaction dynamics in the system will partially determine the best modeling methods. With respect to PFAS, there are several mechanisms of interaction between the contaminant, the fluid, and the IX resin, including van der Waals forces, electrostatic interactions, and hydrogen bonding (Mousavi et al. 2023). Classical MD simulations can explore these bonding forces with respect to the IX resins and may be used to examine complex mixtures of PFAS, as well as various resins to determine which formulations are likely to work best, based on how they have been formulated.

Developing better models for PFAS and other contaminants for IX resin not only addresses the knowledge gaps described in Section 2.0, but can also increase the number of variables that can be tested with less in-depth laboratory-scale testing. As MD simulations become more accurate, they will be able to examine the inter-ion effects, and experiments can be performed to validate the model's conclusions. Additionally, modeling the needs of the P&T facilities with respect to flow, output, and overall exchange capacity can determine what, if any, changes may be necessary, and this can be expanded from the laboratory scale to a test platform size, which is imperative for scale-up investigations, prior to suggesting any changes to a full-scale P&T system.

4.0 Conclusions

PFAS are an ever-increasing group of contaminants that may yet require remediation as the EPA expands the rules for drinking water and groundwater concentration or if PFAS levels above the current (or future) MCLs are found on the Hanford Site. These compounds, while not currently analyzed for on the Hanford Site, have been discharged historically and if the concentrations are high enough, they would require remediation to remain compliant with a changing regulatory landscape. IX resins have been proven effective at removing PFAS compounds from municipal and industrial waters; however, these systems are not representative of remediation efforts at complex DOE sites such as Hanford, with multiple radioactive and chemically hazardous contaminants. As the Hanford Site looks ahead to regulatory changes with respect to PFAS, it is important to understand what remediation technologies are already active on site and what needs can be addressed quickly and efficiently. If PFAS are found above the current MCL set by the EPA or the Washington State Department of Ecology, the already considerable investment in IX technologies should be levied to approach the problem with tools and techniques that are already used throughout the site.

With the success of P&T operations for other contaminants, and the potential for the IX resins currently in use to uptake PFAS, a fundamental understanding of the influence of the comingled ions is required to technically underpin PFAS removal. If there are PFAS in the past or present influent streams in the Hanford P&T systems, it is possible the P&T systems are also removing some unknown amount of PFAS from the groundwater, and it is likely that this reaction is hampered by competitive IX with other comingled ions. Understanding those interactions will provide insight to the potential for PFAS remediation as an added value to ongoing P&T activities.

The report identified four fundamental knowledge gaps with respect to using IX resin to remove PFAS from groundwater: (i) the influence of dissolved ions in contaminated groundwater on the effectiveness of PFAS removal via IX resin, (ii) the influence of PFAS removal on the effectiveness of IX resins for removal of PCOCs and SCOCs, (iii) the mechanisms of PFAS removal from contaminated water, and (iv) practical solutions to IX resin regeneration and waste disposal. Batch and column experiments would be needed to examine the effects of PFAS on the resins currently in use at Hanford Site P&T facilities to determine if any PFAS remediation has occurred and if those resins are capable of removing PFAS under the complex site-specific conditions. Additionally, modeling opportunities exist that could provide (i) predictive capabilities for PFAS groundwater plume migration; (ii) insights into expanding the use of new PFAS-specific resins from lab scale to field scale, including competitive effects of other ions present in groundwater; and (iii) an understanding of why PFAS interactions with IX resin occur in a site-specific matrix.

While the DOE inventory suggests that there have been discharges of PFAS-containing compounds at the Hanford Site, there are no known PFAS plumes with concentrations that exceed current MCLs. However, EPA regulation for these emerging contaminants is changing and continued advances in instrumentation with sub ng/L detection limits for PFAS allow for finer and finer resolution in measurements. Therefore, should PFAS contamination be found on the Hanford Site, several experimental and modeling approaches have been proposed that could provide a technical basis for making decisions based on impending EPA regulatory changes with respect to PFAS contamination.

5.0 References

Ahrens, L., and M. Bundschuh. 2014. “Fate and Effects of Poly- and Perfluoroalkyl Substances in the Aquatic Environment: A Review.” *Environmental Toxicology and Chemistry* 33 (9): 1921-1929. https://doi.org/https://doi.org/10.1002/etc.2663.

Al-Awqati, Q. 1999. “One Hundred Years of Membrane Permeability: Does Overton Still Rule?” *Nature Cell Biology* 1 (8): E201-E202. https://doi.org/10.1038/70230.

Alexandratos, S. D. 2009. “Ion-Exchange Resins: A Retrospective from Industrial and Engineering Chemistry Research.” *Industrial & Engineering Chemistry Research* 48 (1): 388-398. https://doi.org/10.1021/ie801242v.

Ames, L. L., and R. J. Serne. 1991. *Compilation of Data to Estimate Groundwater Migration Potential for Constituents in Active Liquid Discharges at the Hanford Site.* United States. https://www.osti.gov/biblio/5948721

https://www.osti.gov/servlets/purl/5948721.

Boyer, T. H., Y. Fang, A. Ellis, R. Dietz, Y. J. Choi, C. E. Schaefer, C. P. Higgins, and T. J. Strathmann. 2021. “Anion Exchange Resin Removal of Per- and Polyfluoroalkyl Substances (Pfas) from Impacted Water: A Critical Review.” *Water Research* 200: 117244. https://doi.org/https://doi.org/10.1016/j.watres.2021.117244.

Brennan, N. M., A. T. Evans, M. K. Fritz, S. A. Peak, and H. E. von Holst. 2021. “Trends in the Regulation of Per- and Polyfluoroalkyl Substances (Pfas): A Scoping Review.” *Int J Environ Res Public Health* 18 (20). https://doi.org/10.3390/ijerph182010900. PMCID: PMC8536021.

Buck, R. C., J. Franklin, U. Berger, J. M. Conder, I. T. Cousins, P. de Voogt, A. A. Jensen, K. Kannan, S. A. Mabury, and S. P. van Leeuwen. 2011. “Perfluoroalkyl and Polyfluoroalkyl Substances in the Environment: Terminology, Classification, and Origins.” *Integr Environ Assess Manag* 7 (4): 513-41. https://doi.org/10.1002/ieam.258. PMCID: PMC3214619.

Byrnes, M. E., Simmons, Sally, and Morse, John. 2013. “Startup of the New 200 West Pump-and-Treat, Hanford Site, Richland, Washington.” Waste Management United States.

Campbell, E., T. Levitskaia, M. Fujimoto, V. Holfeltz, S. Chatterjee, and G. Hall. 2018. *Analysis of Uranium Ion Exchange Resin from the 200 West Pump-and-Treat Facility.* PNNL PNNL-28062. DVZ-RPT-007, Rev. 0.

Chambers, W. S., J. G. Hopkins, and S. M. Richards. 2021. “A Review of Per- and Polyfluorinated Alkyl Substance Impairment of Reproduction.” *Front Toxicol* 3: 732436. https://doi.org/10.3389/ftox.2021.732436. PMCID: PMC8915888.

Charbeneau, R. J. 1981. “Groundwater Contaminant Transport with Adsorption and Ion Exchange Chemistry: Method of Characteristics for the Case without Dispersion.” *Water Resources Research* 17 (3): 705-713. https://doi.org/https://doi.org/10.1029/WR017i003p00705.

Chen, Q., G. Fan, W. Na, J. Liu, J. Cui, and H. Li. 2019. “Past, Present, and Future of Groundwater Remediation Research: A Scientometric Analysis.” *International Journal of Environmental Research and Public Health* 16 (20): 3975. https://www.mdpi.com/1660-4601/16/20/3975.

Dąbrowski, A., Z. Hubicki, P. Podkościelny, and E. Robens. 2004. "Selective Removal of the Heavy Metal Ions from Waters and Industrial Wastewaters by Ion-Exchange Method." *Chemosphere* 56 (2): 91-106.

Deutsch, W. J., and R. Siegel. 2020. *Groundwater Geochemistry: Fundamentals and Applications to Contamination*. CRC Press. https://books.google.com/books?id=aOgJEAAAQBAJ.

Dixit, F., B. Barbeau, and M. Mohseni. 2018. "Simultaneous Uptake of Nom and Microcystin-Lr by Anion Exchange Resins: Effect of Inorganic Ions and Resin Regeneration." *Chemosphere* 192: 113-121. https://doi.org/https://doi.org/10.1016/j.chemosphere.2017.10.135.

Dixit, F., R. Dutta, B. Barbeau, P. Berube, and M. Mohseni. 2021. "Pfas Removal by Ion Exchange Resins: A Review." *Chemosphere* 272: 129777. https://doi.org/https://doi.org/10.1016/j.chemosphere.2021.129777.

DOE. 2022a. *Initial Assessment of Per- and Polyfluoroalkyl Substances at Department of Energy Sites.*

DOE. 2022b. *Pfas Strategic Roadmap: Doe Commitments to Action 2022-2025.*

DOE. 2023. *Hanford Annual Site Environmental Report for Calendar Year 2022.* DOE/RL-2023-20, Rev 0. Richland, WA.

Domingo, J. L., and M. Nadal. 2019. "Human Exposure to Per- and Polyfluoroalkyl Substances (Pfas) through Drinking Water: A Review of the Recent Scientific Literature." *Environ Res* 177: 108648. https://doi.org/10.1016/j.envres.2019.108648.

EPA. 1995. *Epa Superfund Record of Decision: Hanford 200-Area (Usdoe) Ou 200-Zp-1, Benton County Wa.* PB95-964609 EPA/ROD/R10-95-114.

2023. Pfas National Primary Drinking Water Regulation Rulemaking. EPA.

Fang, Y., A. Ellis, Y. J. Choi, T. H. Boyer, C. P. Higgins, C. E. Schaefer, and T. J. Strathmann. 2021. "Removal of Per- and Polyfluoroalkyl Substances (Pfass) in Aqueous Film-Forming Foam (Afff) Using Ion-Exchange and Nonionic Resins." *Environmental Science & Technology* 55 (8): 5001-5011. https://doi.org/10.1021/acs.est.1c00769.

Fenton, S. E., A. Ducatman, A. Boobis, J. C. DeWitt, C. Lau, C. Ng, J. S. Smith, and S. M. Roberts. 2021. "Per- and Polyfluoroalkyl Substance Toxicity and Human Health Review: Current State of Knowledge and Strategies for Informing Future Research." *Environ Toxicol Chem* 40 (3): 606-630. https://doi.org/10.1002/etc.4890. PMCID: PMC7906952.

Franke, V., P. McCleaf, K. Lindegren, and L. Ahrens. 2019. "Efficient Removal of Per- and Polyfluoroalkyl Substances (Pfass) in Drinking Water Treatment: Nanofiltration Combined with Active Carbon or Anion Exchange." *Environmental Science: Water Research & Technology* 5 (11): 1836-1843. https://doi.org/10.1039/C9EW00286C.

Gagliano, E., M. Sgroi, P. P. Falciglia, F. G. A. Vagliasindi, and P. Roccaro. 2020. "Removal of Poly- and Perfluoroalkyl Substances (Pfas) from Water by Adsorption: Role of Pfas Chain Length, Effect of Organic Matter and Challenges in Adsorbent Regeneration." *Water Res* 171: 115381. https://doi.org/10.1016/j.watres.2019.115381.

Gao, Y., S. Deng, Z. Du, K. Liu, and G. Yu. 2017. “Adsorptive Removal of Emerging Polyfluoroalky Substances F-53b and Pfos by Anion-Exchange Resin: A Comparative Study.” *J Hazard Mater* 323 (Pt A): 550-557. https://doi.org/10.1016/j.jhazmat.2016.04.069.

García-Romero, E., A. Lorenzo, A. García-Vicente, J. Morales, J. García-Rivas, and M. Suárez. 2021. “On the Structural Formula of Smectites: A Review and New Data on the Influence of Exchangeable Cations.” *J Appl Crystallogr* 54 (Pt 1): 251-262. https://doi.org/10.1107/s1600576720016040. PMCID: PMC7941322.

Glassmeyer, S. T., E. E. Burns, M. J. Focazio, E. T. Furlong, M. O. Gribble, M. A. Jahne, S. P. Keely, A. R. Kennicutt, D. W. Kolpin, E. K. Medlock Kakaley, and S. L. Pfaller. 2023. “Water, Water Everywhere, but Every Drop Unique: Challenges in the Science to Understand the Role of Contaminants of Emerging Concern in the Management of Drinking Water Supplies.” *Geohealth* 7 (12): e2022GH000716. https://doi.org/10.1029/2022gh000716. PMCID: PMC10753268.

Greaves, A. K., R. J. Letcher, C. Sonne, and R. Dietz. 2013. “Brain Region Distribution and Patterns of Bioaccumulative Perfluoroalkyl Carboxylates and Sulfonates in East Greenland Polar Bears (Ursus Maritimus).” *Environmental Toxicology and Chemistry* 32 (3): 713-722. https://doi.org/https://doi.org/10.1002/etc.2107.

Gu, B., Y.-K. Ku, and P. M. Jardine. 2004. “Sorption and Binary Exchange of Nitrate, Sulfate, and Uranium on an Anion-Exchange Resin.” *Environmental Science & Technology* 38 (11): 3184-3188. https://doi.org/10.1021/es034902m.

Gu, Y., T. Liu, H. Wang, H. Han, and W. Dong. 2017. “Hydrated Electron Based Decomposition of Perfluorooctane Sulfonate (Pfos) in the Vuv/Sulfite System.” *Science of The Total Environment* 607-608: 541-548. https://doi.org/https://doi.org/10.1016/j.scitotenv.2017.06.197.

Harland, C. E. 1994. *Ion Exchange: Theory and Practice*. The Royal Society of Chemistry. https://doi.org/10.1039/9781847551184.

Hekster, F. M., R. W. Laane, and P. de Voogt. 2003. “Environmental and Toxicity Effects of Perfluoroalkylated Substances.” *Rev Environ Contam Toxicol* 179: 99-121. https://doi.org/10.1007/0-387-21731-2_4.

Hollingsworth, S. A., and R. O. Dror. 2018. “Molecular Dynamics Simulation for All.” *Neuron* 99 (6): 1129-1143. https://doi.org/https://doi.org/10.1016/j.neuron.2018.08.011.

Hospital, A., J. R. Goñi, M. Orozco, and J. L. Gelpí. 2015. “Molecular Dynamics Simulations: Advances and Applications.” *Adv Appl Bioinform Chem* 8: 37-47. https://doi.org/10.2147/aabc.S70333. PMCID: PMC4655909.

Huang, D., N. A. Khan, G. Wang, K. C. Carroll, and M. L. Brusseau. 2022. “The Co-Transport of Pfas and Cr(Vi) in Porous Media.” *Chemosphere* 286: 131834. https://doi.org/https://doi.org/10.1016/j.chemosphere.2021.131834.

Jiang, S., H. Sun, H. Wang, B. P. Ladewig, and Z. Yao. 2021. “A Comprehensive Review on the Synthesis and Applications of Ion Exchange Membranes.” *Chemosphere* 282: 130817.

Johnson, C. D., J. Q. Wassing, J. P. Loftus, E. J. Engel, T. P. Franklin, and M. A. Perry. 2023. *Online Analytics for Remedy Support at Doe Environmental Management Sites.* United States. https://www.osti.gov/biblio/2308847

https://www.osti.gov/servlets/purl/2308847.

Kadadou, D., L. Tizani, H. Alsafar, and S. W. Hasan. 2024. "Analytical Methods for Determining Environmental Contaminants of Concern in Water and Wastewater." *MethodsX* 12: 102582. https://doi.org/https://doi.org/10.1016/j.mex.2024.102582.

Kugler, A., H. Dong, C. Li, C. Gu, C. E. Schaefer, Y. J. Choi, D. Tran, M. Spraul, and C. P. Higgins. 2021. "Reductive Defluorination of Perfluorooctanesulfonic Acid (Pfos) by Hydrated Electrons Generated Upon Uv Irradiation of 3-Indole-Acetic-Acid in 12-Aminolauric-Modified Montmorillonite." *Water Res* 200: 117221. https://doi.org/10.1016/j.watres.2021.117221.

Lei, X., Q. Lian, X. Zhang, T. K. Karsili, W. Holmes, Y. Chen, M. E. Zappi, and D. D. Gang. 2023. "A Review of Pfas Adsorption from Aqueous Solutions: Current Approaches, Engineering Applications, Challenges, and Opportunities." *Environmental Pollution* 321: 121138. https://doi.org/https://doi.org/10.1016/j.envpol.2023.121138.

Liu, Y.-L., and M. Sun. 2021. "Ion Exchange Removal and Resin Regeneration to Treat Per- and Polyfluoroalkyl Ether Acids and Other Emerging Pfas in Drinking Water." *Water Research* 207: 117781. https://doi.org/https://doi.org/10.1016/j.watres.2021.117781.

Lyons, C. 2007. *Stain-Resistant, Nonstick, Waterproof, and Lethal: The Hidden Dangers of C8*. Praeger. https://books.google.com/books?id=n7enzgEACAAJ.

Maimaiti, A., S. Deng, P. Meng, W. Wang, B. Wang, J. Huang, Y. Wang, and G. Yu. 2018. "Competitive Adsorption of Perfluoroalkyl Substances on Anion Exchange Resins in Simulated Afff-Impacted Groundwater." *Chemical Engineering Journal* 348: 494-502. https://doi.org/https://doi.org/10.1016/j.cej.2018.05.006.

Maroubo, L. A., M. R. Moreira-Silva, J. J. Teixeira, and M. F. S. Teixeira. 2021. "Influence of Rainfall Seasonality in Groundwater Chemistry at Western Region of São Paulo State—Brazil." *Water* 13 (11): 1450. https://www.mdpi.com/2073-4441/13/11/1450.

McGarr, J. T., E. G. Mbonimpa, D. C. McAvoy, and M. R. Soltanian. 2023. "Fate and Transport of Per- and Polyfluoroalkyl Substances (Pfas) at Aqueous Film Forming Foam (Afff) Discharge Sites: A Review." *Soil Systems* 7 (2): 53. https://www.mdpi.com/2571-8789/7/2/53.

Milinovic, J., S. Lacorte, M. Vidal, and A. Rigol. 2015. "Sorption Behaviour of Perfluoroalkyl Substances in Soils." *Science of The Total Environment* 511: 63-71. https://doi.org/https://doi.org/10.1016/j.scitotenv.2014.12.017.

Mousavi, S. Z., H. R. Shadman, M. Habibi, M. Didandeh, A. Nikzad, M. Golmohammadi, R. Maleki, W. A. Suwaileh, A. Khataee, M. Zargar, and A. Razmjou. 2023. "Elucidating the Sorption Mechanisms of Environmental Pollutants Using Molecular Simulation." *Industrial & Engineering Chemistry Research* 62 (8): 3373-3393. https://doi.org/10.1021/acs.iecr.2c02333.

OECD. 2021. *Reconciling Terminology of the Universe of Per- and Polyfluoroalkyl Substances: Recommendations and Practical Guidance Series on Risk Management No 61.*

Palma, D., C. Richard, and M. Minella. 2022. "State of the Art and Perspectives About Non-Thermal Plasma Applications for the Removal of Pfas in Water." *Chemical Engineering Journal Advances* 10: 100253. https://doi.org/https://doi.org/10.1016/j.ceja.2022.100253.

Park, M., K. D. Daniels, S. Wu, A. D. Ziska, and S. A. Snyder. 2020. "Magnetic Ion-Exchange (Miex) Resin for Perfluorinated Alkylsubstance (Pfas) Removal in Groundwater: Roles of Atomic Charges for Adsorption." *Water Research* 181: 115897. https://doi.org/https://doi.org/10.1016/j.watres.2020.115897.

Parker, B. A., D. R. U. Knappe, I. A. Titaley, T. A. Wanzek, and J. A. Field. 2022. "Tools for Understanding and Predicting the Affinity of Per- and Polyfluoroalkyl Substances for Anion-Exchange Sorbents." *Environmental Science & Technology* 56 (22): 15470-15477. https://doi.org/10.1021/acs.est.1c08345.

Pérez, F., M. Nadal, A. Navarro-Ortega, F. Fàbrega, J. L. Domingo, D. Barceló, and M. Farré. 2013. "Accumulation of Perfluoroalkyl Substances in Human Tissues." *Environ Int* 59: 354-62. https://doi.org/10.1016/j.envint.2013.06.004.

Qi, Y., H. Cao, W. Pan, C. Wang, and Y. Liang. 2022. "The Role of Dissolved Organic Matter During Per- and Polyfluorinated Substance (Pfas) Adsorption, Degradation, and Plant Uptake: A Review." *Journal of Hazardous Materials* 436: 129139. https://doi.org/https://doi.org/10.1016/j.jhazmat.2022.129139.

Rahman, M. F., W. B. Anderson, S. Peldszus, and P. M. Huck. 2022. "Ion-Exchange Treatment of Perfluorinated Carboxylic Acids in Water: Comparison of Polystyrenic and Polyacrylic Resin Structures and Impact of Sulfate on Their Performance." *ACS ES&T Water* 2 (7): 1195-1205. https://doi.org/10.1021/acsestwater.1c00501.

Saslow, S. A., E. A. Cordova, N. M. Escobedo, O. Qafoku, M. E. Bowden, C. T. Resch, N. Lahiri, E. T. Nienhuis, D. Boglaienko, T. G. Levitskaia, P. Meyers, J. R. Hager, H. P. Emerson, C. I. Pearce, and V. L. Freedman. 2023a. "Accumulation Mechanisms for Contaminants on Weak-Base Hybrid Ion Exchange Resins." *Journal of Hazardous Materials* 459: 132165. https://doi.org/https://doi.org/10.1016/j.jhazmat.2023.132165.

Saslow, S. A., T. G. Levitskaia, E. A. Cordova, N. M. Avalos, D. Boglaienko, Y. Fang, X. Song, A. Lawter, H. Emerson, J. Szecsody, C. D. Johnson, C. I. Pearce, V. L. Freedman, and R. D. Mackley. 2023b. "Part I: Predicting Performance of Purolite A532e Resins for Remediation of Comingled Contaminants in Groundwater." *Journal of Environmental Chemical Engineering* 11 (3): 109618. https://doi.org/https://doi.org/10.1016/j.jece.2023.109618.

Saslow, S. A., T. G. Levitskaia, E. A. Cordova, N. M. Avalos, D. Boglaienko, Y. Fang, X. Song, A. Lawter, H. Emerson, J. Szecsody, C. D. Johnson, C. I. Pearce, V. L. Freedman, and R. D. Mackley. 2023c. "Part Ii: Predicting Performance of Dowex 21k Resin for Remediation of Comingled Contaminants in Groundwater." *Journal of Environmental Chemical Engineering* 11 (3): 109620. https://doi.org/https://doi.org/10.1016/j.jece.2023.109620.

Sookhak Lari, K., G. B. Davis, A. Kumar, J. L. Rayner, X.-Z. Kong, and M. O. Saar. 2024. "The Dynamics of Per- and Polyfluoroalkyl Substances (Pfas) at Interfaces in Porous Media: A Computational Roadmap from Nanoscale Molecular Dynamics Simulation to Macroscale Modeling." *ACS Omega* 9 (5): 5193-5202. https://doi.org/10.1021/acsomega.3c09201.

Tamanna, T., P. J. Mahon, R. K. Hockings, H. Alam, M. Raymond, C. Smith, C. Clarke, and A. Yu. 2023. "Ion Exchange Miex® Gold Resin as a Promising Sorbent for the Removal of Pfas Compounds." *Applied Sciences* 13 (10): 6263. https://www.mdpi.com/2076-3417/13/10/6263.

Townsend, R. P., and E. N. Coker. 2001. "Chapter 11 Ion Exchange in Zeolites." In *Studies in Surface Science and Catalysis*, edited by H. van Bekkum, E. M. Flanigen, P. A. Jacobs, and J. C. Jansen, 467-524. Elsevier. https://doi.org/https://doi.org/10.1016/S0167-2991(01)80253-6.

Vaaramaa, K., and J. Lehto. 2003. "Removal of Metals and Anions from Drinking Water by Ion Exchange." *Desalination* 155 (2): 157-170.

Wang, J., and Z. Wan. 2015. "Treatment and Disposal of Spent Radioactive Ion-Exchange Resins Produced in the Nuclear Industry." *Progress in Nuclear Energy* 78: 47-55. https://doi.org/https://doi.org/10.1016/j.pnucene.2014.08.003.

Williams, A. J., C. M. Grulke, J. Edwards, A. D. McEachran, K. Mansouri, N. C. Baker, G. Patlewicz, I. Shah, J. F. Wambaugh, R. S. Judson, and A. M. Richard. 2017. "The Comptox Chemistry Dashboard: A Community Data Resource for Environmental Chemistry." *Journal of Cheminformatics* 9 (1): 61. https://doi.org/10.1186/s13321-017-0247-6.

Woodard, S., J. Berry, and B. Newman. 2017. "Ion Exchange Resin for Pfas Removal and Pilot Test Comparison to Gac." *Remediation Journal* 27 (3): 19-27. https://doi.org/https://doi.org/10.1002/rem.21515.

Zaggia, A., L. Conte, L. Falletti, M. Fant, and A. Chiorboli. 2016. "Use of Strong Anion Exchange Resins for the Removal of Perfluoroalkylated Substances from Contaminated Drinking Water in Batch and Continuous Pilot Plants." *Water Research* 91: 137-146. https://doi.org/https://doi.org/10.1016/j.watres.2015.12.039.

Pacific Northwest
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902 Battelle Boulevard
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