PNNL-36648 Rev 0
DVZ-RPT-110 Rev 0

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U.S. DEPARTMENT OF ENERGY

Prepared for the U.S. Department of Energy
under Contract DE-AC05-76RL01830

PACIFIC NORTHWEST NATIONAL LABORATORY
*operated by*
BATTELLE
*for the*
UNITED STATES DEPARTMENT OF ENERGY
*under Contract DE-AC05-76RL01830*

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# Summary

During operations at the U.S. Department of Energy Hanford Site, releases of chemical and radioactive waste resulted in contamination of the soil and groundwater beneath portions of the site, including inadvertent releases of carbon-14 in the 100-K Area. Ongoing environmental cleanup efforts in the 100-K Area are focused on hexavalent chromium [Cr(VI)] and thus have not yet addressed the two carbon-14 groundwater plumes. This is reflected in the positioning of the groundwater wells, where extraction wells are outside the carbon-14 plume areas and only monitoring wells are placed within the plume areas. Based on a literature review of studies on carbon-14-contaminated sites, this report provides context and offers conceptualized options for implementing targeted *ex situ* remediation strategies for carbon-14 using the ion exchange (IX) water treatment technology within the 100-K Area.

Carbon-14 has a relatively long half-life, is persistent in the environment, and is readily available for biological uptake, so it is important to implement a remedy for carbon-14 groundwater plumes that will meet regulatory requirements, such as the drinking water standard. Carbon-14 detected in the groundwater will likely be in the form of (bi)carbonate anions, which can be removed using commercial IX resins. Commercially available anion exchange resins (sometimes advertised as dealkalizers) are designed for capture and removal of the anions associated with alkalinity in water (i.e., bicarbonate and carbonate). While aqueous carbon-14 is not a common contaminant of concern, there are a few examples of IX treatment to remove carbon-14 (Carlton and Baumann 1991; Nuclear Decommissioning Authority 2014). At the end of the resins' treatment life, there are multiple options for long-term storage, immobilization, or disposal of spent IX resins loaded with carbon-14.

This report outlines three options for implementing IX resin technology for treatment of carbon-14 in groundwater in the 100-K Area. The first option consists of modifying the pre-existing aboveground treatment facilities for the 100-KX and -KW pump and treat (P&T) systems, in which an additional IX treatment train for carbon-14 removal is operated before the existing IX treatment trains that use the SIR-700-HP resin for Cr(VI) removal. The second option consists of replacing SIR-700-HP resin from some of the existing IX vessels with a carbon-14 targeted IX resin, which has the benefit of minimal infrastructure modifications. The feasibility of option 2 depends on whether (i) the current adjustment from pH 8 to 7 [implemented to optimize SIR-700-HP resin effectiveness for Cr(VI) removal] will impact carbon-14 removal by the new IX resin, and (ii) fewer SIR-700-HP IX vessels in the treatment train is still adequate to meet the requirements for Cr(VI) treatment. The advantage of options 1 and 2 would be leveraging the established network of P&T injection and extraction wells and the existing aboveground treatment facility. The third option is to use a mobile skid for IX treatment of carbon-14 at impacted wells. The advantage of the mobile skid is deploying the treatment at targeted wellheads rather than undergoing modifications to the 100-KX and -KW P&T facilities.

To support a decision on these implementation options, some uncertainties should be addressed regarding candidate commercial resin performance under conditions relevant to 100-K Area and P&T system operational parameters. Since the findings in this report are based on a literature review, laboratory experiments are recommended to resolve these site-specific uncertainties so calculations can be performed for developing an intermediate-scale IX design with operational specifications for IX treatment of carbon-14.

This initial screening evaluation determined IX treatment of carbon-14 is possible with commercial IX resins designed for (bi)carbonate removal. To support the expansion of IX treatment to include carbon-14 remediation at 100-K P&T systems, additional information is needed to evaluate treatment performance under site-specific conditions and determine the feasibility of different implementation designs.

# Acknowledgments and Quality Assurance

Funding for this work was provided by the U.S. Department of Energy (DOE) Richland Operations Office under the Deep Vadose Zone – Applied Field Research Initiative. Pacific Northwest National Laboratory (PNNL) is operated by Battelle Memorial Institute for DOE under Contract DE-AC05-76RL01830.

This work was performed in accordance with the PNNL Nuclear Quality Assurance Program (NQAP). The NQAP complies with 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.

# Acronyms and Abbreviations

| | |
|---|---|
| CANDU | Canada Deuterium Reactor |
| DOE | U.S. Department of Energy |
| DWS | drinking water standard |
| EPA | U.S. Environmental Protection Agency |
| ERDF | Environmental Restoration Disposal Facility |
| HIC | high-integrity container |
| ISTP | intermediate-scale test platform |
| IX | ion exchange |
| KE | K East (portion of the 100-K Area) |
| KW | K West (portion of the 100-K Area) |
| OU | Operable Unit |
| P&T | pump and treat |
| ROD | record of decision |
| SCEPTER | Selective Carbon Extraction Process |
| SCOC | secondary contaminant of concern |

# Chemical List

| | |
|---|---|
| C-14 or $^{14}C$ | carbon-14 |
| $CO_3^{2-}$ | carbonate |
| Cr(VI) | hexavalent chromium |
| $HCO_3^-$ | bicarbonate |
| $H_2CO_3$ | carbonic acid |
| $NO_3^-$ | nitrate |
| PFAS | per- and polyfluorinated substances |
| Sr-90 | strontium-90 |
| Tc-99 | technetium-99 |
| TCE | trichloroethene |
| U | uranium |

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# 1.0 Introduction

During operations at the U.S. Department of Energy (DOE) Hanford Site in southeastern Washington state, multiple pollutants were released through waste disposal and unintended releases to the soil at multiple locations, with subsequent impacts on groundwater. This included releases of aqueous condensate containing carbon-14 to gas condensate cribs, resulting in two small areas of groundwater contamination in the 100-K Area. In 2021, the total approximate plume area above the water quality standard was 0.06 $km^2$ (Figure 1).

Ongoing environmental cleanup efforts in the 100-K Area are focused on hexavalent chromium [Cr(VI)] and have not yet specifically addressed the carbon-14 plumes. The current pump and treat (P&T) facilities use ion exchange (IX) treatment to remove the Cr(VI). However, the IX resin used in the Cr(VI) treatment does not capture carbon-14 from the groundwater (U.S. DOE 2023). As a result, the groundwater wells in the 100K-Area are positioned such that the extraction wells are outside the two carbon-14 plume areas and only monitoring wells are placed within the plume areas.

The extraction wells adjacent to the carbon-14 plumes have measurable levels of carbon-14, but after blending in the P&T influent tank with groundwater from wells without carbon-14, the concentrations of carbon-14 entering and leaving the IX treatment are below the drinking water standard (DWS). However, by continuing to blend the groundwater and reinjecting it back into the subsurface with untreated carbon-14, the potential exists for the carbon-14 to move from its original source area(s) into new locations in the 100-K Area subsurface. This becomes especially plausible if the carbon-14 plumes begin to migrate into areas with established Cr(VI) extraction wells.

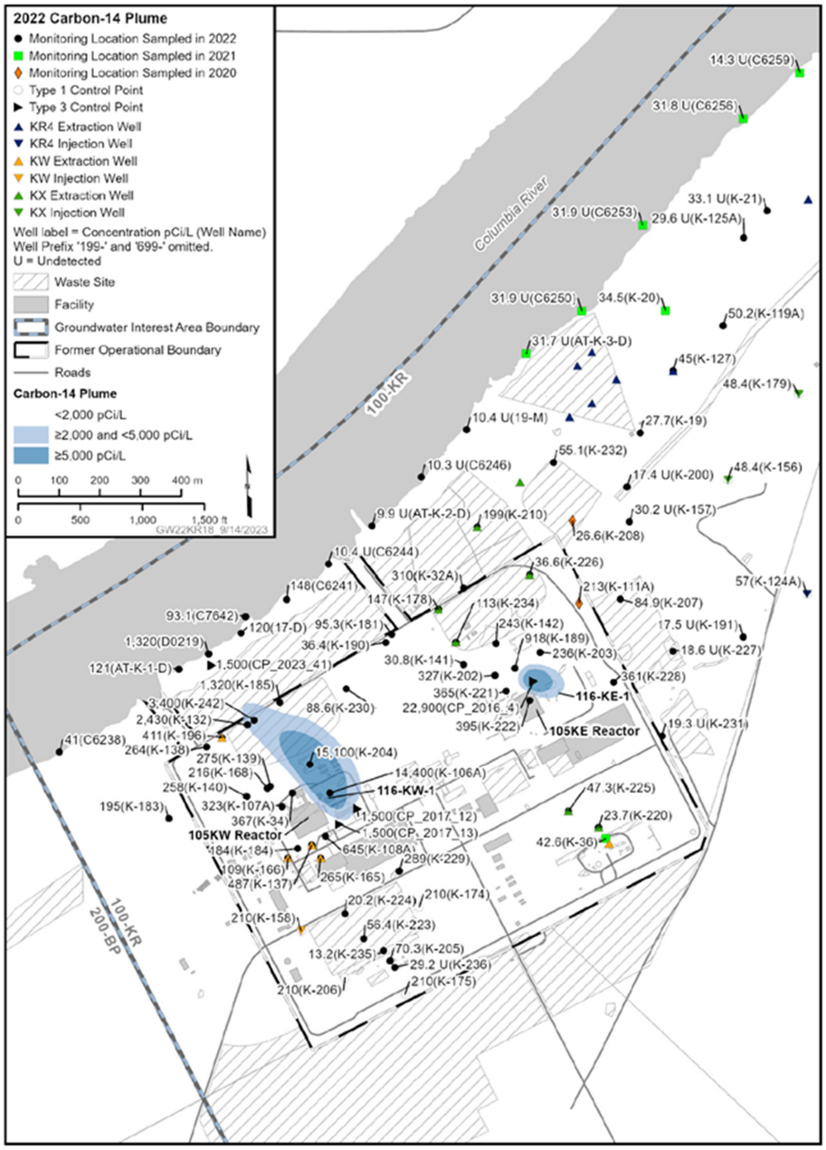

Figure 1. Carbon-14 plume map of the 100-KR-4 Operable Unit (from U.S. DOE 2023).

Carbon-14 exists in the 100-K Area groundwater in several chemical forms, such as bicarbonate ($HCO_3^-$) and carbonate ($CO_3^{2-}$) anions, which have been removed by IX resins at other field sites with carbon-14 contamination (Carlton and Baumann 1991; Nuclear Decommissioning Authority 2014). Because IX treatment is already applied at 100-K Area P&T facilities, the possibility exists to expand this technology to include an IX resin that targets carbon-14 removal.

This report is organized into four sections. Section 1.0 provides (i) an overview of current groundwater conditions and ongoing remediation efforts in the 100-K Area; (ii) information on carbon-14 contamination and its presence at the Hanford Site; and (iii) a brief introduction of IX resins and current application in remediation activities at the Hanford Site. Section 2.0 presents the current state of knowledge about the use of IX resins for carbon-14 treatment. Section 3.0 discusses three potential implementation options for including IX treatment of carbon-14 in remediation activities at the 100-K Area. Section 4.0 recommends future experimental work to resolve uncertainties and support the decision-making process regarding the implementation options.

## 1.1 Current Groundwater Conditions and Remediation Activities in the Hanford 100-K Area

Groundwater in the 100-K Area was contaminated from past operations of the K East and K West reactor facilities, which were active from 1955-1971 (Gerber 1993). By the end of 2022, 76% of the 100-K Area groundwater had either been successfully remediated or no additional remediation efforts were required (U.S. DOE 2023; U.S. EPA 1999, 1996). Remediation of the remaining areas will continue in accordance with current U.S. Environmental Protection Agency (EPA) records of decision (RODs) (U.S. EPA 1999, 1996).

Table 1 summarizes the groundwater contamination in the 100-K Area. Contaminants in the 100-K unconfined aquifer include chromium [total and Cr(VI)], tritium, nitrate, strontium-90, trichloroethene (TCE), and carbon-14 (U.S. DOE 2023). Figure 1 provides a map of carbon-14 contaminant plumes in the 100-K Area (using data from 2022). Chromium is the primary contaminant of concern in the 100-K Area, while carbon-14, nitrate, strontium-90, TCE, and tritium are secondary contaminants of concern (SCOCs). Appendix A provides more information on the groundwater SCOC concentrations. Carbon-14 in the 100-K Area is discussed in depth in Section 1.3.

Table 1. Summary of groundwater contamination in the 100-KR Groundwater Interest Area from the 2022 Hanford Site Groundwater Monitoring Report (U.S. DOE 2023).

| Contaminant | Water Quality Standard | Year | Maximum Measured Concentration | Plume Area[(a)] (km$^2$) |
|---|---|---|---|---|
| Hexavalent chromium | 48/10 µg/L[(b)] | 2022 | 236 µg/L (199-K-188) | 0.4[(c)] |
| | | 2021 | 114 µg/L (199-K-240) | 0.71[(c)] |
| Total chromium (filtered) | 100 µg/L | 2022 | 240 µg/L (199-K-188) | Not Mapped |
| | | 2021 | 112 µg/L (199-K-240) | Not Mapped |
| Tritium | 20,000 pCi/L | 2022 | 131,000 pCi/L (199-K-207) | 0.04 |
| | | 2021 | 234,000 pCi/L (199-K-207) | 0.04 |
| Nitrate | 45 mg/L | 2022 | 104 mg/L (199-K-188) | 0.04 |
| | | 2021 | 112 mg/L (199-K-230) | 0.04 |
| Strontium | 8 pCi/L | 2022 | 179 pCi/L (199-K-141) | 0.02 |
| | | 2021 | 3,940 pCi/L (199-K-222) | 0.03 |
| Carbon-14 | 2,000 pCi/L | 2022 | 24,200 pCi/L (199-K-242) | 0.03 |
| | | 2021 | 30,900 pCi/L (199-K-106A and 199-K-204) | 0.06 |
| Trichloroethene | 4 µg/L | 2022 | 8.7 µg/L (199-K-11) | 0.11 |
| | | 2021 | 8.2 µg/L (199-K-11) | 0.13 |

(a) Estimated area based on concentration higher than the water quality standard.
(b) 48 µg/L (WAC 173-340, "Model Toxics Control Act—Cleanup"); 10 µg/L (WAC 173-201A-240, "Water Quality Standards for Surface Waters of the State of Washington," "Toxic Substances"). It is anticipated that the 10 µg/L standard will be the applicable cleanup level for 100-KR-4 Operable Unit (OU) groundwater.
(c) Includes the hexavalent chromium plume on the border between 100-KR and 100-NR.

P&T operations are ongoing, in accordance with the interim action ROD, across the Hanford Site (U.S. DOE 2022). Most of the chromium found on the Hanford Site exists as Cr(VI) (Thornton et al. 1995), and the interim remedial target for Cr(VI) in the 100-KR groundwater OU is 20 μg/L, with the assumption that the groundwater mixes with the river water to meet the 10 μg/L surface water standard (U.S. DOE 2023; Hulstrom 2024). There are three P&T facilities in the 100-K Area (KE, KW, and KR4) designed for removing Cr(VI) and total chromium from the groundwater. Table A.1 in Appendix A provides more detail on each P&T facility. There were three Cr(VI) plumes in the 100-K Area resulting from (i) spills, leaks, or limited intentional discharges of concentrated sodium dichromate solutions (used for conditioning reactor cooling water) or (ii) limited intentional discharge of spent reactor cooling water to the 116-K-1 Crib and 116-K-2 Trench and retention basin leaks (Thornton et al. 1995); however, the K North plume has since separated into several small areas of remaining contamination.

SCOCs co-located with the Cr(VI) plumes are extracted by the P&T extraction wells along with the Cr(VI)-contaminated groundwater. However, these SCOCs are not specifically targeted by the specialized IX resin implemented by the P&T systems for Cr(VI) removal and may be returned to the aquifer via injection wells, where the SCOCs are injected at concentrations below their respective DWSs, which is consistent with requirements of the interim action ROD. However, injection could result in redistribution of contaminants (i.e., TCE, strontium-90, tritium, and carbon-14) into portions of the aquifer not originally impacted (U.S. DOE 2022). To minimize this cycling of untreated SCOCs through the P&T systems, the extraction wells have been placed outside the concentrated SCOC plumes and focus primarily on the Cr(VI) plumes. This is true for the two carbon-14 plumes in the 100-K Area, where the nearest extraction wells are adjacent to the plumes and only monitoring wells are operated within the main plume areas.

In 2022, a new well (199-K-242) was drilled in the KW Area (north of the KW Reactor), which currently functions as a monitoring well. Sampling of this well in 2022 showed that it contained the maximum concentration of carbon-14 measured across the monitoring wells in the 100-K Area (Table 1). However, this dual-purpose well design includes the option to be reconfigured into an extraction well for the KW P&T system once a remedial pathway is selected for carbon-14 (U.S. DOE 2023).

## 1.2 Sources of Carbon-14 in the Nuclear Fuel Cycle and Historical Interest in Environmental Releases of Carbon-14

Carbon-14 is a radioisotope (beta emitter, 5,730-year half-life) found as a byproduct in nuclear reactor systems (IAEA 2004; Asmussen et al. 2021). Several other radiocarbon isotopes exist, but their half-lives are extremely short, and they are not a concern for DOE environmental management sites. In the nuclear fuel cycle, carbon-14 is produced by neutron interaction with other elements ($^{13}C$, $^{14}N$, $^{15}N$, $^{16}O$, $^{17}O$) present in the nuclear fuel, moderator, and/or primary coolant systems of nuclear reactors (IAEA 2004). The carbon-14 produced in nuclear reactors is often emitted as gaseous carbon dioxide ($^{14}CO_2$); however, it is also possible for the carbon-14 to become condensed and incorporated into aqueous systems as different polyatomic anions, such as bicarbonate ($HCO_3^-$), carbonate ($CO_3^{2-}$), or carbonic acid ($H_2CO_3$) (IAEA 2004).

Carbon-14 has a relatively long half-life, is persistent in the environment, and is readily available for biological uptake, so it is important to address carbon-14 groundwater plumes. To limit public health hazards associated with carbon-14, the EPA has set a DWS of 2,000 pCi/L (74 Bq/L) (IAEA 2004; U.S. DOE 2023).

The treatment of aqueous carbon-14 species was a topic of interest to the scientific community in the 1980s and 1990s due to the prevalence of Canada Deuterium Uranium (CANDU) reactors and advancements to accommodate activities at the Savannah River Site (Aiken, SC) and Sellafield (Cumbria, England) (Carlton and Baumann 1991; Nuclear Decommissioning Authority 2014). During this time, conventional treatment options included precipitation of the carbonates by calcium, barium, or strontium at high pH, which can be advantageous for certain downstream immobilization options, such as cementation (Hodkin et al. 2016). Another treatment option involved removing the aqueous carbon-14 through conventional water alkalinity treatments, such as IX (Carlton and Baumann 1991). However, there has been limited research in the U.S. since then, partially because regulatory practices and requirements do not address carbon-14 waste management (Yim and Caron 2006).

## 1.3 Carbon-14 Contamination at the Hanford Site

At the Hanford Site, carbon-14 was generated primarily as a byproduct of plutonium production. During operation of the 100-KE and 100-KW reactors, carbon-14 concentrations in the gas dryer condensate ranged from $2.9 \times 10^8$ pCi/L at the KW Reactor to $1.04 \times 10^9$ pCi/L at the KE Reactor (U.S. DOE 2023). Carbon-14 was subsequently released from reactor gas dryer regeneration condensate during discharges into the 116-KE-1 and 116-KW-1 gas condensate cribs and fuel storage basins (U.S. DOE 2012). The fate and transport of carbon-14 in the vadose zone can ultimately be affected by a range of factors, including unsaturated water content, extent of microbial biomass production, microbial carbon dioxide production, temperature, diffusion rates, and carbonate equilibriums (Cole and Prairie 2024; Liu et al. 2021).

Carbon-14 exists in the 100-K Area groundwater in various chemical forms, such as $H^{14}CO_3^-$, $^{14}CO_3^{2-}$, and $H_2CO_3$, depending on the pH of the groundwater (U.S. DOE 2012). These chemical forms contribute to the alkalinity of the groundwater, which averages between 150 and 180 mg/L total alkalinity and 2.5 mg/L $CO_3^{2-}$ in the 100-K Area (averaged from 2019-2023 data from the Hanford Environmental Information System). To date, there has been no active remediation to remove carbon-14 in the 100-K Area (Johnson 2016; U.S. DOE 2023).

Currently, there are two carbon-14 plumes in the 100-KR-4 OU with a total area of ~0.06 km$^2$ (Figure 1). In 2021 and 2022, the maximum concentrations measured were 30,900 and 24,200 pCi/L, respectively (U.S. DOE 2023). In the 100-K Area, groundwater flow is generally toward the Columbia River. Some carbon-14 goes through the P&T aboveground treatment systems because it is comingled with the Cr(VI) contamination. However, carbon-14 is not removed by the current IX treatment process. As the carbon-14 plume migrates, carbon-14 concentrations in the P&T influent may become high enough that blending at the P&T facility may not be sufficient to reduce the carbon-14 concentration to below the DWS, which would significantly impact operations for the 100-K Area P&T systems (U.S. DOE 2022).

## 1.4 Contaminated Groundwater Treatment with Ion Exchange Resins

Generally, IX in water treatment is the process of exchanging an aqueous, undesired ion with an innocuous ion attached to solid media. A common media is a cross-linked polymer matrix (called resin) capable of interchanging ions between two phases (e.g., solid and liquid). The polymer serves as an insoluble backbone onto which an ion is electrostatically bound. When contacted with a solution containing ions of the same charge, an exchange can occur (Figure 2). This exchange is determined by factors such as the concentration of the ion(s) in solution, the affinity of the ion(s) for the insoluble media phase, and the chemistry of the solution (e.g., pH, redox potential, additional solutes). Both cation (positively charged) and anion (negatively charged) exchange resins are manufactured.

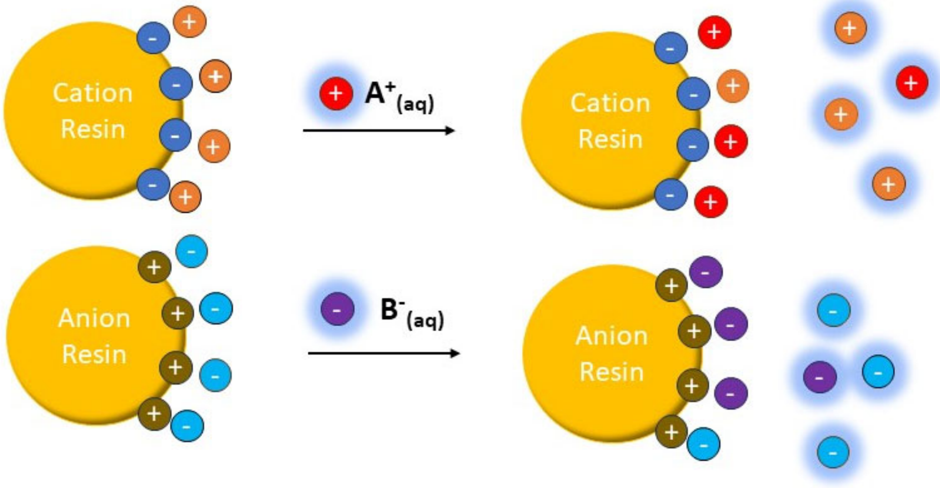

Figure 2. Simplified depiction of single-ion exchange between an insoluble polymer resin (initially loaded with innocuous ions, orange and light blue) and a solution phase containing the undesirable ions (red and purple). For the cation exchange (above), the aqueous, red $A^+$ cation is exchanged with the orange ions originally found on the resin exchange sites. Anion exchange occurs similarly, with the light blue anions on the resin exchanging with the aqueous, purple $B^-$ anion.

IX polymer backbones can also be functionalized with covalent ligands that can further tune the selectivity of the resin for a specific ion (Saslow et al. 2023a). Most IX resins are synthesized in one of two ways: (i) post-functionalization after polymerization with an ion-exchange ligand or (ii) incorporation of a functionalized monomer which is then polymerized into the resin. Functionalized resins are further subdivided into categories based on the functional group activity. For example, strong-acid cation resins are synthesized with anionic functional groups, such as sulfonate ($SO_3^-$), bound to the polymer matrix. Similarly, a weak-acid cation resin has a weaker organic acid ligand such as carboxylic acid (R–COOH). There are also strong- and weak-base IX resins, named for featuring quaternary amino groups or primary, secondary, or tertiary amino groups, respectively (Alexandratos 2009).

Additional characteristics must be considered when selecting an appropriate IX resin, including the following (Harland 1994):

- *Capacity:* determines the quantity of ions exchanged, often expressed as mass of ion per unit mass of resin (mg/g) or as ion equivalence per volume of resin (eq/L) (Schwartz and Loken 2019).
- *Swelling:* relates to the change in physical size of the IX resin beads when exposed to the solution being treated, often expressed as a percent. The degree of swelling is correlated to the amount of cross linkage in the polymer structure, where the greater the degree of cross-linking, the lower the swelling (Volli et al. 2023).
- *Selectivity:* preference of the IX resin for particular ions. The selectivity can be tuned by altering the chemical formulation of the IX resin (Schwartz and Loken 2019).
- *Stability:* overall resilience of the resin to mechanical and chemical degradation over time (Schwartz and Loken 2019).

- *Pore size:* distance of the void space within the individual resin bead. Pore sizes range from 2 nm to greater than 50 nm and are often ranked as micro-, meso-, or macro-porous. Pore size controls the capillary condensation, particle distribution within the pore, and the electrostatic potential of the pores, all of which impact removal performance (Volli et al. 2023; Mohamed and Wilson 2012).

Due to the insolubility of the polymer backbone, IX resins are easily adapted to a variety of continuous processes and systems. The resin media can be removed from solution via filtration and some resins can be regenerated, allowing them to be reused after reaching maximum capacity (Barman et al. 2023; Alexandratos 2009). IX resins have been used for a wide range of water treatment applications, such as water softening, removal of toxic or radioactive metals from the environment, and wastewater recovery (Barman et al. 2023; Alexandratos 2009). Commercial water treatment facilities have seen considerable success removing contaminants from the groundwater using IX technology, as have other DOE sites such as the Savannah River Site, Oak Ridge Reservation, and Paducah Gaseous Diffusion Plant (Kyser 2021; U.S. EPA 2007; U.S. DOE 2007).

## 1.5 Current Implementation of Ion Exchange Resins at the Hanford Site

The Hanford Site is currently using IX resins to treat groundwater in the 200 West, 100-K, 100-D, and 100-H areas. The five P&T facilities along the river corridor (KR4, KW, KX, DX, and HX) use SIR-700-HP IX resin (ResinTech, Camden, New Jersey), which comes loaded with chloride on the exchange sites, to remove Cr(VI) (U.S. DOE 2020, 2022; Saslow et al. 2023a). SIR-700 was renamed SIR-700-HP (where HP means high performance) when it received the Water Quality Association's Gold Seal, which means it meets the requirements of NSF/ANSI-61, *Drinking Water System Components – Health Effects*, for use in all potable water applications.

SIR-700-HP is a weak-base hybrid anion exchange resin due to its ability to remove the Cr(VI) by two mechanisms: (i) pH-dependent IX with chloride ions and (ii) reduction to Cr(III) and subsequent capture within the resin (Saslow et al. 2023a). The Cr(VI) reduction reaction occurs under acidic conditions, so the pH of the slightly alkaline groundwater is decreased to ~7.0 by addition of sulfuric acid, prior to entering the IX columns. The advantage of using a weak-base hybrid anion resin (like SIR-700-HP) versus strong-base anion resins (like Dowex 21K and Purolite A532E, which are used in the 200 West P&T system for uranium and technetium-99 removal) is the ability to maintain removal performance in the presence of high concentrations of competing anionic species (Saslow et al. 2023a-c). The specificity of the SIR-700-HP resin for Cr(VI) removal means that it is unsuitable for the capture of aqueous carbon-14 in groundwater (U.S. DOE 2022).

To address carbon-14 in the 100-K Area, a different IX resin than those currently deployed in the Hanford Site P&T systems will need to be identified and evaluated (Saslow et al. 2023a). The following sections review information from the literature, IX resin manufacturers, and Hanford P&T systems to determine if it is feasible to incorporate IX treatment of carbon-14 in groundwater into ongoing P&T operations. A technical basis for evaluating three implementation options for IX to remediate carbon-14 in the 100-K Area is also provided, including consideration of a wellhead treatment using a mobile IX skid deployed to specific wells.

# 2.0 State of Knowledge for Carbon-14 Treatment by Ion Exchange Resins

Aqueous carbon-14 is likely present in the groundwater in anionic form as $H^{14}CO_3^-$ or $^{14}CO_3^{2-}$, making it a good candidate for targeted removal by IX resins. There are many commercial IX resins (sometimes advertised as dealkalizers) available for removing $H^{12}CO_3^-$ and $^{12}CO_3^{2-}$. However, once the resin reaches the maximum exchanging capacity, the spent resin may require an immobilization treatment to meet requirements for disposal.

This section covers specific information on removal of aqueous carbon-14 by IX, commercially available resin products, and disposal pathways for the carbon-14 loaded spent resins.

## 2.1 Baseline IX Resin Application for Removal of Aqueous Carbon-14 as $CO_3^{2-}$

Inorganic carbon-14 is predominantly present in groundwater as either $H^{14}CO_3^-$ or $^{14}CO_3^{2-}$ (Stumm and Morgan 1996). The relative proportion of inorganic carbon-14 species is primarily driven by a pH-dependent equilibrium summarized in the speciation diagram in Figure 3 (Ghalei 2015). At pH 6.3, the relative distributions of $H_2CO_3$ and $HCO_3^-$ are equal. At pH levels ranging from 6.4 to 10.2, $HCO_3^-$ will be the dominant carbonate species. At pH 10.3, the relative distributions of $HCO_3^-$ and $CO_3^{2-}$ are equal (Benjamin 2015). Based on the groundwater pH in the 100-K Area, which ranges from 7.0 to 8.3 (Dai et al. 2005), the aqueous carbon-14 is expected to be found predominantly as $H^{14}CO_3^-$.

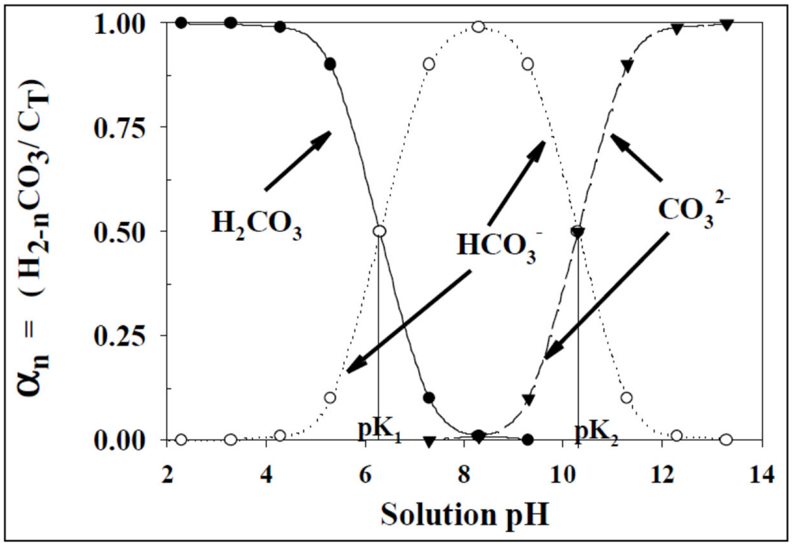

Figure 3. Relative distribution of carbonate species as a fraction of total dissolved carbonate ($C_T$) vs. the pH of the solution. Taken from (Ghalei 2015).

Alkalinity is a measurement of water's ability to neutralize acid and encompasses the presence of $HCO_3^-$, $CO_3^{2-}$, and hydroxide ($OH^-$) species in the water (Water Professionals 2024; Benjamin 2015). Dealkalization is similar to traditional water softening, where $HCO_3^-$ or $CO_3^{2-}$ is removed rather than calcium (Ca) and magnesium (Mg) ions (Water Professionals 2024). IX resins for dealkalization operate primarily through anion exchange via strong-base anion resins where $HCO_3^-$ or $CO_3^{2-}$ is exchanged for chloride ($Cl^-$). This is similar to Figure 2, where the light blue anions represent the $Cl^-$ and the purple anions represent the $HCO_3^-$ or $CO_3^{2-}$.

Dealkalization can also occur through cation exchange via weak-acid cation resins, although the process is not as straightforward. In weak-acid resins, the $H^+$ ion exchanges with hardness cations ($Mg^{2+}$ and $Ca^{2+}$) and the free $H^+$ ions in solution react with the $HCO_3^-$ alkalinity to form $H_2CO_3$. The $H_2CO_3$ then quickly hydrolyzes and is released as gaseous carbon dioxide ($CO_2$), which can be removed via aeration. This cation exchange method is preferred when the ratio of water hardness (dissolved Mg and Ca) to alkalinity is greater than 1.0 (Water Professionals 2024).

It is also common practice to use two resins in a split-stream dealkalization process. In this configuration, two beds of strong-acid cation resins operate in parallel; one bed is sodium (Na)-based and the other is H-based. Water softened by the Na-based resin contains all the alkalinity while the water treated by the H-based resin contains no alkalinity. Then, the blended effluents from each process are degassed to remove $CO_2$, where the ratio of the blended effluents allows the operator to control the alkalinity levels in the final effluent (Water Professionals 2024).

## 2.2 Candidate IX Resins for *Ex Situ* Carbon-14 Removal

There are many commercially available IX resins designed for the removal of $HCO_3^-$ and $CO_3^{2-}$, which should also remove $H^{14}CO_3^-$ and $^{14}CO_3^{2-}$ from groundwater. These types of commercially available resins are often used for water treatment, remediation, and industrial applications. A specific example is at nuclear power plants, especially CANDU reactors, where a large inventory of carbon-14 is captured by IX. The high yield of carbon-14 is primarily due to the presence of deuterated water, which has an increase in oxygen-17 abundance that undergoes neutron capture, producing carbon-14. Unfortunately, the available literature on carbon-14 capture in nuclear power plants does not provide information on the specific IX resins being used.

The investigation of available commercial IX resins designed for removing $HCO_3^-$ and $CO_3^{2-}$ found several options from three manufacturers: Purolite, ResinTech Inc., and DuPont. Table 2 presents an abbreviated list of the commercial resins identified. These specific resins were chosen for their variety in matrix types, functional groups, and ionic forms, which can impact the reported exchange capacity. Section 4.0 describes how these resins can be evaluated under conditions relevant to the 100-K Area.

Table 2. Examples of commercially available IX resins for removal of carbonate species.[(a)]

| Manufacturer | Name | Polymer(s) (matrix type) | Functional Group | Ionic Form | Exchange Capacity | Reference |
|---|---|---|---|---|---|---|
| Purolite | A600E/9149 | Polystyrene-divinylbenzene (gel) | Quaternary ammonium | $Cl^-$ | 1.6 eq/L | Purolite 2024 |
| ResinTech | SBG1 | Styrene (gel) | Trimethylamine | $Cl^-$ | 1.4 eq/L | ResinTech 2024b |
| ResinTech | SBG2 | Styrene (gel) | Dimethylethanolamine | $Cl^-$ | 1.4 eq/L | ResinTech 2024c |
| ResinTech | MBD-10 | Styrene (gel) | Sulfonic acid / trimethylamine | $H^+/OH^-$ | 0.6 eq/L | ResinTech 2024a |
| DuPont | AmberLite IRN 78 OH | Styrene-divinylbenzene (gel) | Trimethylammonium | $OH^-$ | 1.9 eq/L | DuPont 2024b |
| DuPont | AmberLite HPR8400H | Acrylic (macroporous) | Carboxylic acid | $H^+$ | 4.7 eq/L | DuPont 2024a |

(a) Additional resins are available from DuPont and Purolite with the same or lower exchange capacities.

## 2.3 Competitive Effects of Common Groundwater Anions on Carbon-14 Removal Performance

Many studies have documented the effect of competitive ions on the removal of targeted analytes using IX (Inglezakis et al. 2005; Czuprynski et al. 2022; Ates and Incetan 2013; Saslow et al. 2023a; Kang et al. 2004). Other anions (e.g., nitrate, sulfate, and chloride) present in the 100-K Area groundwater may compete with $HCO_3^-$ and $CO_3^{2-}$ for exchange sites and affect carbon-14 removal.

Nitrate ($NO_3^-$) is especially problematic for the targeted treatment of $HCO_3^-$ and $CO_3^{2-}$ due to the affinity that many anion IX resins have for $NO_3^-$. Unless very specifically engineered, most anion IX resins remove anions in descending order by molecular size and valence charge. While this benefits the remediation of $NO_3^-$, the general affinity of strong-base anion exchange resins for $NO_3^-$ will hamper the targeted removal of carbon-14 because the resin will preferentially remove any $NO_3^-$ in the system before $HCO_3^-$ and $CO_3^{2-}$ (Gottlieb 2021). The presence of sulfate ($SO_4^{2-}$) will also likely impact removal performance because $SO_4^{2-}$ is known to interfere with $NO_3^-$ removal by anion IX resins (Gottlieb 2021).

The presence of competitive anions will likely influence the contaminant loading, reaction kinetics, and breakthrough of any resin used for the removal of carbon-14. Many systems used in water treatment simply remove all target anions, such as $SO_4^{2-}$, $NO_3^-$, $HCO_3^-$ and $CO_3^{2-}$, using non-selective resins. However, this approach increases the amount of resin required and decreases operational lifespan of the resins (Owens 1995). Laboratory testing would be needed to determine the degree of competition and the impacts on IX treatment design.

## 2.4 Methods for Disposal of Spent IX Resins

It is important to consider the cradle-to-grave life cycle of any IX resin used for water treatment. At Hanford, the spent SIR-700-HP, Purolite A532E, and Dowex 21K resins are sent to the Environmental Restoration Disposal Facility (ERDF). However, depending on the loading capacity of the targeted carbon-14 resin, it's possible that this spent resin will exceed the maximum limit for disposal in the near-surface (see Section 4.5 for more details). Thus, other disposal processes should be considered, especially given the potential for the carbon-14 to mobilize during resin degradation when stored for extended periods without additional treatment (Yim and Caron 2006). This has led to research into different disposal methods for carbon-14-loaded IX resins, as described below.

### 2.4.1 Removing Carbon-14 from the Resin for Disposal

Regeneration of IX resins allows the spent resin to be restored to its original ionic form, releasing the exchanged (captured) ions (e.g., $H^{14}CO_3^-$) so the resin may be returned to service for further IX. This process can also be used to remove the captured carbon-14 from the resin prior to disposal.

One example of this process was reported by the Savannah River Site, where carbon-14 from reactor primary coolant was mostly retained by the IX resin as $H^{14}CO_3^-$ (Carlton and Baumann 1991). Acid stripping tests showed that more than 99% of the carbon-14 was removed as gaseous $CO_2$ during agitated aeration in nitric acid (2 Normal) according to Eq. (1):

$$\text{Resin-H}^{14}\text{CO}_3 + \text{HNO}_3 \rightarrow \text{Resin-NO}_3 + {}^{14}\text{CO}_2\text{(gas)} + \text{H}_2\text{O} \qquad (1)$$

The $^{14}CO_2$ could then be removed from the gas stream via gas scrubbing (such as alkaline slurry scrubbing, wet scrubbing, ethanolamine scrubbing) or similar technologies (e.g., carbonate precipitation) and further remediated (IAEA 2004).

Another approach to resin regeneration and/or loaded carbon-14 removal uses supercritical conditions. Spent IX resins containing carbon-14 have been shown to undergo rapid isotopic exchange when exposed to $^{12}CO_2$ under supercritical conditions [$CO_2$ transitions to supercritical phase at 7.38 MPa, 304 K (73.8 bar, 31.1 °C)], while leaving other radionuclides unaffected (Dias and Krasznai 1996). This carbon-14-selective process reduces the carbon-14 concentration captured on the resin to below detection limits by incorporating the carbon-14 into the supercritical $CO_2$, which can then be stored or disposed of separately. This allows the spent resins to be re-classified as low-level waste rather than as radioactive waste (assuming no other radionuclides are captured by the resin), and the $^{14}CO_2$ can be disposed separately (Dias and Shapka 2000).

Additional processes use gas-water phase exchanges. One method places the spent IX resins in contact with water and $^{12}CO_2$-enriched air at 70 °C. This causes the carbon-14 to be displaced as $^{14}CO_2$ (gas), which is scrubbed with either barium or calcium hydroxide to form insoluble carbonates, and it can then be disposed as solid waste (Buckley et al. 1989). Alternatively, the resin can be transferred to a tank filled with demineralized water with a $^{12}CO_2$ headspace and treated with a weak organic acid to reduce the pH to 3 (Strohmer and Sempere Belda 2018). This will release the carbon-14 from the resin into the aqueous phase, where it can subsequently be converted to $^{14}CO_2$ (gas) by further lowering the pH. Then, the headspace is collected and further refined through condensation or other processes to treat the $^{14}CO_2$ (gas) (Strohmer and Sempere Belda 2018).

SCEPTER (Selective Carbon Extraction Process) is a commercially available, portable, industrial-scale product designed to selectively remove carbon-14 from spent IX resins used in CANDU reactors. The product removes 95% of carbon-14 from the resin using an extraction reagent and then uses a precipitation reagent to produce a low-volume and low-level waste product containing the carbon-14. The resins are then gently heated to collapse the resin beads to reduce the volume of spent resin by 35-50%. The concentration of carbon-14 into a small volume along with the reduction and reclassification of the spent resin reduces disposal costs (Kinectrics 2024).

Spent IX resins that have been stripped of all carbon-14 and are not fit for reuse are often disposed through vitrification or incineration. However, carbon-14-stripped IX resins can also be disposed of in the same manner as resins loaded with carbon-14 if needed, as described below. For the stripped carbon-14 (as a gas or condensed liquid), the sources cited above do not explicitly state the ultimate disposal pathway, but it would likely depend on the concentration of the carbon-14. If the concentration exceeds the limit for near-surface disposal (8 $Ci/m^3$), then the stripped carbon-14 would need to be stored until a suitable disposal option is available (IAEA 2004). If the stripped carbon-14 concentrations are below the disposal concentration limit, then it could be disposed following the options listed below.

### 2.4.2 Disposal of Resin Loaded with Carbon-14

There are a variety of ways to dispose of spent resin without removing the carbon-14, but immobilization by physical encapsulation is most often used because it prevents re-mobilization of the carbon-14 due to resin degradation. EPA procedures, such as the toxic characteristic leaching procedure, can be used to evaluate the potential of carbon-14 re-mobilization from the resins. If the evaluation shows a need to immobilize resins prior to disposal, physical encapsulation options can include cementation, plastic solidification, storage in high-integrity containers (HICs), or vitrification/bituminization.

Cementation is a common practice used to immobilize radioactive waste at nuclear power plants and legacy nuclear sites such as Hanford (Wang and Wan 2015; Asmussen et al. 2021). In this process, a specially formulated grout is made using water, cement, and other additives that increase contaminant loading, stability, and solidification of the waste (Li and Wang 2006). This grout is mixed with radioactive waste to encapsulate it, and the mixture is poured into a container, where it solidifies into an immobilized waste form for disposal. The final waste forms are typically mechanically strong and have moderate leaching resistance. The raw materials are also widely available and inexpensive (IAEA 2002). IX resins, however, are one of the most difficult materials to cement. Resin beads swell in contact with water and may create cracks in the cement (Wang and Wan 2015). The waste loading of IX resins in a cement grout (i.e., percent of final product that is resin) is low, resulting in a much higher volume of the final waste forms compared to the original resin (Wang and Wan 2015).

Plastic/polymer solidification physically encapsulates spent resin in polymers, such as epoxy resin, polyethylene, formaldehyde, polyesters, or other polymers (IAEA 2002). The resin loading is high and final waste forms are leach resistant (Wang and Wan 2015).

HICs can be used to encapsulate spent IX resins without further immobilization in an additional matrix (Wang and Wan 2015). HICs are reinforced concrete cylindrical containers designed for disposal at facilities for low-level radioactive waste. The container is designed to ensure safe, reliable, below-ground disposal of radioactive waste for a minimum of 300 years while the radioactive isotopes captured by the resins decay. This process is simple, and the final waste volume is low, but HICs are expensive (IAEA 2002).

Vitrification and bituminization are also commonly used technologies for long-term immobilization and storage of IX resins. However, due to the temperatures required (200 °C or higher), the bicarbonate would off-gas as $^{14}CO_2$ (Thorpe et al. 2021). This would defeat the purpose of long-term immobilization and potentially lead to an atmospheric discharge.

Additional preprocessing, including super compaction or incineration, may also be used to increase waste loading and reduce final water form volume (IAEA 2002).

# 3.0 Conceptual Options for Implementing IX Treatment of Carbon-14 for 100-K Area Remediation

This section discusses three possible options for incorporating IX treatment of carbon-14 into ongoing remediation activities at the 100-K Area. One option is to add another IX treatment train to the current P&T facilities. The second option is to replace the existing SIR-700-HP resin in one of the parallel treatment trains with a new carbon-14 targeted IX resin. The third option is to implement wellhead treatment using a mobile IX skid. Section 4.0 discusses how uncertainties in these implementation options can be addressed.

## 3.1 Modification of Pre-existing P&T Infrastructure

The 100-K Area P&T systems (KW, KX, and KR4) already use SIR-700-HP IX resin for removal of Cr(VI) from groundwater (as described in Section 1.5). Thus, incorporation of an additional IX resin for carbon-14 removal could be feasible. Based on groundwater monitoring data from 2022 (Figure 1), the K West associated plume had a carbon-14 concentration of 15,100 pCi/L at 199-K-204, with several other wells downgradient of the 116-K-1 gas condensate crib showing concentrations above the DWS (2,000 pCi/L) (U.S. DOE 2023). In 2022, the K East associated plume had a carbon-14 concentration of 22,900 pCi/L measured at control point CP_20216_4; however, carbon-14 concentrations measured at wells downgradient of the 116-KE-1 Crib were below the DWS, with a maximum of 918 pCi/L measured at well 199-K-189 (U.S. DOE 2023). The K West associated plume is located near the KW P&T facility wells and the K East associated plume is near KX P&T facility wells. The KR4 P&T facility does not have any wells in proximity to the carbon-14 plumes.

In the KW and KX P&T systems, groundwater from extraction wells is blended in a central tank (separate tanks for each system) and the groundwater pH is adjusted from ~ 8 to 7 with sulfuric acid. This adjustment is necessary to increase the efficiency of the SIR-700-HP resin for Cr(VI) removal. However, decreasing the pH could negatively affect the performance of a carbon-14-targeted resin by changing the (bi)carbonate speciation (pH dependent) and would add extra $SO_4^{2-}$ ions that could compete with the $H^{14}CO_3^-$ and $^{14}CO_3^{2-}$ anions for uptake onto the resin. Schematics of the 100-KR-4 P&T facilities can be found in the 2022 annual summary report for the 100 Area P&T operations (Hulstrom 2024). The two options (described below) could apply to both KW and KX P&T facilities, or the carbon-14-impacted groundwater could potentially be routed to only one of the aboveground treatment facilities to reduce the scope of modifications.

The first option would require the current IX treatment process to be adapted to include an additional IX treatment train for a carbon-14 targeted resin (see Figure 4). Here, the native groundwater (approximately pH 8) from carbon-14-impacted extraction wells would (i) feed a separate holding tank, (ii) enter a new IX treatment train for carbon-14 removal, (iii) proceed to the original blending tanks (T-W1 for the KW P&T system and T-X3 for the KX P&T system) for pH adjustment with sulfuric acid, and (iv) continue to the SIR-700-HP treatment trains for Cr(VI) removal.

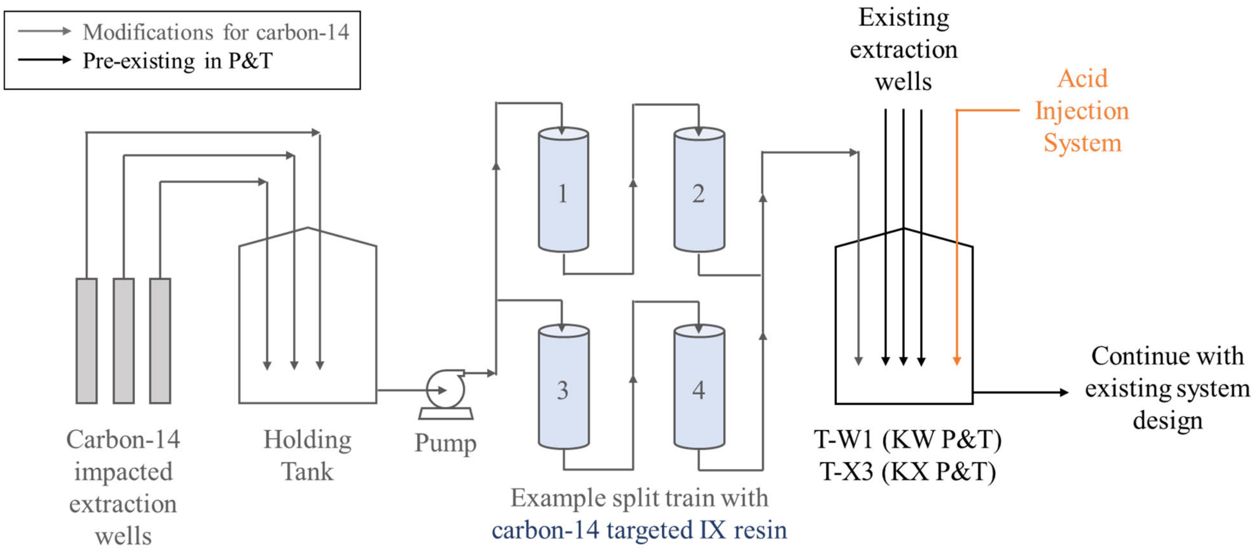

Figure 4. Conceptual schematic for modifying the KW and KX P&T systems to incorporate an additional IX treatment train for carbon-14 removal before entering the blending tank and continuing with the existing system design. The split train for the carbon-14 targeted resin is just an example, where a second split train should be added for redundancy. See Hulstrom (2024) for the existing system schematics for the KW and KX P&T systems.

A second option is to swap out the SIR-700-HP resin in one of the parallel treatment trains with a new carbon-14 targeted IX resin (Figure 5). This would require re-plumbing the split train from a parallel to a series configuration, such that flow enters the two SIR-700-HP resin columns followed by the two carbon-14 targeted resin columns. Then, the effluent would be delivered to the holding tanks (T-W3 for the KW P&T system and T-X5 for the KX P&T system) before proceeding through the existing system design. This approach would require the fewest facility modifications. The effectiveness of this approach would be contingent on the impact of the sulfuric pH adjustment (from 8 to 7) on carbon-14 removal performance, since the additional $SO_4^{2-}$ ions could reduce carbon-14 removal. If the carbon-14 removal is not affected by the sulfuric pH adjustment, then the impact on the efficiency and efficacy of Cr(VI) removal with one less SIR-700-HP treatment train would need to be evaluated to ensure continued compliance with cleanup regulations.

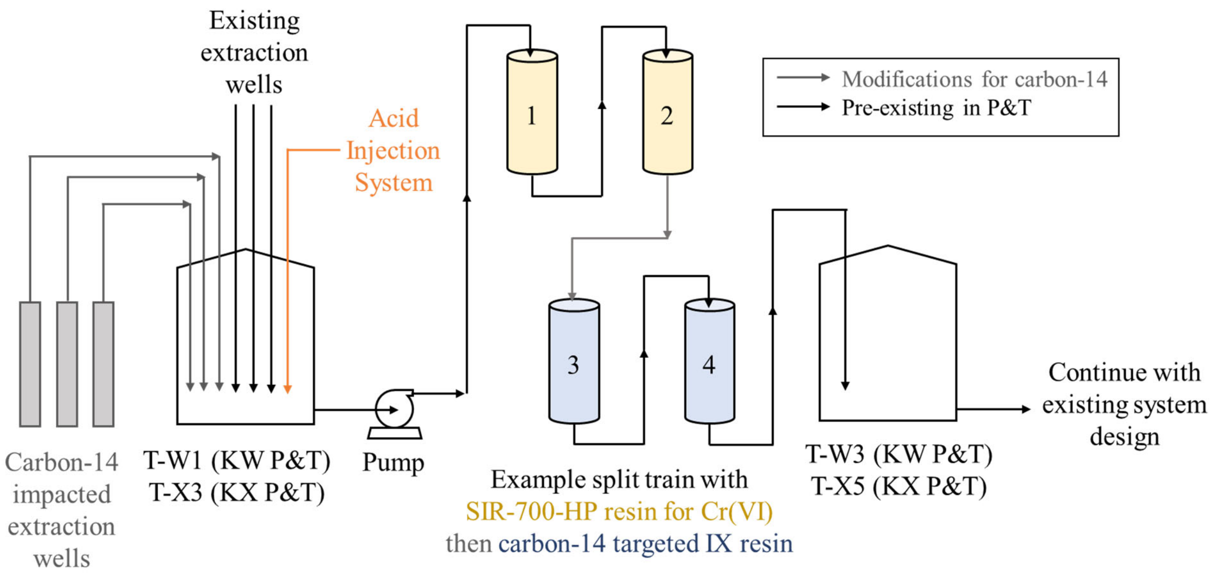

Figure 5. Conceptual schematic for modifying the KW and KX P&T systems to incorporate a carbon-14 targeted resin into the existing split trains. Here, two of the four resin vessels would swap out the SIR-700-HP resin for the carbon-14 resin. Then, the split train would be operated in a series configuration, where flow enters the SIR-700-HP vessels followed by the carbon-14 targeted resin vessels. The effluent would then flow into the holding tank before continuing through the existing system design. The split train for the carbon-14 targeted resin is just an example, where a second split train should be added for redundancy. See Hulstrom (2024) for the existing system schematics for the KW and KX P&T systems.

## 3.2 Treatment at Affected Groundwater Wells

Mobile skids for wellhead groundwater remediation have been used at many sites. For example, Oak Ridge National Laboratory demonstrated a modular, mobile IX system for the treatment of cesium-137 and strontium-90 (Taylor et al. 1998). The design consisted of three compact, skid-mounted modules for (i) storing the feed solution, (ii) performing IX treatment, and (iii) managing the spent IX resin. The first skid contained two feed pumps, while the second skid consisted of a filter and two IX columns that could be used individually, in parallel, or in series. The third skid contained equipment for handling, dewatering, and drying the spent IX resin. A similar design could be used for the treatment of carbon-14 in the 100-K Area, with an extra IX column in the second skid module to allow for the lead-lag-polish configuration commonly used at existing P&T facilities at the Hanford Site.

Another example is from the U.S. Army Corps of Engineers, who designed and implemented a compact trailer-mounted IX skid (with 20-gpm capacity) for the treatment of water contaminated by per- and polyfluorinated substances (PFAS) (Waisner et al. 2022). This system was composed of a pump, filtration system, and three media tanks, one with granular activated carbon and two with IX resin placed in series, mounted on a utility trailer that was towed by a pickup truck (see Figure 6).

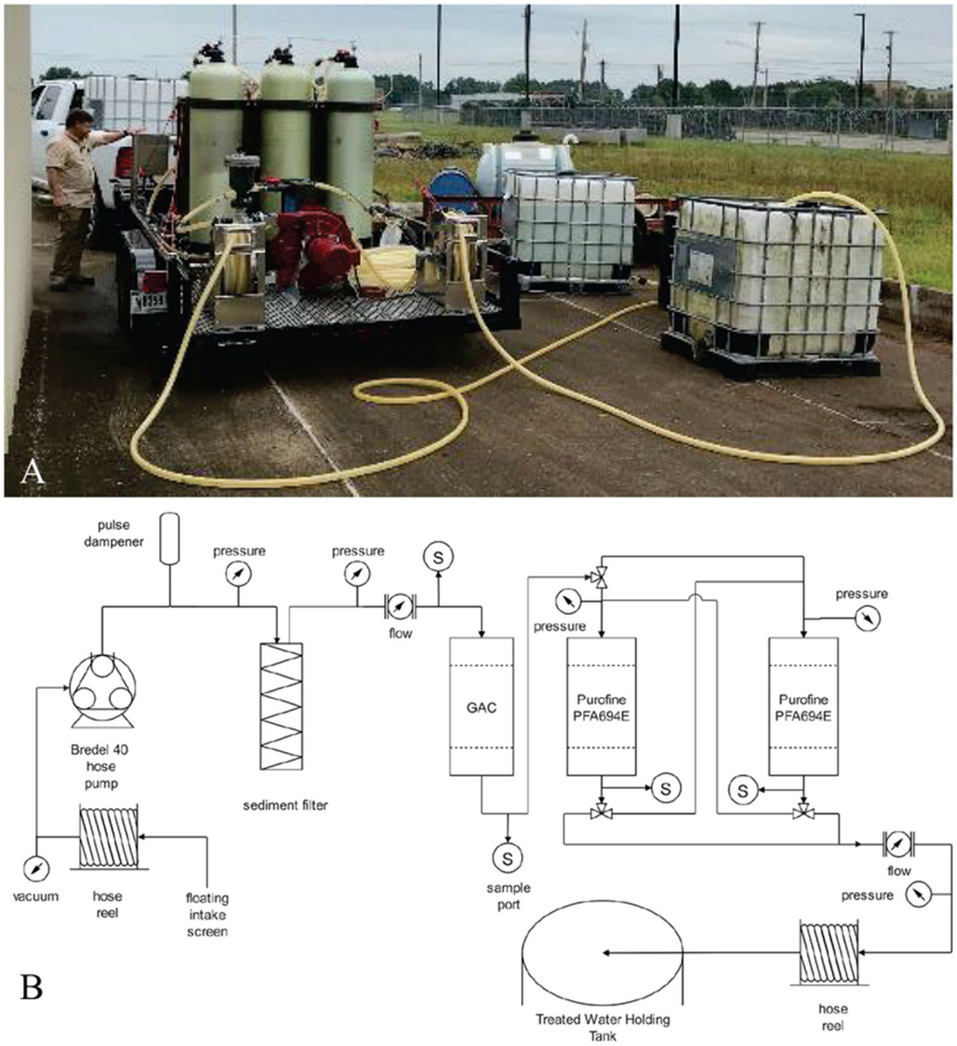

Figure 6. U.S. Army Corps of Engineers mobile treatment skid using granular activated carbon and IX resins for PFAS removal at field sites: (A) treatment system deployed during a treatment demonstration at a field site in Tennessee; (B) basic process flow diagram of the treatment system (Waisner et al. 2022).

Building a mobile IX treatment skid for wellhead treatment of carbon-14-affected wells would provide additional flexibility and mobility compared to using the existing fixed aboveground treatment facilities. A treatment skid also foregoes the expense and disruption of modifications to the P&T facilities. The treatment skid would not require pH adjustments of the groundwater prior to treatment because the native groundwater already has a pH of ~8, where the targeted $HCO_3^-$ anions are the dominant carbonate species and can be captured by the carbon-14 targeted resin.

A mobile IX treatment system would allow the system to be deployed at each carbon-14-impacted well. It also offers flexibility in repurposing the skid for treatment of other SCOCs since the IX resin can be easily replaced within the vessel and the skid can be moved to the desired groundwater well(s). When comparing the skid vs. P&T implementation options, it’s important to consider (i) skid design for integration with the existing monitoring wells, and (ii) how long the skid will need to operate at each well to reach the targeted removal, which will depend on the loading capacity of the resin and treatment capacity of the skid.

# 4.0 Recommendations to Address Uncertainties and Support Remediation Decisions

This report provides a limited screening evaluation, where IX treatment is determined to be a promising remediation option for carbon-14 removal from groundwater. Based on this evaluation, several candidate commercial IX resins were identified (Section 2.2) that can be tested with strategic lab-based experiments to address uncertainties about removal performance and operational approaches under field-specific conditions. To support a decision on the implementation of IX for carbon-14 treatment in the 100-K Area, the recommended experimental work is outlined below.

## 4.1 Addressing Operational and Experimental Uncertainties

There are many parameters, such as resin characteristics and operational conditions, to consider before starting calculations for specific recommendations for modifying the existing 100-K Area P&T facilities. In a previous PNNL report, an intermediate-scale test platform (ISTP) for IX treatment at the 200 West P&T facility was developed based on extensive bench-scale research on specific resins under site relevant conditions (Saslow et al. 2024). The report provided calculations to support the design and operational approach for testing these resins at an intermediate scale. The calculations included the following parameters:

- *Resin characteristics*
  - Physiochemical: bead size, affinity, and selectivity
  - Performance: measured total exchange capacity, breakthrough time, and effect of competing anions
- *Groundwater chemistry*
  - Influent chemistry characteristics: pH, oxidation-reduction potential, electrical conductivity, temperature, concentration of contaminant and other native ions
  - Effluent stream regulations: targeted contaminant removal, contaminant concentration thresholds
- *Operational design*
  - Mechanical: column diameter, bed depth, vessel size
  - Hydrological: flow rates necessary to reach linear velocities, residence time
  - Additional processing: filtration, pH adjustment

While the ISTP calculations can be used as basis for evaluating field applicability, these were developed after several years of laboratory evaluations of specific resins under conditions relevant to the 200 West Area. For the candidate carbon-14 resins, there are still many uncertainties to resolve regarding the resin performance and the 100-K Area P&T systems (Figure 7).

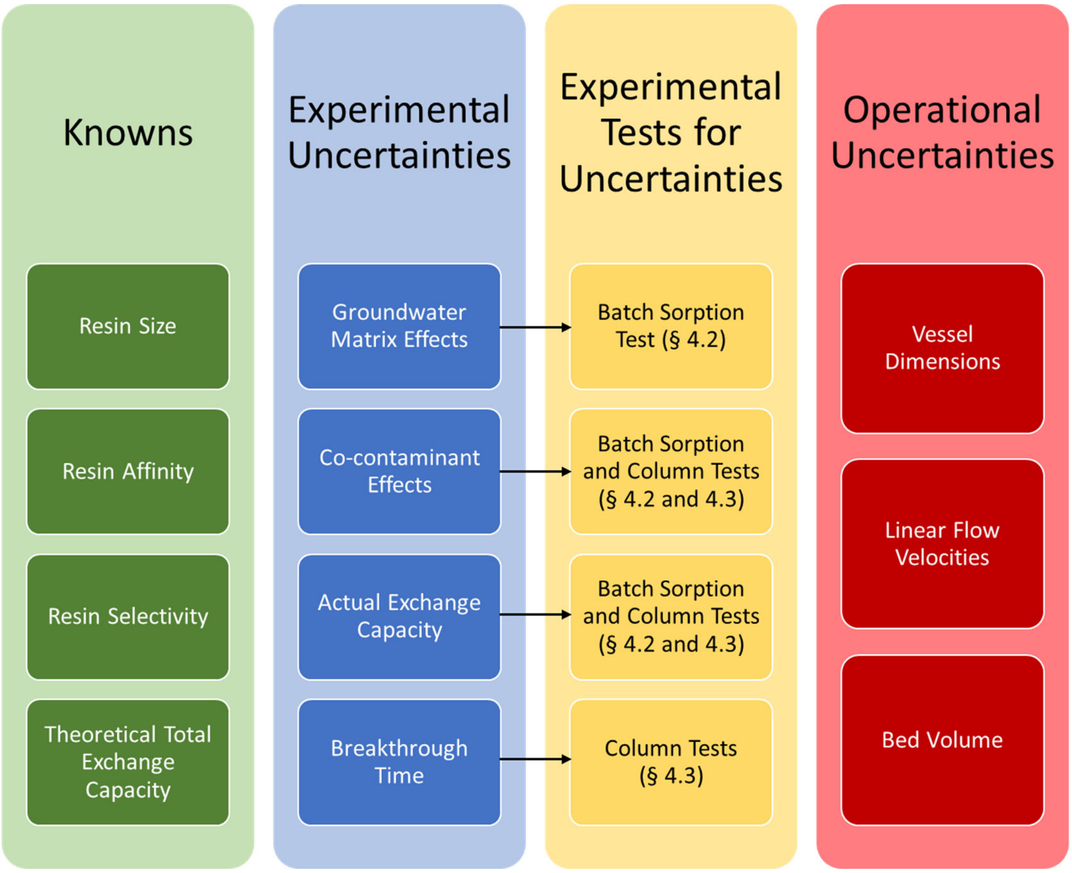

Figure 7. Knowns, uncertainties, and recommended experimental tests to determine the effectiveness of the resin and to optimize conditions for a P&T system. The knowns (in green) include the resin size, affinity, selectivity, and theoretical (maximum) exchange capacity as provided by the manufacturers. The experimental uncertainties (in blue) include resin performance characteristics and groundwater chemistry, which can be addressed by batch sorption and column tests (in yellow). Operational uncertainties (in red) for a P&T system include vessel dimensions, linear flow velocities, and bed volume.

For the resin characteristics, some of the information [e.g., affinity, selectivity, theoretical (maximum) total exchange capacity] can be obtained from the resin manufacturer. However, many of the resin performance characteristics will depend on the groundwater chemistry. The 100-K Area influent groundwater matrix will likely contain native anions (nitrate, sulfate, chloride, etc.) and other contaminants that may compete with the $H^{14}CO_3^-$ and $^{14}CO_3^{2-}$ for exchange sites on the resin. The groundwater pH may also play a role since the distribution of the carbonate species ($H_2CO_3$, $HCO_3^-$, and $CO_3^{2-}$) is pH dependent. Also, adjusting the pH to 7.0 with sulfuric acid (to mimic 100-K P&T operations) will introduce more sulfate anions that can impact performance. These uncertainties can be addressed with batch sorption tests (Section 4.2) to evaluate candidate resin performance under different conditions (e.g., groundwater chemistry, pH) by measuring exchange capacities and identifying any competitive anion effects.

To understand how flow conditions, like those in 100-K Area P&T systems, can further impact resin performance, measured exchange capacity and breakthrough time of carbon-14 can be determined with column tests (Section 4.3). The column tests would also incorporate groundwater matrix and co-contaminant effects identified in the batch tests. If the column tests show effective removal of the carbon-14 by the candidate resin(s) under 100-K Area relevant conditions, the results can inform operational uncertainties such as vessel dimensions, linear flow velocities, and bed volumes required. After addressing the experimental and operational uncertainties, these values can be used as inputs for scale-up calculations based on the ISTP report calculations (Section 4.5). The resulting scale-up parameters would inform the options for incorporating a carbon-14 targeted resin into the KW and KX P&T systems. A disposal pathway for carbon-14 loaded resins can also be determined if the spent resins will not be eligible for disposal at ERDF (Section 4.5).

## 4.2 Batch Sorption Tests

Batch sorption experiments are used to determine reaction kinetics at laboratory scale, which can easily test variables such as concentration, time, solid to liquid ratio, and competitive ion concentration. Adsorption isotherms are an empirical relationship used to quantify the amount of solute (i.e., ion of interest) adsorbed by the substrate of interest (i.e., resin). This graphical representation can then be extrapolated to the amount of solute adsorbed by unit weight of substrate and the amount of solute remaining in a test at equilibrium, which directly correlates to the exchange capacity.

These experiments are carried out in small-scale vessels at static conditions, which allows for many tests to be done simultaneously. While they are not wholly representative of field conditions, they are less labor intensive as they do not require flowing conditions. These experiments are conducted with a known ratio of solid (quantity of resin) to solution [deionized water (as a control) or synthetic Hanford groundwater] and would be spiked with known concentrations of $^{12}HCO_3^-$ and $^{12}CO_3^{2-}$.

The results would provide kinetic information and values for the adsorption isotherm at equilibrium. Then, the amount of resin necessary for $H^{12}CO_3^-$ removal from the system can be calculated. The impact of other ions on resin performance would be evaluated by adding co-mingled co-contaminants and common Hanford groundwater anions to the synthetic groundwater. The results would be used to down-select the commercial resins to a subset that may be best suited for use in the 100-K Area and advanced into column tests.

## 4.3 Column Tests

Column tests expand on batch tests by adding a single-flow directionality (1-D flow) to the experiment. While batch tests are an excellent method for narrowing variables and selecting top performers, the results do not account for fluid dynamics (e.g., flow rates). Column tests enable the determination of loading capacity, lag times, and breakthrough of the constituent of interest (important parameters for evaluating resin performance) by measuring effluent solution concentrations over time. This work could be done with $H^{12}CO_3^-$ and $^{12}CO_3^{2-}$ for initial validation of loading capacity under simulated 100-K Area conditions, followed by tests using $H^{14}CO_3^-$ and $^{14}CO_3^{2-}$ to validate carbon-14 specific uptake. If possible, groundwater retrieved from the carbon-14-affected wells could also be used to account for any differences between the native groundwater and the simulated groundwater recipe. The results from this scale of testing would be used to further down-select the best performing commercial resins.

## 4.4 Intermediate-Scale Development and Pilot Studies

Scale-up is required to evaluate the feasibility of field-scale implementation of a carbon-14 targeted IX resin in the 100-K Area. It also helps address the uncertainties associated with maximizing capacity and operational lifetime of the IX resin under relevant groundwater conditions. Based on the laboratory study results recommended above, the calculations outlined in the 200 West ISTP report can be used as a basis to design an ISTP relevant to the 100-K Area. Once built, the effectiveness of the selected carbon-14 targeted resin(s) can be tested before full-scale implementation and/or modification of the 100-K Area P&T systems.

## 4.5 Waste Form Determination

Evaluating the overall partitioning and effectiveness (e.g., loading capacity) of the resin (Sections 4.1 and 4.4) is also important for determining if the spent resin would be eligible for near-surface disposal. The maximum limit for near-surface disposal of carbon-14 is 8 $Ci/m^3$; however, the International Atomic Energy Agency has reported that spent IX resins for carbon-14 capture in heavy water reactors are often ineligible for near-surface disposal as the spent resin exceeds the limit (IAEA 2004). If the measured loading capacity indicates the resin will not be suitable for disposal in ERDF, a suitable disposal pathway for spent resin loaded with carbon-14 must be identified. Multiple technologies are available for disposal of low-level waste and spent resin (see Section 2.4), but an evaluation of the effectiveness of those technologies would require laboratory-scale testing. The testing would involve waste form production, leach and stability testing, and overall effectiveness of the waste form.

# 5.0 Conclusions

The 100-KR-4 groundwater OU has three P&T systems (KR4, KW, and KX) to remove Cr(VI) using IX treatment with the SIR-700-HP resin. In addition to the Cr(VI) plumes, there are secondary contaminant plumes, including carbon-14. Ongoing remediation efforts in the 100-K Area are focused on the Cr(VI) plumes, where extraction wells are currently placed outside the two carbon-14 plumes. This is because the groundwater from the extraction wells is blended prior to the IX treatment process, where only the Cr(VI) is captured by the SIR-700-HP IX resin. Thus, any carbon-14 co-mingled with the Cr(VI) remains untreated when the groundwater is later injected back into the subsurface.

This ongoing cycling through the network of extraction and injection wells can potentially distribute the carbon-14 from the original source areas to locations where it was not previously present. It also makes it challenging to remediate the Cr(VI) co-mingled with the carbon-14 plumes because the current groundwater concentrations of carbon-14 may cause P&T effluent concentrations to increase above DWSs, which could spur a change to the interim action for 100-K Area P&T operations (Hulstrom 2024). In preparation for future carbon-14 remediation efforts, a new dual-purpose well was drilled in 2022 within the carbon-14 plume in the KW Area that can function as a monitoring well and later be reconfigured as an extraction well for the KW P&T facility (U.S. DOE 2023).

Carbon-14 can exist in the 100-K Area groundwater in various chemical forms, such as $H^{14}CO_3^-$, $^{14}CO_3^{2-}$, and $H_2^{14}CO_3$, depending on the pH of the groundwater. The groundwater in 100-K is approximately pH 8, which indicates that $HCO_3^-$ will be the dominant carbon-14 species. $H^{14}CO_3^-$ can be removed from the groundwater via IX resins. There are various commercially available IX resins designed to capture $HCO_3^-$ and $CO_3^{2-}$. Removal of aqueous carbon-14 by IX resins has been demonstrated at a few field sites, including the Savannah River Site and Sellafield. For disposal of the carbon-14-loaded IX resins, there are many options, including removing the carbon-14 from the resin for separate disposal or leaving the carbon-14 bound to the resin. In the latter case, if there is concern about the carbon-14 mobilizing due to post-disposal resin degradation, the resin can undergo cementation or be stored in HICs. However, the cabon-14 loading capacity of the spent resins will be important for determining eligibility for near-surface disposal.

Three options were conceptualized for implementing carbon-14 targeted IX treatment in the 100-K Area. One option would modify the pre-existing P&T facilities to add an additional IX treatment train before the existing SIR-700-HP IX treatment trains for Cr(VI) removal. A second option would swap out the SIR-700-HP resin in some of the parallel resin trains with a new IX resin for carbon-14 treatment, but this would be dependent on the impacts of the groundwater pH adjustment and maintaining compliance with Cr(VI) cleanup regulations. The third option would construct a mobile IX treatment skid for wellhead treatment of carbon-14-affected wells. This would allow for greater flexibility and mobility with targeted carbon-14 treatment and avoid modifying the existing P&T systems. However, before implementation decisions can be made, there are many uncertainties to resolve regarding the carbon-14 removal performance under conditions relevant to the 100-K Area and operational parameters for the KW and KX P&T systems. To address these uncertainties, a series of laboratory experiments are recommended to provide a technical basis for the decision-making process.

Based on this initial screening evaluation, treatment for carbon-14 in groundwater with commercially available IX resins in a P&T remedy appears promising. To support remedial design and implementation decision for the 100-K Area, additional information is needed to resolve uncertainties and evaluate site-specific conditions.

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# Appendix A – Hanford 100-K Area Background Information

## A.1 Overview

The Hanford Site is a 1,450-km$^2$ (560-mi$^2$) federal facility located in Benton County in southeastern Washington State along the Columbia River. It was established as part of the Manhattan Project during World War II in 1943 to produce the plutonium used in the Trinity Test and the atomic bomb dropped on Nagasaki, Japan, in 1945 (U.S. DOE 2024; Gephart 2010). Plutonium production continued through the Cold War era until 1987, when operations transitioned to an environmental cleanup focus (U.S. DOE 2024). The ongoing remediation efforts are governed by the Tri-Party Agreement to bring the Hanford Site into compliance with the remedial action provisions of the Comprehensive Environmental Response Compensation and Liability Act and with the Resource Conservation and Recovery Act treatment (U.S. DOE 2024).

The Hanford Site is divided into alphanumerically designated areas. The 100 Area, which encompasses approximately 68 km$^2$ (26 mi$^2$), borders the southern shore of the Columbia River and is the site of nine retired plutonium-production reactors (U.S. DOE 1992). The 100-K Area is 9 km$^2$ (3.5 mi$^2$) and consists of two retired reactors, K East (KE) and K West (KW), as well as basins that provided temporary storage of irradiated fuel discharged prior to shipment to processing facilities (U.S. DOE 1992). The 100-K Area encompasses the operable units (OUs) for the KE Reactor and KW Reactor and includes the 100-KR-1 and 100-KR-2 Source OUs and the 100-KR-4 groundwater OU (U.S. EPA 1999). Existing land use in the 100 Area includes facilities support, waste management, and undeveloped land (U.S. DOE 2023).

Construction of the twin 100-K Area reactors began in 1952 and operation began in 1955, with the primary mission being plutonium production for national defense (Gephart 2010). This continued until 1971, when the plutonium production was eventually phased out and the reactors decommissioned. The reactors had a secondary operational phase from 1975 until 2007, when the reactor fuel storage basins were repurposed to store spent fuel from the N Reactor.

During plutonium production, various radionuclides were produced, with a wide range of half-lives. The short-lived radionuclides (e.g., manganese-54, iodine-131, and zinc-65) were primarily a concern during operation as they were discharged to the river (U.S. EPA 1999). During KE and KW reactor operations, the short-lived radioisotopes represented more than 98% of the radioactivity in the reactor effluents (Cannon et al. 2002). These very short-lived radionuclides have since decayed to concentrations below regulatory limits. Long-lived radioisotopes (e.g., cobalt-60, strontium-90, cesium-137, europium-152, carbon-14, and tritium) have a half-life greater than 3 years and are the radioactive primary contaminants of concern for Hanford restoration activities, including those in the 100-K Area (Cannon et al. 2002).

## A.2 Geology

The 100-K Area is located on the southern bank of the Columbia River, downstream from 100-BC and upstream from other Hanford Site reactor areas. Topographically, 100-K is relatively flat inland from the Columbia River with the steepest slopes at the riverbank. The water table ranges from the riverbank, 0 m (0 ft) to 37 m (120 ft) inland (U.S. EPA 1999). The water table, mimicking the topography, is also mostly flat; however, there is variation due to ongoing P&T activities. Major geologic units from shallowest to deepest depths are the Holocene sediments, the Hanford formation, the Ringold Formation, and the Columbia River Basalt Group (Hartman 2011). Figure A.1 shows a stratigraphic column.

The Hanford formation is an informal name used to describe these Pleistocene-age cataclysmic flood deposits. The vadose zone ranges in depth from 0 m (0 ft) at the riverbank to 32 m (105 ft) inland and mimics the topography. The vadose zone includes superficial soil, Hanford formation sediments, and Ringold Formation Unit E sediments. The dominant unit in the vadose zone is the Hanford formation, which consists predominantly of very poorly to moderated sorted unconsolidated sediments, from boulder-sized gravel to sand, silty sand, and silt of a primarily basaltic origin (Lindsey 1992).

The Ringold Formation Unit E is a gravel-dominated unit consisting primarily of fine-to-course gravels and sands, though there are locally interbed sand-dominated areas (Reidel et al. 1998). This unit forms the unconfined aquifer in 100-K Area. Aquifer testing suggests that the horizontal hydraulic conductivity of the Hanford formation is generally three times greater than the Ringold Formation Unit E, although variable cementation can influence the transmissivity in both units. Horizontal hydraulic conductivities of the Ringold Formation generally range from ~$10^{-5}$ to $10^{-4}$ m/s (3 to 28 ft/d) (U.S. DOE 2011). There is limited recharge for the groundwater except for the Columbia River influence because there are no other natural bodies of water in the area and the climate is generally hot and arid with limited precipitation (Stone et al. 1983). Artificial anthropogenic recharge may result from leakages from facilities with water supplies.

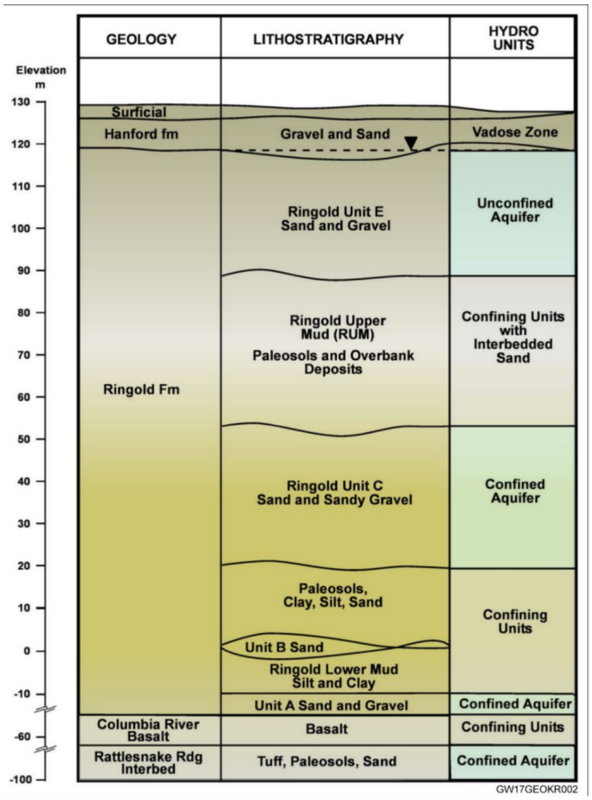

Figure A.1. Stratigraphic view of the 100-K Area, separated into geologic units, the lithostratigraphy, and hydro units (from U.S. DOE 2023).

## A.3 Current Groundwater Conditions

The groundwater in the 100-K Area was contaminated from the KE and KW reactor facilities during their period of operation (1955-1971). By the end of 2022, 76% of the 100-K waste sites had either been successfully remediated or did not require additional remediation (U.S. DOE 2023; U.S. EPA 1999, 1996). The remaining 24% are undergoing continued remediation in accordance with current U.S. Environmental Protection Agency records of decision (RODs) (U.S. EPA 1999, 1996). Table 1 in the main report provides a summary of the groundwater contamination. Contaminants in the 100-K unconfined aquifer include chromium (total and hexavalent chromium [Cr(VI)]), tritium, nitrate, strontium-90, trichloroethylene (TCE), and carbon-14 (U.S. DOE 2023). Carbon-14 contamination plumes in the 100-K Area (using data from 2022) are shown in Figure 1 of the main report (U.S. DOE 2023). Chromium is the primary contaminant of concern in the 100-K Area, while carbon-14, nitrate, strontium-90, TCE, and tritium are secondary contaminants of concern.

Chromium contamination at Hanford is undergoing remediation via groundwater P&T facilities. Most of the chromium found on the Hanford Site exists as Cr(VI) (Thornton et al. 1995), and the interim remedial target for Cr(VI) in the 100-KR groundwater OU is 20 µg/L, with the assumption the groundwater mixes with the river water to meet the 10 µg/L surface water standard (U.S. DOE 2023; Hulstrom 2024). There are generally three Cr(VI) plumes, which resulted from two different historical releases (either spills, leaks, or limited intentional discharges) of concentrated sodium dichromate solutions or spent reactor cooling water that was discharged to the 116-K-1 Crib and 116-K-2 Trench (Thornton et al. 1995).

Major historical sources of tritium in the 100-K Area include releases of reactor gas dryer condensate (concentrations up to $10 \times 10^{10}$ pCi/L; Peterson et al. 2002), fuel storage basin water (up to $10 \times 10^{9}$ pCi/L; Johnson 1995), contaminated reactor cooling water (Johnson 1995), and disposal of solid waste (up to 13,400 pCi/g; Farris and Sulloway 2008). The extent of the tritium plume has decreased over time, and much of the tritium will continue to undergo monitored natural attenuation without further remediation (Farris and Sulloway 2008).

Nitrate plumes decreased significantly between 2003 and 2015 due to ongoing remediation, including the P&T operations; however, the concentrations of many wells continue to exceed the 45 mg/L drinking water standard (DWS) (Johnson 2016). The nitrate plumes in 100-KR are linked to the discharge of reactor gas dryer condensate ammonia that has oxidized over time, while in other areas the plumes are the result of discharges of nitric acid (Johnson 2016).

Strontium-90 is a fission product generated during regular nuclear reactor operation. It was historically released during fuel failure events, resulting in contamination of reactor cooling water. The contaminated cooling water was released to the 116-K-2 Trench under off-normal conditions and to the reactor fuel storage basins during discharge of irradiated fuel from the reactors (Dorian and Richards 1978). Contaminated cooling water was held in the 107KE or 107KW retention basins (which are known to have leaked) and was subsequently discharged to the 116-K-2 Trench.

The highest Sr-90 concentrations in groundwater are linked to drainage systems (i.e., 116-KW-2 and 116-KE-3 cribs and reverse wells), and leaks (e.g., UPR-100-K-1). Concentrations of Sr-90 in aquifer tube 22-M suggest a downgradient migration toward the river from the distal end of the trench (U.S. DOE 2023). Sr-90 plumes in the 100-KR-4 area will naturally decay below the DWS in 200 to 300 years (U.S. DOE 2023). Other technologies have been unable to significantly reduce the cleanup period. Long-term monitoring will be necessary to confirm that decay occurs as expected and no unexpected migration occurs.

TCE is often used as a solvent and degreaser during equipment maintenance and is known to migrate into sanitary systems and piping. This is the likeliest source for TCE in 100-K as no specific release points have been identified. The proposed cleanup standard for TCE is 4 µg/L. Two pockets within the larger TCE plume exceed 5 µg/L; however, the TCE present in the treated groundwater being injected into the aquifer from the KW P&T system is below the cleanup standard (U.S. DOE 2023).

Carbon-14 is discussed in depth in Section 1.3 of the main report.

## A.4 Current Remediation Efforts in the 100-K Area

Pump and treat (P&T) operations are ongoing in accordance with the interim action ROD in various locations across the Hanford Site (U.S. DOE 2023; U.S. EPA 1996). There are multiple P&T systems for the removal of Cr(VI) and total chromium from the groundwater, as outlined in Table A.1 (U.S. DOE 2022, 2023).

Table A.1. Summary of ongoing chromium P&T activities.

| P&T Name | Location and Startup Year | Cr(VI) Plume Regions | Avg Influent Cr(VI) (µg/L) | Avg Effluent Cr(VI) (µg/L) | Secondary Contaminants | Avg Effluent C-14 (pCi/L) |
|---|---|---|---|---|---|---|
| KR4 | Downgradient from 116-K-2 Trench; 1997 | K North; K-N Boundary | 4.7 | < 2 | C-14, $NO_3^-$, Sr-90, H-3 | < 32.8 |
| KW | Near KW Reactor; 2007 | K West | 38 | < 2 | C-14, $NO_3^-$, Sr-90, H-3, TCE | 237.8 |
| KX | Between 116-K-2 Trench and N Reactor; 2009 | K East; K North; K-N Boundary | 11.6 | < 2 | C-14, $NO_3^-$, Sr-90, H-3, TCE | 50 |

Table is a summary of information available in (U.S. DOE 2022, 2023).
Key: C-14: carbon-14; $NO_3^-$: nitrate; Sr-90: strontium-90; H-3: tritium; TCE: trichloroethene

Combined, the three P&T systems located in the 100-K Area can treat up to 5,910 L/min (1,560 gal/min) of groundwater, which is then returned to the aquifer through a network of injection wells (U.S. DOE 2023). During 2022, the three 100-K P&T facilities treated a combined 1,928 million L (509 million gal) of groundwater and removed 17.7 kg Cr(VI). Since the startup of these three P&T facilities (1997-2022), 35,486 million L (9,375 million gal) of groundwater has been treated and 1,049 kg Cr(VI) has been removed (U.S. DOE 2023).

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