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Analysis of Uranium Ion Exchange Resin from the 200 West Pump-and-Treat Facility

September 2018

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U.S. DEPARTMENT OF
ENERGY

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

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Executive Summary

The 200 West Area Pump-and-Treat (P&T) Facility at the Hanford Site is a multifunctional groundwater treatment facility consisting of unit processes to remove radionuclides such as uranium (U) and technetium (Tc-99) as well as other inorganic (nitrate and hexavalent chromium), and organic (carbon tetrachloride and trichloroethene) contaminants. The RAD building of the P&T Facility removes U and Tc-99 using ion exchange chromatography. In 2016, the Purolite A530E resin used for the Tc-99 removal was replaced and the spent resin was analyzed. In addition to Tc-99, the Purolite A530E resin also retained I-129 and Co-60; however, the resin loading was dominated by common groundwater constituents such as calcium, iron, silicon, and sulfate.[1]

In 2017, the lead column for U removal was replaced, providing an opportunity for a similar analysis of the spent DOWEX 21K resin and identifying if common groundwater constituents are interfering with U adsorption. Results demonstrated a high U loading at 18,500 µg/g resin (± 10%), which equates to about 12 – 24% of the theoretical capacity of the resin (based on the presence of U(VI) species with negative charges on the resin of 2 and 4). The second and third most abundant anions retained by the resin were sulfate at 27,500 µg/g resin (± 11%) and nitrate at 17,280 (± 13%), which accounted for about 21.5% of the resin capacity. Overall, the combined U(VI), sulfate, and nitrate loading accounted for approximately 67% of the resin capacity. Only insignificant quantities of other anionic species were retained on the resin. This indicates that the spent DOWEX 21K resin was near capacity and approached breakthrough.

Among common groundwater constituents, Ca and Fe appeared at high concentrations of 11,000 and 3,000 µg/g resin, respectively. Both are known foulants of ion exchange resins and reduce their overall performance. No appreciable quantities of other elements were found on the resin.

Among radioactive contaminants, a significant quantity of I-129 at 0.11 µg/g resin (± 9%) was retained on the resin while the concentration of the non-radioactive I-127 was 45 µg/g resin (± 9%), resulting in their concentration ratio of about 400. The retention of I-129 and I-127 isotopes by the spent P&T Purolite A530E resin used for the Tc-99 treatment[1] was about 0.062 and 51 µg/g resin, respectively, corresponding to their concentration ratio of about 1000. Comparison of these results indicates that the feed water treated by the U ion exchange unit contained about 2.5 times greater concentration of I-129 than the feed water treated by the Tc-99 ion exchange unit. No Tc-99 was detected on the resin, confirming the lack of the DOWEX 21K resin affinity for the pertechnetate anion.

The redox and chemical speciation of U retained by the DOWEX 21K resin was also examined. Structural characterization techniques including X-ray absorption spectroscopy and X-ray photoelectron spectroscopy provided strong evidence for the presence of U in an oxidation state of +6 on the resin; so that uranyl (UO_2^{2+}) complexes are the dominant U species occurring on the P&T DOWEX 21K resin. The chemical composition of these species could be attributed to the negatively charged sulfate and carbonate complexes such as $UO_2(SO_4)_2^{2-}$, mixed ligand complexes such as $UO_2(CO_3)(SO_4)^{2-}$, $UO_2(CO_3)_n^{2-n}$ (where n = 2, 3), and $CaUO_2(CO_3)_3^{2-}$. Uranyl complexes were also found to vary by pH, which means that perturbations in the conditions of the influent groundwater to the P&T Facility may impact the DOWEX 21K resin efficiency.

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[1] Levitskaia TG, Campbell EL, Chatterjee SD, Hall GB. 2017. *Analysis of Technetium Ion Exchange Resin from the 200 West Pump-and-Treat Facility.* PNNL-26933; RPT-DVZ-AFRI-049, Rev. 0, Pacific Northwest National Laboratory, Richland, WA.

In addition to the U resin analysis, an analytical method for the selective and rapid determination of ferrocyanide on the DOWEX 21K resin was developed to better understand potential impacts of cyanide on the treatment system. Ferrocyanide ($Fe(CN)_6^{4-}$) is strongly retained by the DOWEX 21K resin. A protocol for the sequential stripping of the loaded DOWEX 21K resin is proposed where U(VI) is selectively stripped, followed by a strip to elute $Fe(CN)_6^{4-}$. This eliminates U(VI) spectral interference for the UV-vis measurement of the oxidized $Fe(CN)_6^{3-}$ in the solution. Further testing is warranted to validate the analytical method for measuring ferrocyanide $Fe(CN)_6^{4-}$ retention on the DOWEX 21K resin.

Acknowledgments

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Acronyms and Abbreviations

APS	Advanced Photon Source
CAWSRP	Conducting Analytical Work in Support of Regulatory Programs
CCV	continuing calibration verification
CHPRC	CH2M Hill Plateau Remediation Company
DI	deionized
DOE	U.S. Department of Energy
EQL	estimated quantitation limit
ESL	Environmental Sciences Laboratory
EXAFS	extended X-ray absorption fine structure
FIO	for information only
FTIR	Fourier transform infrared spectroscopy
GEA	gamma energy analysis
GW	groundwater
HASQARD	Hanford Analytical Services Quality Requirements Document
HPGe	high-purity germanium
IC	ion chromatography
ICP-MS	inductively coupled plasma mass spectroscopy
ICP-OES	Inductively coupled plasma optical emission spectroscopy
ICV	initial calibration verification
IX	ion exchange
LSC	liquid scintillation counting
NIST	National Institute of Standards and Technology
NQAP	Nuclear Quality Assurance Program
P&T	pump-and-treat
PNNL	Pacific Northwest National Laboratory
PTFE	polytetrafluoroethylene
QA	quality assurance
QC	quality control
RSD	relative standard deviation
SEM	scanning electron microscopy
UV-vis	ultraviolet-visible
XANES	X-ray absorption near edge spectroscopy
XAS	X-ray absorption spectroscopy
XFS	X-ray fluorescence spectroscopy
XPS	X-ray photoelectron spectroscopy

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1.0 Introduction

1.1 Background

During World War II and the Cold War era, uranium was used as fuel in nine nuclear reactors along the Columbia River corridor in southeastern Washington State to generate weapons-grade plutonium for the production of the first nuclear weapons. During this time, the 200 Areas in the Central Plateau of the Hanford Site housed facilities for irradiated fuel reprocessing (REDOX plant) and uranium recovery (U Plant) along with associated waste management activities. (DOE-RL 2017a). Plutonium processing and separation generated a significant amount of chemically hazardous and radioactive waste that was discharged to retention ponds, cribs, and ditches, as well as underground storage tanks for temporary disposal in the 200 Areas (DOE-RL 2017a). Migration and percolation of this waste into the soil resulted in contamination of the deep vadose zone and groundwater (Wellman et al. 2011).

Groundwater contamination beneath the 200 East and West Areas is challenging due to the complex mixture of metals, radionuclides, inorganic, and organic contaminants. In 1989, the U.S. Department of Energy (DOE) entered the Tri-Party Agreement with the U.S. Environmental Protection Agency (EPA) and Washington State Department of Ecology to collectively address groundwater and vadose zone contamination for remediation on the Hanford Site. This agreement aims to (1) prevent further contamination of the Columbia River and groundwater, (2) develop a remediation/cleanup plan, and (3) restore groundwater to below the EPA drinking level limits (DOE-RL 2017a). Towards this effort, CH2M Hill Plateau Remediation Company (CHPRC) designed a 2500-gpm Pump-And-Treat (P&T) Facility, concurrent with an extraction and injection system, to capture and treat contaminated groundwater in the 200 West Area. This facility utilizes a combination of ion exchange (IX), granulated activated carbon, and biological treatment pathways to treat contaminants of concern, including technetium-99 (Tc-99), iodine-129 (I-129), uranium (U), tritium, carbon tetrachloride, trichloroethene, chromium (Cr, total and hexavalent), and nitrate (DOE-RL 2017b).

Operation of the 200 West P&T Facility was initiated in August of 2012, with uranium treatment capability commissioned in September 2015. The RAD building of the P&T Facility removes Tc-99 and U using IX chromatography. Contaminated groundwater from the uranium plume is pumped to the 200 West P&T Facility through a series of above ground pipes, then combined in an influent tank and pumped through particulate filters to remove suspended particles. The filtered groundwater is passed through an IX treatment train of three DOWEX 21K resin columns in series, prior to pertechnetate removal by two parallel IX Purolite A530E columns to achieve clean-up levels of 30 µg/L and 900 pCi/L for uranium and Tc-99, respectively (DOE-RL 2017b). The effluent then undergoes follow-on treatment to remove other inorganic (nitrate and hexavalent chromium), and organic (carbon tetrachloride and trichloroethene) contaminants.

In fiscal year 2017, Pacific Northwest National Laboratory (PNNL) evaluated samples of the P&T spent resin Purolite A530E utilized for the uptake of Tc-99 (Levitskaia et al. 2017). Overall, results from these analyses showed that loading of the spent P&T Purolite A530E resin with Tc-99 was small and utilized approximately 0.034% of the resin theoretical capacity. Results also demonstrated that an appreciable quantity of iodine was also retained on the resin. The concentrations of I-127 and I-129 on the resin were found to be about 2.5 times greater and 350 times smaller than that of Tc-99, respectively. This means that a significant amount of non-radioactive iodine was being retained on the resin, and radioactive iodine to a much lesser extent.

After operating for nearly 2 years, the lead column used for uranium removal was removed from service. Three subsamples of the spent P&T resin were analyzed after the P&T system treated 5 million gallons of contaminated groundwater and removed nearly 20 kg of uranium. Results described in this report include quantification of uranium and co-contaminants (radionuclides, metals, inorganic anions, total cyanide) retained by the DOWEX 21K P&T resin through a combination of destructive and nondestructive analytical techniques. Relevant information on uranium sorption, selective stripping of the P&T resin, and sulfate affinity toward DOWEX 21K is also discussed.

1.2 DOWEX 21K Ion Exchange Resin

Commercial DOWEX 21K IX resin, suited for mineral processing and groundwater remediation, was implemented in the 200 West P&T Facility to remove uranium from contaminated groundwater plumes. DOWEX 21K is a strong-base anion exchange resin with quaternary amine exchange sites on a polystyrene/divinyl-benzene framework. The high theoretical loading capacity of 1.4 equivalents/L allows processing of very large volumes of groundwater without replacement.

The performance of the DOWEX 21K resin for uranium sorption was previously tested using source water from the Hanford Site well 299-W19-36, and high K_d values were observed at alkaline pH, albeit the sorption was dependent on the nitrate concentration (Mattigod et al. 2010). This resin was also demonstrated to selectively sorb gold/cyanide complexes from its aqueous mixture with the lead/cyanide from industrial waste water (Ok and Jeon 2014).

2.0 Testing Objectives and Methodology

The 200 West P&T system treats a variety of waste streams under different conditions. To support the evaluation of uranium resin treatment, operational conditions, and performance, knowledge of resin capacity and contaminant retention is needed for uranium. In addition, information about the fate of cyanide is also needed to better understand and manage the fate of cyanide in the 200 East waste streams treated at the facility. This information can in part be obtained via quantitative characterization of the representative samples from the homogenized, uranium-loaded IX DOWEX 21K lead column from the 200 Area P&T Facility.

The three primary objectives of this work are as follows:

1. Determine effective loading of U and other contaminants on the spent DOWEX 21K resin.

   This task provides quantitative information of the overall retention of U and other contaminants on the Dowex 21K resin. The resin samples were first subjected to the direct nondestructive evaluation by gamma and low-energy photon spectroscopy to determine the presence on the resin of such radioisotopes as Co-60, Tc-99, I-129, and U-235/238. The second activity involved wet oxidation of the spent resin and determination of the U and other metals in the leachate by inductively coupled plasma optical emission spectroscopy (ICP-OES) / mass spectroscopy (MS) methods. In addition, the spent resin was eluted following literature and newly developed protocols, and the eluate was analyzed for U, other metals, anion, and total cyanide.

2. Determine redox and chemical speciation of U retained by the resin and evaluate the impact of feed composition on the retention of U by the resin.

   This task provided information on the nature of the uranium complexes on the spent resin so that the binding process can be identified and used to evaluate the impact of water chemistry variation on uranium retention. The objective was to determine the effects of pH and concentrations of sulfate and other constituents in the feed on U retention.

   Uranium speciation on the resin was determined using structural characterization techniques, including (1) X-ray absorption fine structure (XAFS) spectroscopy to determine the molecular coordination environment and U oxidation state; (2) X-ray photoelectron spectroscopy (XPS), yielding information on U oxidation state and number of the sorbed U species; and (3) optical spectroscopy (Raman and Fourier transform infrared spectroscopy [FTIR]) to obtain information on the nature of the ligands coordinated to U and identity of the sorbed complexes.

   Pristine Dowex 21K resin was used as a control sample to obtain K_d values for U complexes. In this effort, aqueous U speciation was determined and served as a guide for designing the batch experiments with the pristine Dowex 21K resin. Concentrations of the U species in the contacting solutions before and after equilibration with the resin were measured by inductively coupled plasma mass spectrometry (ICP-MS) and the equilibrium K_d values for each U species were determined. This allowed determination of U sorption isotherms.

   To determine the effect of the feed composition, uranium K_d values were determined using a range of feeds containing nitrate, sulfate, and other constituents of the contaminated groundwater at variable pH. Once conditions impairing U uptake by the pristine resin were identified, partially loaded spent resin obtained from the 200 W P&T system was challenged by the feed containing constituents identified to have the most pronounced impact on the U retention at variable pH.

3. Develop a method for quantification of ferrocyanide retained on the resin.

The objective of this task was to determine the partitioning of ferrocyanide $Fe(CN_6)^{4-}$ to the Dowex 21K resin. The main outcome is the development of a new analytical method to measure ferrocyanide loading on an IX resin. Once the method is demonstrated using loaded pristine Dowex 21K resin, it will be validated using actual spent Dowex 21K resin obtained from the 200 W P&T Facility.

The method development involves two main activities. First, an analytical method was developed for the rapid determination of ferrocyanide in solution. It is based on the initial oxidation of ferrocyanide $Fe(CN_6)^{4-}$ to ferricyanide $Fe(CN_6)^{3-}$ followed by the measurement of the ferricyanide aqueous concentrations before and after oxidation using ultraviolet-visible (UV-vis) absorbance. The second activity was focused on measuring ferrocyanide retention on the pristine Dowex 21K resin and following a protocol for its quantitative and selective stripping.

3.0 Methods

Resin samples for the laboratory analyses were collected by CHPRC during a variety of operations at the 200 West P&T Facility. Sample handling upon arrival at PNNL facilities is described in Section 3.1. The laboratory analysis methods used for the resin are presented in Section 3.2.

3.1 Resin Sample Handling

3.1.1 Spent 200 West P&T DOWEX™ 21K 16/20 Resin

The specification sheet for the DOWEX 21K 16/20 resin can be found in **Error! Reference source not found.**. Three homogenized resin samples cataloged as B3FM14, B3FM23, and B3FM32 were selected for analyses and obtained at PNNL in coordination with CHPRC personnel responsible for operation of the P&T Facility. Resin was sampled into amber glass bottles. For preservation at PNNL, it was tightly capped and refrigerated. Visual inspection indicated that the resin bead size within the samples varied, with predominantly dark brown resin beads with occasional white beads intermixed. There was no visible difference among the three resin samples received.

3.1.2 Loading Pristine DOWEX™ 21K XLT with Uranium

Dow manufacturer discontinued DOWEX 21K 16/20 resin and replaced it with DOWEX 21K XLT resin characterized by the same functionality but uniformly sized beads resulting in the improved IX process, stability, and hydrolytic performance (see Specification Sheet in Appendix B). Pristine Dowex 21K XLT procured from the manufacturer (Dow Chemical Company) was pre-conditioned with 1 M HCl to convert the resin to the chloride form. The resin was then rinsed with deionized (DI) water until neutral pH was achieved. The conditioned resin was used in the following tests:

- As a control in wet oxidation tests to understand chemical constituents present from resin manufacturing steps or inherent to the styrene/divinyl-benzene resin framework
- Determination of U sorption isotherms
- Development of the resin stripping protocols
- Development of the cyanide analytical method

3.2 Resin Analysis Methods

3.2.1 Nondestructive Methods

3.2.1.1 X-Ray Absorption Spectroscopy (XAS)

To examine the effect of the minor constituents of groundwater on uranium coordination on the resin, a full (or "complex") groundwater simulant was developed based on results from the 200-ZP-1 and 200-UP-1 Operable Unit Pump-and-Treat Operations (DOE-RL 2017b) and Hanford Site Groundwater Monitoring Report (DOE-RL 2017a), as shown in Table 1. The composition was balanced with respect to total concentration of ionic species, resulting in concentrations of some constituents that vary slightly from the average value of the groundwater composition. Stock solutions of components with concentrations of less than ca. 0.5 mM were prepared, and subsequent dilutions were made in order to achieve the very low concentrations of some of the constituents. The simulant was allowed to settle for at least 1 week before use, during which time no precipitation was observed.

Table 1. Complex Groundwater Simulant Composition.

Constituent	Conc. in Simulant (mmol/L)	Average Conc. in Groundwater (mmol/L)
Ca	2.0E+00	2.0E+00
Cl	4.2E+00	6.9E-01
Na	3.1E+00	1.7E+00
NO_3^-	8.1E-01	8.3E-01
Cl	5.0E-01	9.8E-01
Mg	9.8E-01	8.4E-01
SO_4^{2-}	9.8E-01	1.7E-01
K	1.7E-01	2.0E+00
CO_3^{2-}	1.8E+00	--
NO_2^-	6.1E-03	6.1E-03
F	1.8E-02	1.8E-02
B	3.0E-03	3.0E-03
Br	2.9E-03	2.9E-03
Fe	1.2E-03	1.2E-03
Al	1.1E-03	1.1E-03
Mo	5.6E-05	5.6E-05
Cu	5.5E-05	1.4E-05
Se	5.1E-05	5.5E-05
Ni	2.3E-05	5.1E-05
Mn	4.5E-06	2.3E-05
Co	1.8E-04	4.5E-06
Cr(VI)	1.8E-04	1.8E-04
Cr(III)	5.4E-05	2.3E-04
CN (total)	4.4E-03	4.6E-03

Samples were prepared by loading uranyl onto Dowex 21K XLT resin from different matrices as displayed in Table 2. The conditioned resin was pre-equilibrated, in a batch-contact manner with ground water simulant with composition in Table 4. This was done four sequential times where the supernatant was removed and replaced after each contact to equilibrate the resin with anions present in the groundwater simulant.

In addition, the conditioned Dowex 21K XLT (chloride form) was subjected to equilibration with the full (*complex*) groundwater simulant (Table 1).

Batch contacts (24-hour equilibration time) with each pre-equilibrated resin were performed, contacting with groundwater simulant (simple or complex) containing 25 µM uranyl nitrate at pH 8. For each sample, three subsequent batch contacts were performed to maximally load the resin with uranium.

Additionally, a sample of resin in the chloride form was contacted with a solution of 25 µM uranyl nitrate in 50 mM $NaHCO_3$ solution at pH 8. A summary of these samples prepared by batch contact for extended X-ray absorption fine structure (EXAFS) analysis is shown in Table 2.

Table 2. Summary of Control Samples Prepared for EXAFS Experiment.

Resin Form	Pre-equilibration Solution	Contacting Solution
Cl^-	NA	P&T feed influent
Cl^-	Groundwater (GW) simulant	25 µM uranyl nitrate in GW simulant
Cl^-	Complex GW simulant	25 µM uranyl nitrate in *complex* GW simulant
Cl^-	50 mM $NaHCO_3$	25 µM uranyl nitrate in 50 mM $NaHCO_3$

Samples of resin were prepared for XAS by grinding in an agate mortar and pestle to a fine powder, after which they were loaded into a teflon sample holder and encased by Kapton tape. This was further encased by a layer of mylar tape or mylar film, and then by a layer of Kapton film. The uranium L_3 edge at 17.1 keV was probed. Data reduction and analysis was performed in the Demeter package (Ravel and Newville 2005). Samples of resins B3FM14, B3FM23, and B3FM32 were analyzed by EXAFS spectroscopy at beamline 12-BM-B at the Advanced Photon Source (APS). A sample of resin B3FM14 and uranium-loaded resins were analyzed by EXAFS at beamline 20-ID-B at the APS. Spectra were collected in either transmission or fluorescence mode. Energy alignment and calibration was performed using the K edge of a Zr foil. Four uranium compounds, obtained from IBI Labs (Boca Raton, FL) were used as standards: uranyl carbonate, UO_2CO_3, uranyl sulfate trihydrate, $UO_2SO_4{\cdot}3H_2O$, potassium uranyl sulfate, $K_2UO_2(SO_4)_2{\cdot}3H_2O$, and uranium sulfate, $U(SO_4)_2{\cdot}8H_2O$.

3.2.1.2 Gamma Energy Analysis (GEA) and Low-Energy Photon Spectroscopy

Subsamples of resin beads, B3FM14, B3FM23, and B3FM32 were washed several times with DI water to remove any remaining mother liquor. Nominally 10 g of resin and 9 g of DI water were massed into a 125 mL, straight-side, wide-mouth plastic Nalgene jar (stock #2116-125). The sample geometry was selected to provide adequate activity in a flat or pancake geometry to maximize the detection and quantification of low energy X-rays with minimal self-attenuation. A National Institute of Standards and Technology (NIST)-traceable mixed isotope standard (mixed γ, Eckert & Ziegler, source no. 1948-17) and I-129 standard were prepared in the same geometry for detector calibration using conditioned DOWEX 21K XLT resin. The masses of resin and DI water for the samples, blank, and GEA standards are listed in Table 3.

Table 3. Mass of Resin and DI Water Used for GEA Analysis on Spent 200 West P&T Resins.

Sample ID	Resin Mass (g)	Water Mass (g)	Total Mass (g)
B3FM14	10.0175	9.0822	19.0997
B3FM23	9.3794	9.0357	18.4151
B3FM32	7.4851	9.0657	16.5508
Blank	10.0028	8.9626	18.9654
Mixed γ standard	10.0027	9	19
I-129 standard	10.0019	9	19

GEA was performed using a Canberra model GC100 p-type coaxial HPGE detector with 100% relative efficiency. The detector was controlled with a Canberra Lynx digital signal processor (DSP) and data acquired and analyzed using the Canberra Genie 2000 gamma spectroscopy software suite (V3.4.1). A calibration was prepared by quantitative mass transfer of a NIST-traceable mixed isotope standard to a Nalgene container with similar resin and water content. The efficiency calibration was from 46 to 1836 keV. While the samples were low in total activity, they were counted at a position 6.6 cm from the detector face to eliminate the potential of cascade and random summing. Samples were counted for approximately 1 day. A blank background sample prepared similar to the calibration standard and counted for 2 days and used for background subtraction on the resin samples.

Additionally, the samples were counted on a Canberra model GL2015R, planar low-energy germanium (LEGe) detector with a thin carbon composite window allowing transmission of photons down to approximately 6 keV. The thin detector provides for high resolution at low energy while minimizing noise and background from higher energy gamma rays. The active detector area was 2000 mm^2, with an active diameter of 50.5 mm. Like the GEA, the detector was paired with a Canberra Lynx DSP with system control and data acquisition using G2K. The same GEA NIST calibration standard was used to provide a "high-energy" calibration while an I-129 calibration standard was prepared to specifically quantify I-129. Samples were counted on the face of detector. Count times ranged from slightly over 1 day (89,688 s) for B3FM14 sample to 2.06 days for the B2FM32 sample.

3.2.1.3 X-Ray Photoelectron Spectroscopy (XPS)

Photoelectron spectra were recorded using a Kratos AXIS Ultra DLD system equipped with a monochromatic Al Kα X-ray source (1486.7 eV) and a hemispherical analyzer. The resin samples were ground into a powdery paste using mortar and pestle, and subsequently mounted using double-sided Scotch tape attached to a silicon substrate. The instrument work function was calibrated to give a binding energy of 83.96 ± 0.1 eV for the Au $4f_{7/2}$ line for metallic gold and the spectrometer dispersion was adjusted to give a binding energy of 932.62 ± 0.1 eV for the Cu $2p_{3/2}$ line of metallic copper. High-resolution analyses were carried out with an analysis area of 300 µm × 700 µm using a pass energy of 40 eV with a step size of 0.1 eV. Surface charge was eliminated with a charge neutralizer, and data were corrected through referencing the 285.0 eV C 1s peak. The percentages of individual elements were determined from the relative composition analysis of the peak areas of the bands. XPS peak fitting was performed using CasaXPS.

3.2.1.4 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectroscopy was used to analyze various resin samples for qualitative information. Conditioned DOWEX 21K XLT was measured as a control, along with conditioned DOWEX 21K saturated with (1) Na_2SO_4, (2) groundwater simulant, and (3) $Fe(CN_6)^{4-}$ to compare to spent P&T resin. All resin samples were rinsed with DI H_2O thrice and analyzed directly on a Bruker Alpha FTIR spectrometer with single reflection attenuated total reflection diamond plate. An air background was taken between each sample and spectra were generated from the average of 32 scans with 4 cm^{-1} resolution.

3.2.1.5 Scanning Electron Microscopy (SEM) and Energy-Dispersive X-ray Spectroscopy (EDX)

Scanning electron microscopy (SEM) in combination with EDX was performed to visually inspect the surface of the spent P&T resin and observe distribution of chemical components within the resin bead. The resin beads were mounted on a carbon-tape-coated SEM stub. The samples were then carbon coated and placed in the instrument chamber. Resin beads were imaged on a FEI Helios NanoLab 660 FIB/SEM at different voltages.

3.2.2 Destructive Analysis

Quantification of co-contaminants retained on the resin was explored through wet oxidation of the conditioned resin, uranium-loaded Dowex 21K XLT and three spent P&T resin samples. This destructive analysis method utilized ICP-OES, ICP-MS, and ion chromatography (IC) to analyze metals, inorganic anions, and specific isotopes retained on the resin, including U-238, Tc-99, and non-radioactive I-127 to determine concentration of total iodine.

3.2.2.1 Wet Oxidation of DOWEX 21K Resin and Spent P&T Resin

Wet oxidation was employed as a destructive analysis technique to identify and quantify uranium and co-contaminants retained by the DOWEX 21K resin. A series of resin digestion experiments were conducted to destroy the resin by wet oxidation and analyze the digested solution by ICP-OES for metals and ICP-MS for U-238, Tc-99, and I-127.

Partial dissolution of the conditioned DOWEX 21K XLT resin was achieved fairly quickly using a 1:1 mixture of $HNO_3 + H_2O_2$ with heating near 100 °C. Conditioned DOWEX 21K resin was used as a blank in the wet oxidation experiments to assist in assigning constituents resulting from degradation of the resin. Additionally, digestion of the uranium-loaded DOWEX 21K resin served as a control experiment to determine efficiency of the wet oxidation method and quantify recovery of uranium.

Approximately 200 mg of conditioned, uranium-loaded, B3FM14, B3FM23, and B3FM32 resin samples were used in this analysis and underwent the wet oxidation protocol described in Levitskaia et al. (2017). All samples were done in duplicate with two digestions of each sample to drive digestion to completion and remove additional constituents remaining on the resin. Digestion solutions and the respective bubbler scrubs were analyzed independently, but the results are reported as combined µg/g resin. The conditioned resin sample and uranium-loaded sample did not fully dissolve after two digestions, but the P&T resin samples experienced near complete dissolution. Despite the partial dissolution of the control resin samples, quantitative U recovery was demonstrated indicating complete sample oxidation.

The uranium-loaded DOWEX 21K XLT resin sample was prepared as follows. A 0.12 M uranyl nitrate solution was made by dissolving 1.208 g $UO_2(NO_3)_2 \cdot 6H_2O$ in approximately 20 mL of 0.01 M HNO_3. Separately, a 50 mM carbonate solution was prepared by dissolving 1.0506 g $NaHCO_3$ in 250 mL DI water. An 8.5 mL aliquot of the $UO_2(NO_3)_2$ solution was combined with the 50 mM CO_3^{2-} solution for a total volume of 200 mL and a nominal uranium concentration of 5 mM. A spike of U-233 was added as a radiotracer to quantify uranium uptake by liquid scintillation counting (LSC). The pH of the final uranium/carbonate solution was adjusted to 7.82 using NaOH.

Conditioned Dowex 21K XLT resin (10.1525 g) was added to the above solution and agitated on a shaker table at ~300 rpms for 18 hours. The initial uranium/carbonate solution was a distinct yellow color, but after contact with the resin, the supernatant was clear and colorless indicating uptake of U by the resin. The supernatant was removed, and the resin was washed thrice with DI water. Analysis of the initial solution and supernatant by LSC and ICP-MS indicated quantitative (>99.99%) sorption of uranium with a calculated concentration of 26 mg/g of resin.

3.2.2.2 Analysis by Inductively Coupled Plasma (ICP)

Major cations were analyzed quantitatively using a PerkinElmer Optima 8300 dual view inductively coupled plasma-optical emission spectrometer and a PerkinElmer S-10 auto-sampler interface. The instrument was calibrated using standards made by the High-Purity Standards Corporation to generate calibration curves from 50 ppb to 50 ppm. This calibration was verified immediately with an initial calibration verification (ICV) and during sample analysis with a continuing calibration verification (CCV), run every 10 samples at a minimum. Calibration blanks were also analyzed after each calibration verification to ensure background signals and potential carryover effects were minimized. The calibration was independently verified using standards made by Inorganic Ventures. All calibration verification values must be within ±10% of the target concentrations to comply with the quality assurance / quality control (QA/QC) requirements as defined in the Hanford Analytical Quality Assurance Requirements Document (HASQARD), Conducting Analytical Work in Support of Regulatory Program (CAWSRP). A 1 ppm Lu, Sc, and Y solution was added as an internal standard to all samples, standards, and blanks to demonstrate the stability of the instrument and sample introduction system. All samples were run at several dilutions in order to bring their various elemental concentrations within the optimal analytical ranges of the instrument and to provide another level of result confirmation.

Uranium was measured quantitatively at mass 238 using a Thermo Scientific X-Series II quadrupole inductively coupled plasma-mass spectrometer and an Elemental Scientific SC4 DX FAST auto-sampler interface. The instrument was calibrated using (0.05 to 5 ppb) standards made by the High-Purity Standards Corporation to generate calibration curves. The same protocol outline above for ICP-OES was applied to ICV, CCV, and calibration blanks run intermittently. A 10 ppb Rh and Sb solution was added as an internal standard to all samples, standards, and blanks during the analysis to demonstrate the stability of the instrument and sample introduction system.

All samples and standards were diluted with 2% Fisher Scientific Optima trace metal grade nitric acid and twice DI water with resistivity no lower than 18.0 MΩ-cm. Results less than 2x the estimated quantitation limit (EQL) and samples with %RSD >30% are reported, but data is for information purposes and is not quantifiable due to poor reproducibility in duplicate measurements.

3.2.3 Resin Elution Studies

A series of uranium stripping studies were performed to evaluate the effect of the aqueous solution matrix on the retention of uranium by DOWEX 21K. Conditioned resin was contacted with the stripping solutions as a blank, and uranium-loaded DOWEX 21K XLT (Section 3.1.1) was used as a control to investigate the effectiveness of each stripping solution to remove/desorb uranium from the resin. Approximately 100 mg of pristine, uranium-loaded, and all three P&T resins were treated with 6 mL of 1 M HCl, 1 M $NaHCO_3$, or 1.5 M NaOH in duplicate. Samples were contacted for ~24 hours on a shaker table at ambient temperature (23 ± 2 °C), and the resulting supernatant was analyzed by ICP-OES, ICP-MS, and IC for metals and inorganic anions.

Additional stripping studies were performed on conditioned, uranium-loaded resin, and B3FM14 sample in duplicate, with the exception that the mass of P&T resin was increased 4-fold to achieve better detection of contaminants. Nominally 400 mg of the P&T resin was contacted with 6 mL of the following strip solutions: 1 M NaCl, 5 M NaCl, 0.9 M $MgSO_4$, 0.9 M Na_2SO_4, 2 M $CaCl_2$, 2 M $MgCl_2$, or 0.1 M NaOAc at pH 5. The supernatant and pristine strip solutions were analyzed by ICP-OES, ICP-MS, IC, and for total cyanide.

Raman spectroscopy was used to analyze the supernatant from select P&T strip experiments. Nominally 1 g of spent P&T resin was contacted on a shaker table with 3 mL of 1 M $NaHCO_3$, 1 M HCl, or 1 M

NaCl at ambient temperature for ~24 hours. The supernatant was removed and analyzed on the same system described in Section 3.2.3. Raman spectra of pristine strip solution and DI water were taken for reference and baseline corrected using OMNIC software; the baseline of DI water was subtracted from the reported spectrum.

3.2.4 IC Analysis

Anions were analyzed quantitatively using either a Dionex Reagent Free Ion Chromatography System 5000 (RFICS-5000) with an AS-AP auto-sampler or a Dionex Reagent Free Ion Chromatography System 2000 (RFICS-2000) with an AS-1 auto-sampler. Both instruments were calibrated using a multi-component anion solution made by Inorganic Ventures from 0.1 to 7.5 ppm. The calibration was verified with an ICV standard and during sample analysis with a CCV standard run every 10 samples at a minimum. A CCB was analyzed after each CCV to ensure background signals and potential carryover effects were not a factor. The CCV standard was prepared from a multi-component anion solution made by SPEX CertiPrep. All calibration verification values must be within ±10% of the target concentrations to comply with the QA/QC requirements as defined in HASQARD CAWSRP.

3.3 Uranium Batch Contacts

3.3.1 Groundwater Simulant

A simple groundwater simulant was developed, guided by existing data on the composition of the influent groundwater to the uranium train of the P&T Facility provided by CHPRC personnel. Major constituents of the groundwater were included in the simulant, and average concentrations were approximated. Due to charge balance, the concentration of Na^+ exceeds the average groundwater concentration by approximately 1 mM, as shown in Table 4.

Table 4. Constituents of Groundwater Simulant Used in Studies and Average Concentrations of the Same Constituents in P&T Influent to the Uranium IX Train based on results from the 200-ZP-1 and 200-UP-1 Operable Unit Pump-and-Treat Operations (DOE-RL 2017b) and Hanford Site Groundwater Monitoring Report (DOE-RL 2017a).

	Concentration (mM)	
Constituent	Simulant	Groundwater Influent (±σ)
Na	3.45	2.4 (0.7)
Cl	0.85	0.68 (0.01)
Mg	1	0.98 (0.22)
K	0.15	0.16 (0.04)
SO_4^{2-}	1	0.84 (0.01)
CO_3^{2-}	2	1.8 (0.1)
NO_3^-	0.75	0.74 (0.01)

The groundwater simulant was used for sorption experiments to determine the effect of the groundwater constituents on uranium sorption isotherm and K_d values. The simulant pH was adjusted (to pH 5, 6, or 8), uranyl was added at a concentration of 25 µM, and the resulting solution was used for batch contact sorption experiments as described below.

3.3.2 Determination of Uranium Isotherms from Various Aqueous Matrices

A stock solution of 0.0125 M uranyl nitrate in 0.01 M HNO_3 was prepared by dissolving 0.3495 g $UO_2(NO_3)_2 \cdot 6H_2O$ in 50.000 g of 0.01 M HNO_3. This stock solution was used to prepare subsequent working solutions of uranyl (25 or 50 µM) in a variety of matrices and at varying pH, for batch contact sorption experiments. Preparation of solutions used for uranium batch sorption experiments is shown in Table 5. The pH of each solution was adjusted using HCl or NaOH, allowed to equilibrate overnight, and readjusted as necessary before sorption experiments.

Table 5. Solution Compositions Used in Batch Contact Sorption Isotherm Experiments with Dowex 21K, Showing Expected Dominant Uranyl Species in Each Matrix.

Batch ID	Dominant species	pH (initial)	[U] (µg/L, initial)	[$NaHCO_3$] (mM)	[Ca] (mM)	[Mg] (mM)	[$NaSO_4$] (mM)
1	UO_2CO_3	5.0	5447	50	0	0	0
2	$UO_2(CO_3)_2^{2-}$	6.0	5497	50	0	0	0
3	$UO_2(CO_3)_3^{4-}$	7.8	11033	50	0	0	0
4	$UO_2Ca_2(CO_3)_3$	6.0	5587	63	1	0	0
5	$UO_2Ca_2(CO_3)_3$	6.0	5616	50	1	0	0
6	$UO_2Ca_2(CO_3)_3$	7.8	5543	63	1	0	0
7	$UO_2Ca_2(CO_3)_3$	7.8	5670	50	1	0	0
8	$UO_2Mg(CO_3)_3^{2-}$	7.8	5266	50	0	1	0
9	UO_2CO_3	5.0	5235	50	1	0	1
10	$UO_2Ca_2(CO_3)_3$	6.0	5295	50	1	0	1
11	$UO_2Ca_2(CO_3)_3$	7.8	5370	50	1	0	1
12	UO_2CO_3	5.0	6090	Groundwater simulant[(a)]			
13	UO_2CO_3	6.0	6093	Groundwater simulant[(a)]			
14	$UO_2Mg(CO_3)_3^{2-}$	7.8	5993	Groundwater simulant[(a)]			

(a) Groundwater simulant composition given in Table 4.

Batch sorption experiments were performed using the Dowex 21K XLT resin in the chloride form. Conditioning of the resin consisted of soaking in DI H_2O overnight, followed by conditioning in 1 M HCl. The conditioned resin was then rinsed with DI H_2O sufficiently to remove all excess HCl, as determined by the rinse reaching a constant pH. Further matrix-specific conditioning of the resin was performed in order to better simulate the equilibrium conditions of the P&T resin. Prior to a sorption experiment in a given matrix, a portion of the resin was pre-conditioned in the same matrix as the uranium-containing solution (e.g., 50 mM $NaHCO_3$ solution at pH 6, or groundwater simulant at pH 8). This allowed for resin sites to be pre-saturated with any ions from the matrix.

Batch sorption experiments were performed at ambient temperature by contacting varying mass (0.01 to 1.5 g) of pre-conditioned resin with 6 or 7 mL of uranium solution in 15 mL plastic centrifuge tubes. Samples were agitated on an orbital shaker (275 rpm) during the 24-hour contact time, after which time the supernatant was removed and acidified to 2% HNO_3 prior to analysis by ICP-MS. ICP-MS detection limits for U ranged from 0.071-7.1 μg/L.

3.3.3 Sulfate Affinity toward DOWEX 21K

Water retention of the DOWEX 21K XLT resin was determined by weighing 0.5 g of hydrated resin in duplicate and gently heating to 30 °C under vacuum for 72 hours. The dry resin mass was recorded and water retention was calculated. The manufacturer reports 50% to 60% water retention for DOWEX 21K XLT, and the experimental value was found to be in excellent agreement at 61 ± 1%.

Batch contacts using variable masses of DOWEX 21K XLT resin were performed with 25 mM Na_2SO_4 from DI water and groundwater simulant. Samples were contacted on a shaker table for 72 hours at ambient temperature (23±2 °C). A series of calibration solutions (5 to 70 mM Na_2SO_4) were measured by Raman spectroscopy using an InPhotonics RS2000 high-resolution spectrometer equipped with a thermoelectrically cooled charged coupled device; detector operating at –55 °C. A 670 nm, 150 mW diode laser was aimed through the side of a half dram vial with the focused fiber optic RamanProbe operated in a 180° back reflection mode. Ten spectra were averaged using Molecue software with 10-second integration time and spectral window from 400 to 4000 cm^{-1}. The intensity of the S=O peak at 983 cm^{-1} was plotted versus the analytical concentration of Na_2SO_4 to generate a calibration curve in both DI water and groundwater simulant, as shown in Figure 1. The concentration of sulfate sorbed to the resin was quantified by measuring the Raman intensity of supernatant after contact with the resin and calculating the concentration from the calibration curve. Raman spectra of the initial Na_2SO_4 and DI water were taken for reference and all spectra were normalized to the water band at 3350 cm^{-1} for data processing.

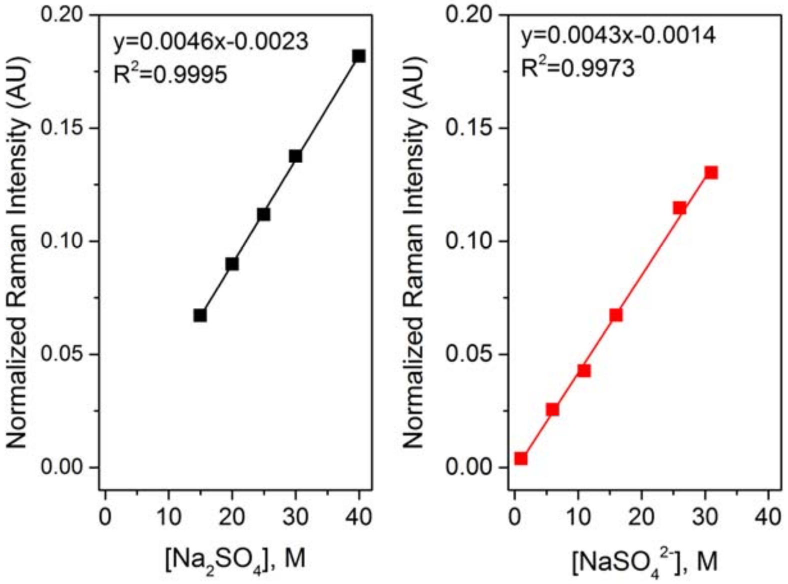

Figure 1. Calibration Curves Generated from (left) 15-40 mM Na_2SO_4 in DI Water Matrix and (right) 2-30 mM Na_2SO_4 in Groundwater Simulant. Spectra were baseline corrected and normalized to the water band at 3350 cm^{-1}.

3.4 Method Development for Ferrocyanide $Fe(CN)_6^{4-}$ Quantification

Ultraviolet-visible (UV-vis) spectroscopy was applied for the determination of ferrocyanide in aqueous solutions. To obtain the highest possible sensitivity by this analytical technique, all solutions were treated with sodium hypochlorite to oxidize $Fe(CN)_6^{4-}$ to $Fe(CN)_6^{3-}$, which possess a higher molar extinction coefficient in the visible region and thus offers a higher limit of detection. To achieve quantitative conversion from $Fe(CN)_6^{4-}$ to $Fe(CN)_6^{3-}$, 10 µL of the $K_4Fe(CN)_6$ solution was added to 840 µL of an aqueous solution consisting of a target matrix applied for the stripping of ferrocyanide from the DOWEX 21K resin. Next, 150 µL of NaOCl (Sigma-Aldrich, reagent grade, 4.00-4.99 % chlorine) was mixed in and allowed to develop for a minimum of 24 hours after addition. Slow oxidation of $Fe(CN)_6^{4-}$ was observed in the high salt solutions, such as 5 M NaCl, with incomplete conversion after 24 hours, and a recommended dilution step. Calibration plots were obtained by measuring absorbance of the developed $Fe(CN)_6^{3-}$ solution in the 0.03 to 1 mM concentration range. In these scoping tests, a total of five calibration data points per solution matrix was used to construct calibration plots. Absorbance spectra of $Fe(CN)_6^{3-}$ were collected on a Cary Bio 50 Spectrophotometer using disposable 10 mm semi-micro cuvettes. The experimental setup utilized automatic background subtraction with a medium scan rate (300 nm/min). The spectral window was 200 to 800 nm measured in 1 nm increments.

3.4.1 Loading of Ferrocyanide on the DOWEX 21K Resin

For development of an analytical method to quantify ferrocyanide retained by the Dowex 21K resin, conditioned resin was loaded with a known quantity of $Fe(CN)_6^{4-}$ from carbonate or chloride matrices. For carbonate loading experiments, 0.1069 g $K_4Fe(CN)_6$ and 0.1330 g $NaHCO_3$ were combined in a 25 mL volumetric flask to make a concentration of 10 mM $K_4Fe(CN)_6$ and 50 mM $NaHCO_3$. The pH of the solution was adjusted to 8.1 using dilute HCl.

Pre-conditioned Dowex 21K XLT resin (2.0035 g) was added to 13 mL of the above solution and agitated on a shaker table at ambient temperatures for ~2 hours. The clear and colorless supernatant was removed and set aside for analytical analysis to quantify the residual $Fe(CN)_6^{4-}$ remaining in the solution and determine $Fe(CN)_6^{4-}$ loaded on the resin. The loaded resin was rinsed three times with DI water.

Additionally, retention of $MgFe(CN)_6^{2-}$ onto Dowex 21K resin was explored since Mg^{2+} is a common groundwater constituent and is likely to associate with $Fe(CN)_6^{4-}$. The conditioned resin was first saturated (10 times) with a concentrated GW simulant. The supernatant was decanted, and the resin beads were washed three times with DI water in order to ensure that any residual supernatant was removed. Separately, 0.1050 g $MgCl_2$ and 0.0580 $K_4Fe(CN)_6$ were combined in a 50 mL volumetric flask for final concentrations of 10 and 2.75 mM, respectively. Nominally 3 g of the GW-saturated resin was contacted with 48 mL of the $Fe(CN)_6^{4-}/MgCl_2$ solution for ~18 hours. The supernatant was removed for analysis and the resin was washed three times with DI water before stripping studies.

Analysis of the initial solution and supernatant by UV-vis and colorimetric analysis indicated that both $Fe(CN)_6^{4-}$ and $MgFe(CN)_6^{2-}$ sorbed quantitatively with a respective loading capacity of 13.7 mg $Fe(CN)_6^{4-}$/g resin and 11.0 mg $Fe(CN)_6^{4-}$/g resin.

3.4.2 Stripping of Ferrocyanide from the Loaded DOWEX 21K Resin

Nominally 200 mg of the loaded resin was contacted with the following stripping solutions: 2 M $CaCl_2$, 1 M $NaHCO_3$, 0.9 M Na_2SO_4, NaCl (0.5, 1, 2, 3, 4, 5 M), 0.1 M NaOAc at pH 5, and KCl (0.05, 0.5, 2 M) in a solution/resin ratio of 33. Strips were done in duplicate and analyzed by UV-vis analysis. 850 µL of the direct strip solution was mixed with 150 µL of NaOCL and allowed to develop for 24 hours in case the absorbance was observed to be high enough to saturate the charge coupled detector, the resulting solution was diluted as needed using corresponding solution matrix containing the same concentration of NaOCl as in the developing step.

Selective stripping of the P&T resin was performed by contacting nominally 1 g of resin with 6 mL of 1 M $NaHCO_3$ in duplicate. The resin was agitated for ~ 2 hours and the supernatant was removed and replaced with 6 mL of fresh stripping solution. This was repeated three times in total to selectively strip the uranium. The remaining P&T resin was rinsed three times with water and then contacted with 6 mL of either 2 M CaC_2 and 5 M NaCl for ~2 hours. The supernatant was removed, diluted, and treated with NaOCl, and then analyzed using the developed UV-vis method.

3.4.3 Total Cyanide Determination by Micro-Distillation and Spectrophotometric Analysis

In this method, hydrogen cyanide (HCN) is liberated through acidification of the sample and separated using micro-distillation. The freed HCN is collected in the upper part of a micro-distillation tube containing sodium hydroxide (NaOH) absorption solution. The trapped cyanide (CN^-) is converted to cyanogen chloride (CICN) by reaction with chloramine-T, which reacts with a pyridine-barbituric acid reagent to form a purple color. The absorbance of this compound is proportional to the cyanide concentration and is measured using a calibrated spectrophotometer in the visible spectrum at 580 nm wavelength. Note: This cyanide procedure is for the determination of total cyanide in liquid or solid samples that contain only acid soluble cyanide compounds.

4.0 Results

4.1 Dowex 21K Resin Analysis

4.1.1 Nondestructive Analysis

4.1.1.1 X-Ray Absorption Spectroscopies

The position of the edge feature in EXAFS spectra can provide information regarding the oxidation state of the element being probed. In the U L_3 edge EXAFS performed on samples of the spent P&T resin and on lab-prepared samples (Figure 2), the edge feature appears at energy corresponding to that expected for U(VI) (Zhang et al. 2016).

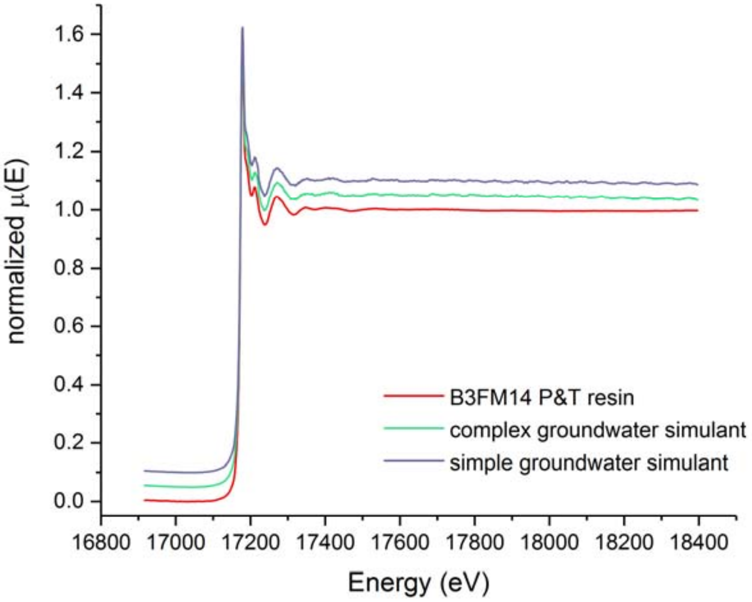

Figure 2. Normalized μ(E) EXAFS Spectra of the U L_3 Edge of P&T resin sample (red), Dowex 21K XLT Resin Loaded from Complex Groundwater Simulant (green) and Dowex 21K XLT Resin Loaded from Simple Groundwater Simulant (blue). FIO

The U L_3-edge EXAFS of three samples of P&T resin (B3FM14, B3FM23, B3FM32) was measured. The resulting spectra (Figure 3) showed no discernable differences between these three samples.

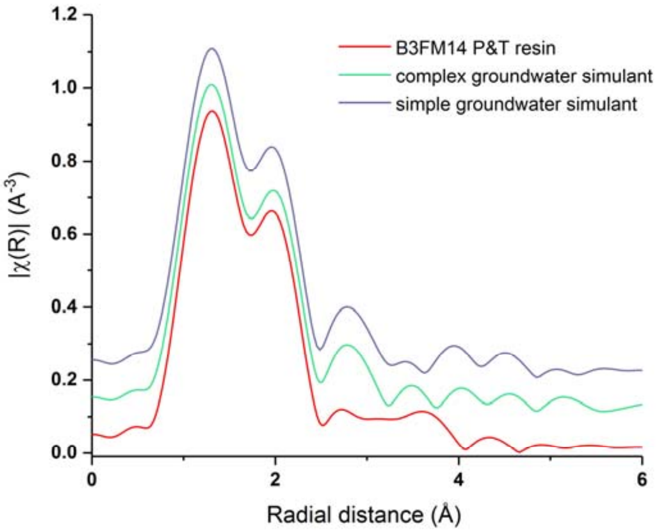

Figure 3. Magnitude of the Fourier Transform of U L_3-Edge k^2-Weighted EXAFS Data, over the Range k = 3.2 – 9.4 Å^{-1} for Three Samples of P&T Resin. FIO

The magnitude of the Fourier transform of U L_3-edge k^2-weighted EXAFS data, over the range k = 3.2 – 9.4 Å^{-1}, of B3FM14 resin and three control samples is shown in Figure 4. The control samples were prepared by loading Dowex21K XLT resin with uranyl from (green trace) complex groundwater simulant at pH 8, (blue trace) simple groundwater simulant at pH 8, and (pink trace) 50 mM $NaHCO_3$ solution at pH 8. From the comparison of these spectra, it is observed that the bond length of the first coordination shell (R = 1.3 Å), which due to its very short distance can be assigned as the U=O oxygen, is identical in all samples. The second coordination shell, at R = 1.96 Å, is also consistent among all samples, and is likely a coordinating O or N (which cannot be resolved by EXAFS). Due to the limited k range of the data, coordination shells at longer R are less sensitive.

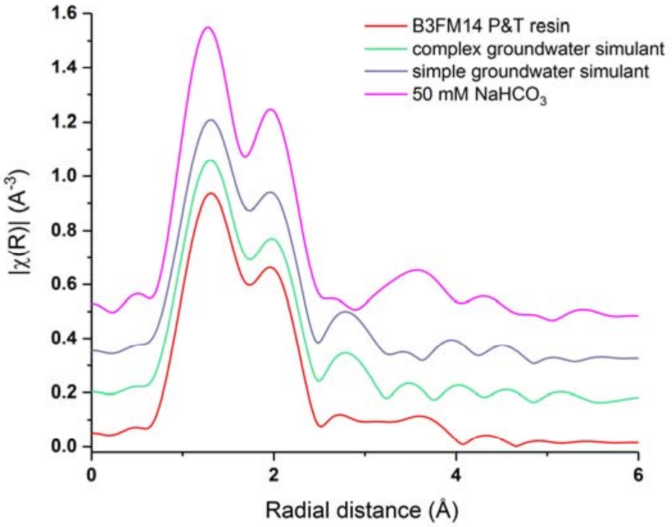

Figure 4. Magnitude of the Fourier Transform of U L_3-Edge k^2-Weighted EXAFS Data, over the Range k = 3.2 – 9.4 Å^{-1} of P&T Resin (red); Dowex 21K Sorbed with Uranyl from Complex Groundwater Simulant (green); Dowex 21K Sorbed with Uranyl in Simple Groundwater

Simulant (blue); and Dowex 21K Sorbed with Uranyl from 50 mM $NaHCO_3$ Solution (pink). Initial pH of all solutions were adjusted to 8 for spectra shown. FIO

These results confirm that the spent P&T resin retains U in +6 oxidation state in a chemical form of uranyl complexes.

4.1.1.2 X-Ray Photoelectron Spectroscopy (XPS)

XPS is a powerful tool to probe the chemical and oxidation environment for the various different elements; however, care should be given to ensure that there are no interferences of other elements in the spectra assigned to a particular element. The entire range of energies from 0-1400 eV were scanned for all three resin samples. Subsequently, specific emphasis was given to the elements U (4f region), Tc (3d region), Fe (2p region), Cr (2p region), S (2p region), Cl (2p region), P (2p region), N (1s region), and C (1s region). For the U region of spectrum, due to proximity of U f4 binding energies with the N 1s, the region of monitoring was carefully delineated to eliminate the interference effects due to the abundance of the quaternary amine binding sites. Weak U and non-detectable S spectra were observed in the resin B3FM14, possibly suggesting attenuation of the X-ray beam by the protective tape used in the sample preparation or non-representative sampling for the XPS analysis. The B3FM23 and B3FM32 samples showed the presence of both U and S. No detectable presence of Tc, Fe, Cr, Cl, or P was observed for any of the spent P&T resin samples.

The U $4f_{7/2}$ line was used to investigate the chemical and oxidation environment of U in the resins, as the $4f_{5/2}$ lines were too close in energy to the N 1s lines. In the B3FM23 and B3FM32 samples, the U $4f_{7/2}$ line could be resolved into two U species with binding energies of 380.4 and 382.2 eV, and with observed respective relative percentages of 8 and 92 for the B3FM23 sample and 28 and 72 for the B3FM32 sample (Figure 5, Table 6). An overlapping spectral feature observed at a binding energy of 385.6 eV, which could be attributed to a satellite of the U $4f_{7/2}$ line. Both binding energies are in the range with that reported for several U(VI) species with the 380.4 and 382.2 eV values consistent with U(VI) alkali urinates and hydrated uranyl hydroxides and inorganic salts (Ilton and Bagus 2011). The representative examples include $UO_2(NO_3)_2.6H_2O$ (binding energy = 382 eV), Li_2UO_4 (binding energy = 381.4 eV), and $CaUO_4$ (binding energy = 380.7 eV) (Chadwick 1973). However, the U $4f_{7/2}$ line binding energy of 380.4 eV can also be attributed to the reduced U(IV) species (Stubbs et al. 2015). It has been reported that consideration of the satellite-primary U $4f_{7/2}$ peak binding energy separation can help to resolve this uncertainty, so that the separation ranges of 3.5–4.9 and 5.8–7.3 eV are indicative of U(VI) and U(IV) respectively (Ilton and Bagus 2011). The satellite-U 4 peak separation values of 5.2 and 3.4 eV are observed for the respective 380.4 and 382.2 eV binding energies, suggesting the presence of U(VI) in the B3FM23 and B3FM32 resin samples.

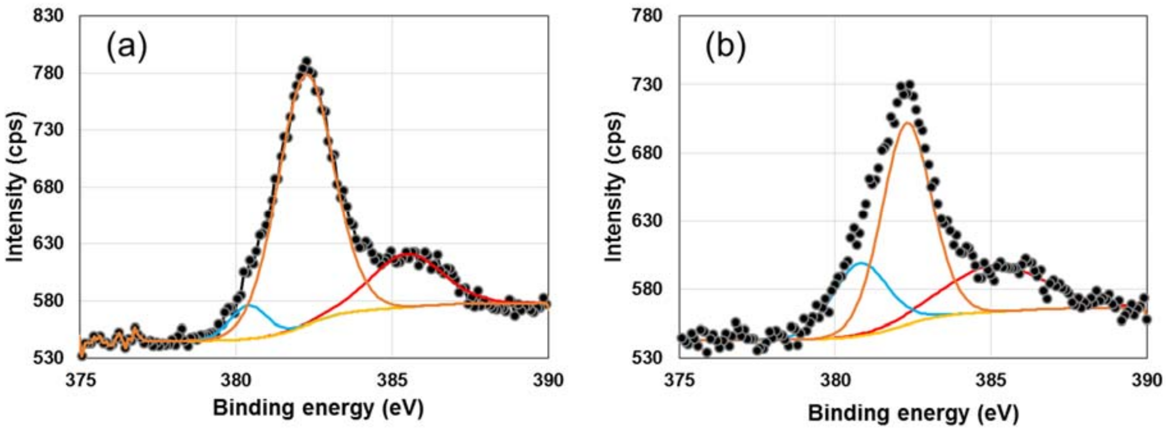

Figure 5. Photoelectron Spectra of U $4f_{7/2}$ Lines in (a) B3FM23 and (b) B3FM32.
(black circles) Experimental data, (orange trace) U(VI) fit, (blue trace) U(IV) fit, (red trace) satellite of the U $4f_{7/2}$ line, (yellow trace) baseline. FIO

The S $2p_{3/2}$ line in B3FM23 can be resolved into two components with binding energies 168.2 eV and 169.3 eV, respectively, in a 60:40 ratio as shown in Figure 6. While both the binding energies fall within that observed in case of organic and inorganic SO_4^{2-} (Barbaray et al. 1978), the former is presumably attributed to SO_4^{2-} bound on the resin functional groups, while the latter is presumably attributed to a complexed form of SO_4^{2-} such as $UO_2(SO_4)_2^{2-}$. The S $2p_{3/2}$ line in B3FM32 shows a similar behavior.

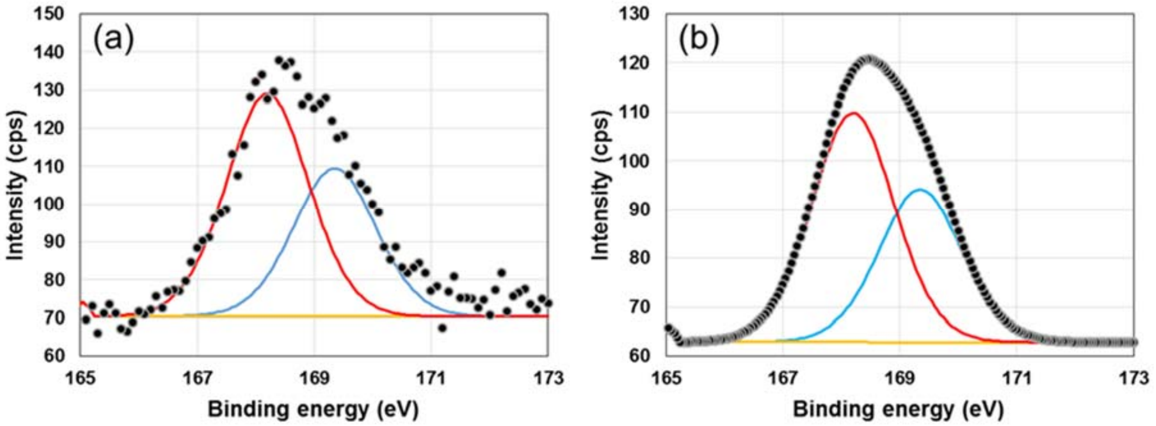

Figure 6. Photoelectron Spectra of S $2p_{3/2}$ Lines in (a) B3FM23 and (b) B3FM32.
(black circles) Experimental data, (red and blue trace) SO_4^{2-} fit, (yellow trace) baseline. FIO

Table 6. Tabulation of Binding Energies and Percentages of Key Elements in the Resins. FIO

Resin	Element	Binding Energy	% Observed
B3FM23	U	380.4	8
		382.2	92
	S	168.2	60
		169.3	40
B3FM32	U	380.7	28
		382.3	72

	S	168.2	60
		169.3	40

4.1.1.3 FTIR of DOWEX 21K Resin Beads

FTIR spectra of spent P&T resin compared to the pristine DOWEX 21K resin treated with various aqueous matrices are shown in Figure 7. The top spectrum (red trace) corresponds to conditioned DOWEX 21K where N—R and C—H stretches from the resin framework can be observed at the finger print region of 900 – 1800 cm^{-1} and at ~ 2800 – 3000 cm^{-1}. Broad peak at 3000 – 3600 cm^{-1} corresponds to the —OH stretching envelope of water. DOWEX 21K saturated with sulfate from a 25 mM Na_2SO_4 solution in DI water is represented by the green trace. It is evident that sulfate is loaded onto the resin from the strong S=O stretch observed at 1085 cm^{-1} (Pretsch et al. 2009). DOWEX 21K resin contacted with groundwater simulant, concentrated by 10 times, is shown by the blue trace. The sulfate S=O stretch at 1085 cm^{-1} and the NO_2 symmetric stretch at 1335 cm^{-1} can be observed, indicating sorption of both nitrate and sulfate from the groundwater simulant discussed in Section 3.3.2. Lastly, the black trace is representative of the spent 200 West P&T resin. The spectrum is nearly identical to that of the resin loaded with concentrated (10 times) groundwater simulant with the presence of S=O and NO_2 vibrations at 1085 and 1335 cm^{-1}, respectively. These results clearly indicate significant retention of the sulfate and nitrate anions by the Dowex 21K resin.

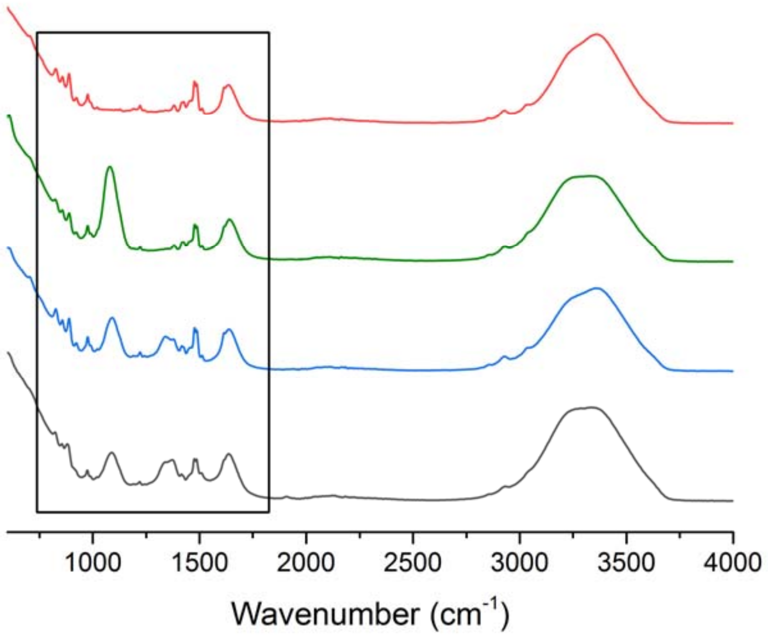

Figure 7. FTIR Spectrum of DOWEX 21K Resin after (red) Conditioning with 1 M HCl, (green) Saturation with Na_2SO_4, and (blue) Contact with a Concentrated (10 times) Groundwater Simulant in Comparison to the (black) Spent Resin from the 200 West P&T Facility.

4.1.1.4 Scanning Electron Microscopy (SEM) and Elemental Mapping

SEM images of spent P&T resin are shown in Figure 8. The size, color, and surface morphology of the resin beads vary within the small subset of resin beads imaged. Some of the resin beads appear in excellent condition, while other beads are fractured or split in half. All of the resin beads imaged appear to be less than 1 mm in diameter.

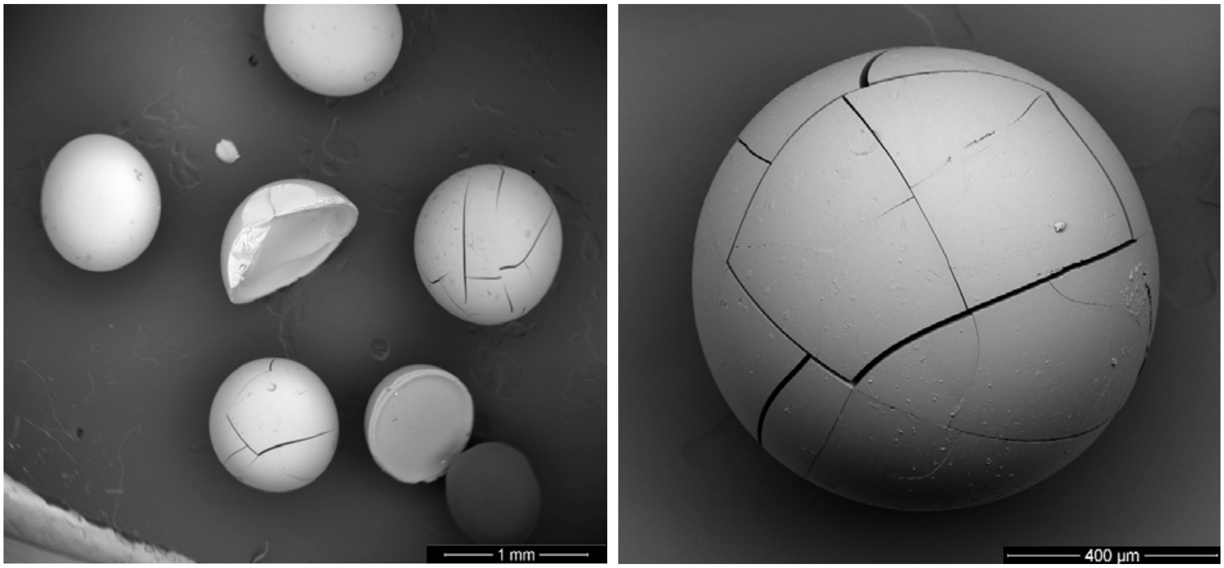

Figure 8. SEM Images of Spent 200 West P&T Resin Beads. FIO

Elemental mapping can provide useful information on distribution of elements within the sample. In the case of the cross-sectioned resin bead in Figure 9, the EDX shows that the uranium is located in the highest concentration on the outside of the bead, with negligible concentration present within the bead. This indicates that the DOWEX 21K from the P&T site operates by sorption to the surface of the resin bead.

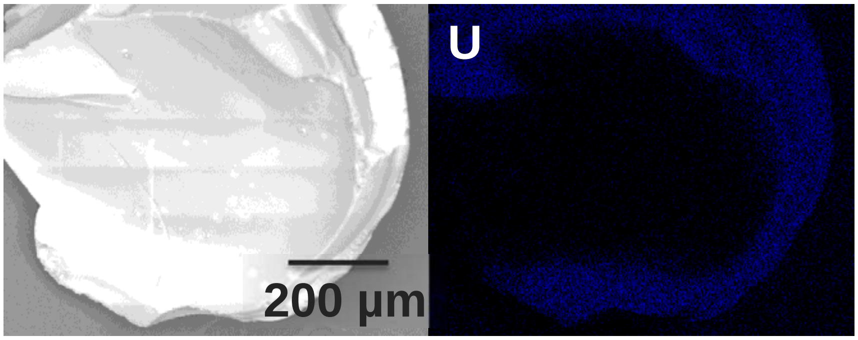

Figure 9. Elemental Distribution of Uranium on a Cross-Sectioned Spent P&T Resin Bead. FIO

4.1.1.5 Radiochemical Analyses

GEA was performed using a combination of high-purity germanium (HPGe) and LEGe detectors to quantify radionuclides in samples B3FM14, B3FM23, and B3FM32. LEGe allows for quantification of gamma emitting radionuclides with energies below 40 keV, whereas HPGe detectors are necessary to quantify radionuclides at higher energies.

GEA results indicate Co-60, U-235, and U-238 as the primary isotopes identified in all three resin samples. The activities and associated concentrations are given in Table 7. The U-235 activity is reported based on the 185.7 keV line (57% intensity), while the U-238 activity is based on the 1001 keV (0.84%

intensity) line of Pa-234 (half-life = 1.16 minutes), which is assumed to be in secular equilibrium with the U-238 and Th-234 parents. Overall, the results are in good agreement among the three P&T samples with a U-238 concentration of 21.2 mg U/gram of resin.

Table 7. Activities and Associated Concentrations of Radionuclides Retained by DOWEX 21K Resin Samples from the 200 West P&T Facility as Quantified by GEA. The results are expressed in Bq or µg nuclide per gram of hydrated resin.

	Co-60[(a)]		U-235[(b)]		U-238[(a)]	
Sample	Bq/g	pg/g	Bq/g	µg/g	Bq/g	µg/g
B3FM14	5.0	0.12	11.7	146	267	21451
B3FM23	5.0	0.12	11.7	146	257	20647
B3FM32	5.3	0.13	12.3	154	268	21531
Average	5.1	0.12	11.9	149	264	21210

(a) Relative uncertainty = 2% at 1 standard deviation

(b) Relative uncertainty = 3% at 1 standard deviation

Quantification of low-energy X-rays, such as those associated with the decay of I-129, can be measured using a LEGe detector. The activity of I-129 was quantified based on the weighted average of X-rays at 29.461 keV (19.5% intensity) and 29.782 keV (35.9% intensity) as shown in Figure 10.

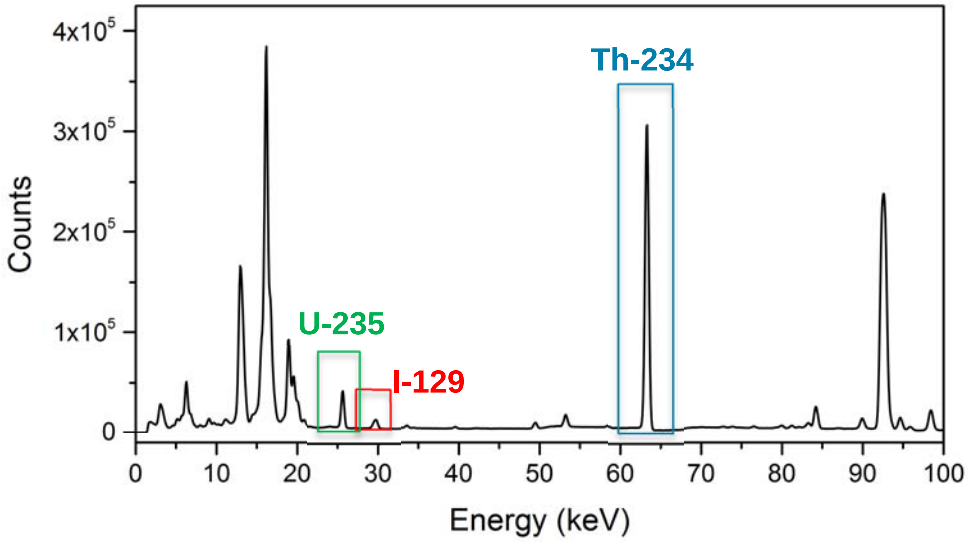

Figure 10. Low-Energy Spectrum of B3FM23 P&T Resin with X-Ray Energies Assigned to I-129, U-235, and Th-234 (decay daughter of U-238).

Additionally, quantification of U-235 and U-238 by low-energy analysis was used to cross-validate the low-energy technique with HPGe analysis. The 185.7 keV line was used to quantify U-235 and the 63.3 keV line (3.7% intensity) from the Th-234 decay daughter was used to quantify the U-238. The Th-234 daughter, with a half-life of 24.1 days, is assumed to be in secular equilibrium with the U-238 parent. The gamma rays from Co-60 were outside the effective energy range or the LEGe detector and thus were not quantifiable using this technique. The calculated activities and concentrations of I-129, U-235, and U-238 are given in Table 8. The concentration of U-235 with respect to U-238 was calculated to be 0.70%, consistent with natural abundance of uranium-235.

Table 8. Activities and Associated Concentrations of Radionuclides Retained on the DOWEX 21K 200 W P&T Resin Samples as Quantified by Low Energy Analysis. The results are expressed in Bq or µg nuclide per gram of hydrated resin.

	I-129[(a)]		U-235[(b)]		U-238[(c)]	
Sample	Bq/g	µg/g	Bq/g	µg/g	Bq/g	µg/g
B3FM14	0.66	0.10	11.9	149	266	21370
B3FM23	0.67	0.10	11.9	149	266	21370
B3FM32	0.76	0.12	13.1	164	292	23459
Average	0.70	0.11	12.3	154	275	22067

Relative uncertainty = (a) 5%, (b) 2%, or (c) 11% at 1 standard deviation

Overall, there is excellent agreement between the HPGe and LEGe results for the U-235 and U-238 specific activities for all three P&T resin samples. The slight increase in specific activity reported for B3FM32 for all radionuclides is likely due to the change in geometry of the counted sample as reported in Table 3. The mass of the resin was approximately 30% less than samples B3FM14 and B3FM23. There is reason to believe with less resin mass, there was less “self-attenuation” of the low-energy X-rays used to calculate the specific activities. Regardless, collating the three P&T resin samples, the average U-238 concentration from the combined GEA equates to 0.0216 ± 0.001 mg ^{238}U/g of resin.

No Tc-99 was detected on the spent P&T resin samples.

4.1.2 Destructive Analysis of Resin Samples

Digestion of the pristine conditioned and uranium-loaded DOWEX 21K XLT resin, as well as spent P&T resin, was performed to destroy the resin and quantify metals and radionuclides of interest by ICP-OES and ICP-MS. All three P&T resin samples underwent two successive wet oxidation digestions with HNO_3 + $H2O_2$ in duplicate and the average concentrations (in µg/gram of resin) and relative standard deviations (RSDs) are shown in Table 9.

Table 9. ICP-OES and ICP-MS Results for Wet-Oxidation Treatment of Conditioned Dowex 21K, in Comparison to a Uranium-Loaded Dowex 21K Control and Three Samples of Spent Resin from the 200 W P&T Facility.

Elemental Composition Reported as μg/g of Resin											
	Dowex 21K	RSD	U-loaded	RSD	B3FM14	RSD	B3FM23	RSD	B3FM32	RSD	P&T(b)	RSD
Aluminum(c)	22	80	ND	-	ND	-	39	141	ND	-	39	141
Barium	47	108	74	6	39	62	83	39	137	40	86	57
Ba-138(a)	54	101	75	7	46	67	84	41	149	53	93	56
Boron	**1576**	**0**	**1688**	**13**	**1600**	**7**	**1459**	**5**	**1658**	**2**	**1572**	**6**
Cd-111(a)	ND	-	ND	-	ND	-	ND	-	ND	-	ND	-
Calcium(c)	3735	100	7601	34	6261	77	10760	39	16317	46	11111	45
Chromium	**122**	**24**	**16**	**141**	**68**	**11**	**57**	**7**	**75**	**22**	**67**	**14**
Cr-52(a)	**122**	**17**	**25**	**36**	**78**	**7**	**67**	**8**	**93**	**2**	**79**	**16**
Cobalt(c)	29	141	95	141	ND	-	ND	-	ND	-	ND	-
Copper(c)	5	141	ND	-	ND	-	ND	-	ND	-	ND	-
Cu-63(a) (c)	9	141	15	107	9	62	6	141	10	26	8	30
I-127(a)	**0.3**	**141**	**3**	**5**	**38**	**1**	**30.0**	**0**	**38**	**3**	**35**	**13**
Iron	**486**	**29**	**120**	**39**	**3427**	**10**	**2942**	**2**	**2894**	**2**	**3088**	**10**
Lead	ND	-	ND	-	ND	-	ND	-	ND	-	ND	-
Pb-208(a)	ND	-	ND	-	ND	-	ND	-	ND	-	ND	-
Magnesium(c)	22	91	44	39	34	70	49	35	78	23	53	42
Manganese	7	29	ND	-	ND	-	ND	-	ND	-	ND	-
Mo-95(a)	**7**	**86**	**2**	**141**	**7**	**4**	**5**	**31**	**6**	**17**	**6**	**12**
Nickel(c)	64	39	ND	-	ND	-	ND	-	ND	-	ND	-
Potassium	ND	-	ND	-	ND	-	ND	-	ND	-	ND	-
Ru- 101(a)	**ND**	-	**ND**	-	**4**	**2**	**4**	**11**	**5**	**10**	**4**	**10**
Silicon	1642	13	420	33	ND	NA	ND	NA	207.5	141	207	141
Sodium	**1686**	**0**	**1763**	**15**	**1781**	**5**	**1625**	**1**	**1962**	**1**	**1789**	**9**
Strontium(c)	3	141	ND	-	ND	-	ND	-	ND	-	ND	-
Sulfur	**430**	**102**	**371**	**27**	**7732**	**9**	**7182**	**11**	**8196**	**3**	**7703**	**7**
Tc-99(a)	ND	-	ND	-	ND	-	ND	-	ND	-	ND	-
Titanium(c)	ND	-	15.9	19	ND	-	6.1	141	ND	-	6	141
U-238(a)	**1**	**79**	**25853**	**1**	**19224**	**10**	**16685**	**10**	**19577**	**2**	**18496**	**9**
Zinc	545	101	969	33	800	79	1357	32	1988	42	1382	43

(a) Analyzed by ICP-MS

(b) Average of B3FM14, B3FM23, and B3FM32

(c) Poor reproducibility, analytical concentration <2x EQL, or RSD greater than 30%

ND = not detected

Conditioned DOWEX 21K, used as a blank, indicates a significant concentration of sodium, silicon, and boron. The concentrations of boron and sodium in the P&T samples are at or below the concentration of the blank, which likely indicates these analytes are leaching from the glass vials used for sample digestion. The concentrations of chromium and iron in the blank resin are somewhat surprising, but these may be a result of resin manufacturing activities. The fact that chromium was not detected on the uranium-loaded DOWEX resin can be explained by the displacement of the chromium (likely chromate) by uranium during loading. Calcium appeared at seemingly high concentrations; however, definitive conclusions about its presence on the control resin cannot be drawn due to poor analytical statistics.

Near quantitative recovery (99±1%) of the uranium loaded onto the DOWEX 21K XLT was observed using the wet oxidation method. The first digestion step solubilized 96% of the total uranium, with only 4% recovered in the second digestion step. This was used as the experimental control, but it should be noted that the pristine conditioned DOWEX 21K XLT resin and the uranium-loaded DOWEX 21K XLT resin sample did not fully dissolve during the wet oxidation procedure; however, the spent P&T samples did. This leads to the conclusion that the complete wet oxidation of the resin is achieved without its physical dissolution in the digestion solution.

The uranium concentration reported for the P&T resin is in excellent agreement among the three samples measured, with an average concentration of 1844 µg/g resin (± 10%). This equates to 0.018 g U/gram of resin on the lead IX column after 2 years of operation at the 200 West P&T Facility and is in satisfactory agreement (within 15%) with the U-238 concentration determined from GEA.

Dissolution results for the spent P&T resin samples indicate that multiple elements co-sorb to the resin in addition to uranium, most notably iron, sulfur, chromium, and I-127. Iron and sulfur are present in much higher concentrations, as expected due to the nature of the groundwater, but sorption of chromium and iodine, which are also targeted for groundwater remediation, cannot be discounted. Consistent with radiochemical analysis, there was no detectable concentration of Tc-99 on the spent P&T resin by ICP-MS, which is surprising considering the uranium plume also contains a significant concentration of Tc-99, existing primarily as the anionic pertechnetate (TcO_4^-) species. This clearly indicates lack of the DOWEX 21K resin selectivity for the pertechnetate anion.

Sulfur constitutes the highest concentration of co-contaminant on the DOWEX 21K resin, with an average concentration of 7604 µg/g resin (± 8%) for the three P&T samples. The sulfur composition likely exists as the inorganic sulfate anion, which was found to have strong affinity towards DOWEX 21K, vide infra.

The iron concentration in the blank, although still quantifiable, is much less than the concentration of iron reported for the B3FM14, B3FM23, and B3FM32 P&T samples. Iron was reported as the second highest co-contaminant concentration on the P&T resins, with an average of 3015 µg/g resin (± 10%), which is a factor of 6 less than the uranium concentration loaded on the resin.

Additionally, although quantification proved difficult and reproducibility between duplicate measurements was poor, there are notable quantities of both calcium and magnesium on the P&T resins at the respective 11 (±45%) mg/g resin and 53.4 µg (±45%) µg/g resin. These species are both present in the groundwater and are known to form complexes with uranium in aqueous solutions.

4.1.3 Uranium Stripping Studies

The P&T resin samples were exposed to different aqueous stripping solutions to quantify co-contaminants and inorganic anions retained by DOWEX 21K resin. Initially, 1 M HCl, 1 M $NaHCO_3$, and 1.5 M NaOH solutions were used to strip the three P&T resins (in duplicate), and the results are shown in Table 10. The same stripping solutions were used with the uranium-loaded DOWEX 21K control resin to judge stripping efficiency of each solution.

Table 10. Elemental Composition of Contaminants Stripped from B3FM14, B3FM23, and B3FM32 Resins from the 200 West P&T Facility. Analytes with reported concentrations < 2x EQL and/or %RSD>30% were omitted from analysis. The complete analytical worksheet is shown in **Error! Reference source not found.**.

Elemental Composition Reported as µg/g of Resin						
	1 M HCl	%RSD	1 M $NaHCO_3$	%RSD	1.5 M NaOH	%RSD
B3FM14 Spent P&T Dowex21K Resin						
Chromium	45	6	25	NA	(c)	(c)
Cr- 52(a)	42	7	30	7	26	12
Iron	(b)	NA	59(c)	NA	(b)	NA
I-127(a)	16	13	31	9	7	5
Sulfur	8259	5	9132	7	7838	2
U-238(a)	19148	5	17372	2	2009	1
B3FM23 Spent P&T Dowex21K Resin						
Chromium	49	6	29	1	29	6
Cr- 52(a)	47	6	30	1	28	8
Iron	160	2	ND	NA	ND	NA
I-127(a)	19	1	32	0	8	8
Sulfur	8544	2	9320	1	8150	7
U-238(a)	20640	2	19487	4	1902	10
B3FM32 Spent P&T Dowex21K Resin						
Chromium	51	13	26	NA	31	6
Cr- 52(a)	49	14	27	3	29	1
Iron	240	46	ND	NA	ND	NA
I-127(a)	19	9	31	4	8	4
Sulfur	8387	3	8449	3	8517	2
U-238(a)	19843	4	18041	1	1952	3

(a) Analyzed by ICP-MS
(b) Poor reproducibility, analytical concentration <2x EQL, or RSD greater than 30%
(c) Result based on single measurement

Table 10 indicates the main components stripped from the three P&T samples are uranium, chromium, I-127, and sulfur. This is in excellent agreement with the results of the wet oxidation experiment, with the exception that iron concentration was too low to be reliably quantified.

The concentration of uranium in eluate was largely impacted by the nature of the stripping solution. Analysis of the stripping solutions from the control samples with uranium-loaded DOWEX 21K, indicates that 1 M HCl and 1 M $NaHCO_3$ stripped the uranium nearly quantitatively at 98% and 90%, respectively, whereas the NaOH only stripped 4% of the uranium from the resin. Using the concentration of uranium from the wet oxidation method to calculate the theoretical uranium concentration on the P&T resin indicates quantitative stripping with 1 M HCl, 90% stripping for 1 M $NaHCO_3$ and only 10% of the uranium removed by NaOH.

Chromium concentrations for the 1 M HCl stripping solution appear to be the highest, but still slightly less than those reported for the wet oxidation experiment. Cr concentrations for 1 M $NaHCO_3$ and 1.5 M

NaOH strips are nearly half of what is reported for HCl, suggesting greater stripping efficiency with the acidic stripping solution.

I-127 concentration is in excellent agreement with the wet oxidation value when stripped with the manufacturer-recommended regeneration solution of 1 M $NaHCO_3$. Treatment with 1 M HCl results in only partial stripping of the iodine. 1 M NaOH exhibited poor iodine stripping.

The sulfur concentration remains unchanged for all three P&T resin samples regardless of stripping conditions, with an average concentration of 8511 µg/g resin (± 5%). This is 10% higher than that observed for the wet oxidation experiments, but is still within analytical tolerance.

Additional strip solutions were explored, and the mass of resin was increased by a factor of 4 to assist in detection of additional analytes. Results from the wet oxidation experiment indicated there was no distinguishable difference between B3FM14, B3FM23, and B3FM32; thus, further stripping studies were performed only with B3FM14. The analytes and their respective concentrations are given in Table 11.

The main co-contaminants on the P&T resin are cobalt, chromium, iodine, iron, lead, manganese, molybdenum, and sulfur. A majority of these contaminants have already been discussed from both wet oxidation and the first set of stripping experiments. The increase in mass of resin subjected to the stripping led to the detection of cobalt, iron, lead, manganese, and molybdenum. The concentration of chromium in the second series of strips was significantly lower than the chromium concentrations quantified by acidic stripping and wet-oxidation.

Iron was detected in the second series of strips, but in concentrations much lower than those observed for the wet-oxidation. The chloride strip solutions appeared to be most effective for stripping iron, with the highest concentration of 539 µg/g resin for 5 M NaCl, which is significantly less than 3354 µg/g resin quantified by wet-oxidation for B3FM14.

Lead and Mo-95 were quantified for the series of strip solutions, but the concentrations varied significantly across the matrices. Comparison with corresponding results from the wet oxidation method indicates that the concentrations of these analytes were too low for their quantification. The concentration of manganese, on the other hand, remained constant at 1.4 µg/g of resin for all the strip solutions, except for 0.1 M NaOAc, which was a very poor stripping solution, even for uranium.

The concentration of I-127 from chloride stripping solutions remained fairly constant at 45 ± 3 µg/g resin. This value is higher that the concentration of I-127 of 38 ± 1 µg/g determined by wet oxidation method. This potentially suggests that the acidic matrix of the samples generated during the wet oxidation might attenuate the analytical ICP-MS determination of I-127.

Comparing the I-127 concentrations from stripping to the I-129 concentration from nondestructive GEA analysis provides that the amount of I-127 on the spent resin is approximately 400 times greater than that of I-129. This is significantly lower compared to the corresponding ratio of about 1000 observed for the Purolite IX train at the 200 West P&T Facility (Levitskaia et al. 2017). This suggests that there is 2.5x greater bulk concentration of I-127 in the feed entering the Purolite IX train of the 200 West P&T Facility relative to the lead IX column.

Inorganic anions, sulfate, and nitrate were quantified by IC for all strip solutions. The concentrations were below the detection limits for 1 M HCl, 1 M $NaHCO_3$, and 1.5 M NaOH due to the smaller mass of resin used. The nitrate concentration in the chloride strip solutions was 17.3 mg/g resin (± 13%), as compared to the sulfate stripping solutions, which measured 8.82 mg/g resin (± 17%).

The sulfate concentration in chloride strips was 26.4 mg/g resin (± 11%), with the exception of $CaCl_2$, which was significantly lower at 16.0 mg/g resin. This equates to approximately 8786 µg/g resin, which is comparable to the sulfur concentration quantified by ICP-OES. This confirms that the sulfur absorbed to the resin exists predominantly as sulfate.

The effectiveness of the stripping solutions can be evaluated through comparison of loaded DOWEX 21K control resin and the spent P&T resin for uranium recovery. Using the known mass of U/g of resin on the control uranium-loaded resin, the concentration of uranium in solution can be calculated in the event that the uranium was stripped completely and compared to the concentration quantified by ICP-MS, giving the percent recovery for uranium. The same methodology can be applied to the P&T resin using the concentration of uranium determined by the wet-oxidation. The ratio of uranium quantified in the strips of the P&T resin to the concentration of uranium expected from the wet-oxidation results provides a pseudo percent recovery of uranium. The uranium recovery from the control resin and spent P&T resin for all 10 stripping solutions is given in Figure 11.

The P&T resin is nearly quantitatively stripped by 1 M HCl, 1 M $NaHCO_3$, and 5 M NaCl. Uranium recovery lies below 40% for 1 M NaCl, 2 M $CaCl_2$, 2 M $MgCl_2$, 0.9 M $MgSO_4$, 0.9 M Na_2SO_4, and 0.1 M NaOAc at pH 5. Surprisingly, the $CaCl_2$ and $MgCl_2$ with nominally 4 M Cl^- concentrations do not strip either the control resin or the P&T resin effectively. One explanation is the solubility of the Ca/U/CO_3 or Mg/U/CO_3 complexes that likely form. If those precipitate, then the uranium concentration in the supernatant is artificially less than stripped from the resin. In support of this hypothesis, the I-127 concentration for $CaCl_2$ and $MgCl_2$ strips lie between the concentrations resulting from stripping with 1 and 5 M NaCl, indicating the poor uranium recovery is likely not attributed to incomplete stripping.

One interesting note is the behavior of the 5 M NaCl strip for the uranium-loaded control resin and the spent P&T resin. The P&T resin was nearly completely stripped of uranium with 5 M NaCl, whereas the control only stripped around 38%. One thing to note is that the uranium on the control resin was loaded from a carbonate matrix, which indicates a uranium carbonate complex. However, uranium speciation on the P&T resin is unknown. If the uranium speciation on the P&T resin forms a weaker complex than the U-carbonate species, that could explain the discrepancy in the stripping efficiency of the 5 M NaCl between the P&T resin and the control sample. Aside from the 5 M NaCl, the stripping of the control resin and the P&T resin from the other nine stripping solutions appear to be within error of one another with no significant anomalies.

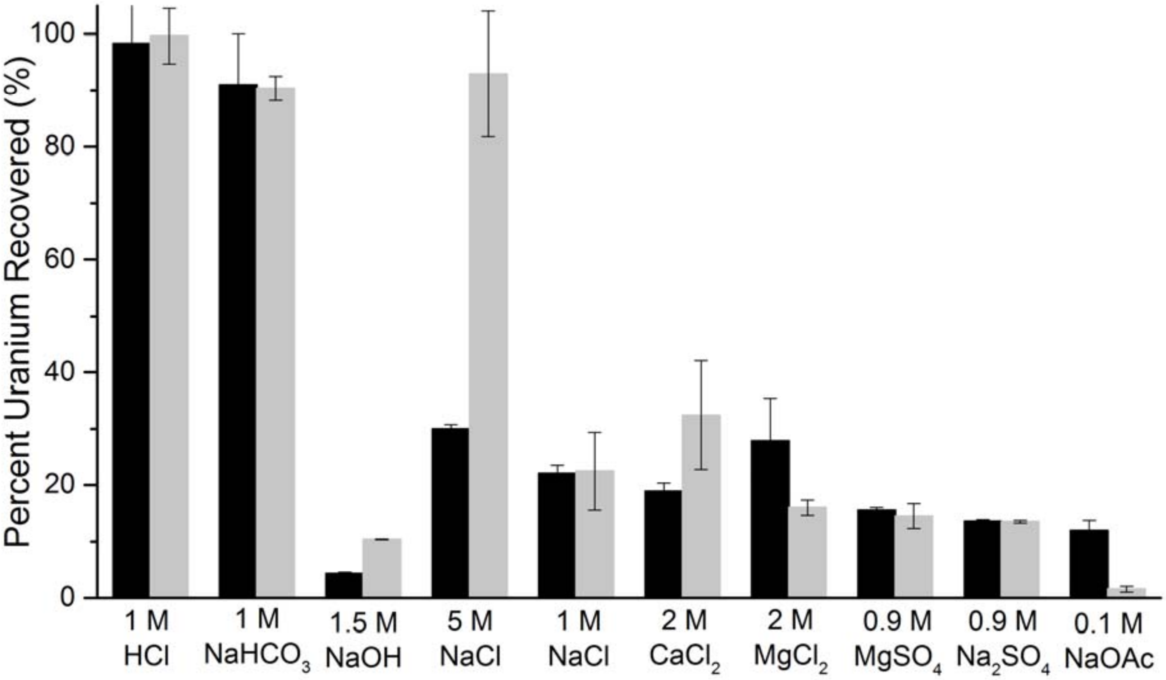

Figure 11. Percent Uranium Recovered from (black) Uranium-Loaded Resin and (grey) B3FM14 P&T Resin Sample. The P&T sample is calculated from a theoretical uranium loading concentration of 19224 µg/g resin based on results from wet oxidation analysis.

Table 11. Elemental Composition of Contaminants Stripped from B3FM14 Resin from the 200 West P&T Facility. Analytes with reported concentrations < 2x EQL and/or %RSD>30% were omitted from analysis.

Elemental Composition Reported as µg/g of Resin Stripped with Various Eluents														
	5 M NaCl	%RSD	1 M NaCl	%RSD	2 M $CaCl_2$	%RSD	2 M $MgCl_2$	%RSD	0.9 M $MgSO_4$	%RSD	0.9 M Na_2SO_4	%RSD	0.1 M NaOAc pH 5	%RSD
Chromium	17	3	19	1	11.3	1	13.7	11	11.4	4	14.4	5	4.2	10
Cobalt	6	5	3.2	2	5.7	1	3.5	10	1.6	24	1.6	5	ND	-
I-127(a)	48	0	43	2	45.7	3	45	6	14.7	4	12.3	1	0.2	20
Iron	539	2	118	5	456	10	274	10	5.4	6	5.2	3	ND	-
Lead	17	3	15	2	(c)	-	12.5	8	6.3	3	8.3	14	ND	-
Manganese	1.4	1	1.3	4	1.2	2	1.3	4	1.3	3	1.3	5	ND	-
Mo-95	4.1	4	4.2	3	2.6	12	2.4	1	3.5	8	4	5	ND	-
Nitrate	20365	5	17334	1	15910	4	15527	7	7779	6	9866	5	ND	-
Sulfate	27498	5	28500	2	16024	15	23078	8	NM	-	NM	-	ND	-
Sulfur	10170	3	8313	0	12314	2	7335	11	NM	-	NM	-	632	8
U-238(a)	17857	12	4317	31	6227	30	3072	8	2789	15	2607	2	296(b)	33(b)

(a) Analyzed by ICP-MS

(b) Poor reproducibility with RSD greater than 30%

(c) Analytical concentration was less than 2x EQL

ND = not detected and NM = not measured

In a companion test, nominally 1 g of P&T resin was contacted with 1 M HCl, 1 M $NaHCO_3$, or 1 M NaCl and the eluates were analyzed qualitatively by Raman spectroscopy. Figure 12 shows the Raman spectra obtained from the eluates (solid traces) overlaid with the pristine stripping solutions (dashed traces). Sulfate, nitrate, and carbonate can be observed at 983, 1050, and 1075 cm^{-1}, respectively. The carbonate strip (blue trace) shows a peak at 820 cm^{-1} that can be attributed to a uranium-carbonate $UO_2(CO_3)_3^{4-}$ species (Nguyen-Trung et al. 1992). This same peak can be observed in the 1 M NaCl strip, where there is also a small CO_3^{2-} peak at 1075 cm^{-1}, which is evidence for the $UO_2(CO_3)_3^{4-}$ species stripped from the resin in the near neutral 1 M NaCl strip. When stripping with the acidic 1 M HCl solution, the anionic uranium complex is broken and the uranium is stripped from the resin as the uranyl ion, which can be observed by the shift to 875 cm^{-1} indicative of UO_2^{2+} (Nguyen-Trung et al. 1992).

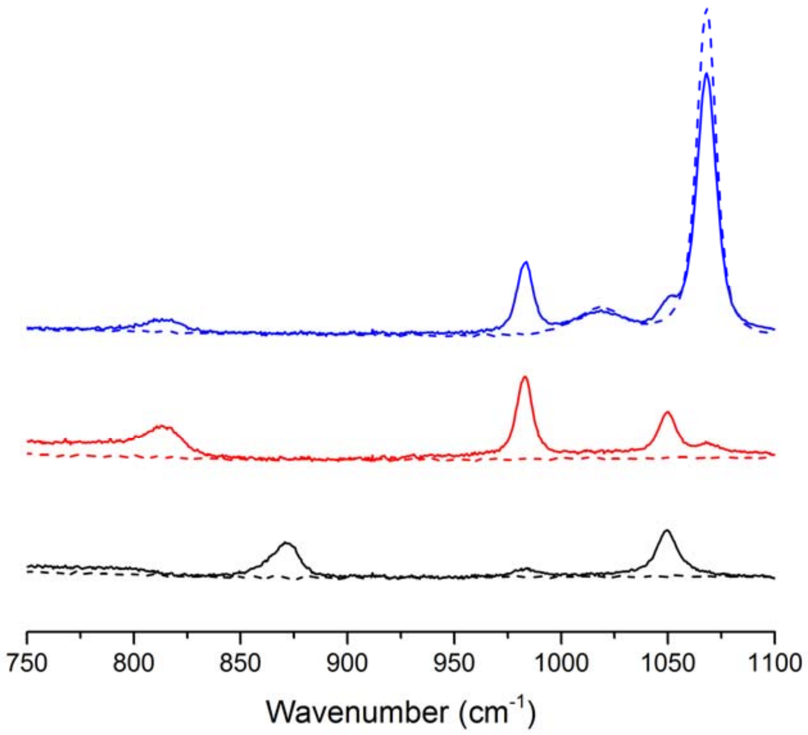

Figure 12. Raman Spectra of (black) 1 M HCl, (red) 1 M NaCl, and (blue) 1 M $NaHCO_3$ Stripping Solutions after Contact with Nominally 1 g of P&T Resin. Dashed traces indicate strip solutions prior to contact with the P&T resin.

4.2 Uranium Sorption Isotherms

4.2.1 Uranium Speciation in Solution

Any environmentally mobile U is expected to be U(VI), which readily forms the dioxo-linear cation, uranyl (UO_2^{2+}). While U(VI) is capable of forming many soluble complexes in groundwater and consequently is very environmentally mobile, U(IV) in environmental groundwater is much less mobile (Morss et al. 2010). Previous studies have established that in the vadose zone porewater at the Hanford Site, the neutral complex $Ca_2UO_2(CO_3)_3$ is a major species (Wang et al. 2004). Other species expected in the groundwater influent based on the previous literature reports include the anionic uranyl carbonate species, $UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$ (Guillaumont 2003). In addition to the neutral $Ca_2UO_2(CO_3)_3$

species, the anionic species, $CaUO_2(CO_3)_3^{2-}$ is also formed (Dong and Brooks 2006), as well as the neutral species UO_2CO_3. Interestingly, Mg^{2+}, a homolog of Ca^{2+}, forms only single $MgUO_2(CO_3)_3^{2-}$ complex (Dong and Brooks 2006, 2008) with stability constant only one order of magnitude smaller than for the calcium analog. This suggests that the formation of the $MgUO_2(CO_3)_3^{2-}$ complex can significantly affect speciation of U(VI) in alkaline groundwater. Previous reports indicate that strongly basic IX resins do not sorb the $MgUO_2(CO_3)_3^{2-}$ complex and have only small affinity for the $CaUO_2(CO_3)_3^{2-}$ (Dong and Brooks 2006, 2008; Riegel and Schlitt 2017), suggesting that at a $pH > 6$, the presence of not only Ca^{2+} but also Mg^{2+} may attenuate sorption of U(VI) on the resin.

Table 12 provides the expected uranyl species in Hanford groundwater, together with their stability constants (log β). The distribution of these species in solution is strongly dependent upon solution conditions (i.e., pH and concentration of Ca, Mg, uranyl, and carbonate/dissolved CO_2), as is illustrated by the speciation diagrams shown in Figure 13). As a result, perturbations in solution conditions are capable of shifting the equilibrium uranyl speciation. In influent groundwater to the P&T Facility, pH and concentration of various ions (e.g., Ca, Mg, SO_4^{2-}) have been observed to fluctuate. Such variations of solution conditions are expected to change the uranyl speciation in the groundwater. Consequently, the fraction of neutral or anionic uranyl species present in groundwater will depend on the pH and concentration of other groundwater constituents. As only anionic species will be complexed by the anion exchange resin, such changes in uranyl speciation have a direct implication for removal efficiency.

While the solution speciation can serve as a useful guide to predict the uranyl behavior in groundwater, it becomes less predictive of the uranyl speciation in vicinity of the resin. The equilibria used to create solution speciation diagrams (Table 12) do not predict speciation of uranium retained on the resin, which contains a high concentration of exchangeable anions (i.e., Cl^-). An excess of other anions on the resin, particularly anions with a strong affinity for uranyl (e.g., SO_4^{2-}, CO_3^{2-}), is expected to be capable of influencing the speciation of neutral uranyl species, through formation of anionic complexes on the surface of the resin, which are then retained.

Table 12. Literature Values for Stability Constants and Solubility Constants for Various Uranium Species Likely Present in Groundwater. FIO

Species	Reaction	log β or log K_{sp}	Source
UO_2OH^+	$UO_2^{2+} + H_2O\ (l) \leftrightarrow UO_2OH^+ + H^+$	-5.25 ± 0.24	(a)
$UO_2OH_2(aq)$	$UO_2^{2+} + 2H_2O\ (l) \leftrightarrow UO_2(OH)_2(aq) + 2H^+$	-12.15 ± 0.07	(a)
$UO_2(OH)_3^-$	$UO_2^{2+} + 3H_2O\ (l) \leftrightarrow UO_2(OH)_3^- + 3H^+$	-20.25 ± 0.42	(a)
$UO_2(OH)_4^{2-}$	$UO_2^{2+} + 4H_2O\ (l) \leftrightarrow UO_2(OH)_4^{2-} + 4H^+$	-32.40 ± 0.68	(a)
$(UO_2)_2(OH)^{3+}$	$2UO_2^{2+} + H_2O\ (l) \leftrightarrow (UO_2)_2(OH)^{3+} + H^+$	-2.70 ± 1.00	(a)
$(UO_2)_2(OH)_2^{2+}$	$2UO_2^{2+} + 2H_2O\ (l) \leftrightarrow (UO_2)_2(OH)_2^{2+} + 2H^+$	-5.62 ± 0.04	(a)
$(UO_2)_3(OH)_4^{2+}$	$3UO_2^{2+} + 4H_2O\ (l) \leftrightarrow (UO_2)_3(OH)_4^{2+} + 4H^+$	-11.90 ± 0.30	(a)
$(UO_2)_3(OH)_5^+$	$3UO_2^{2+} + 5H_2O\ (l) \leftrightarrow (UO_2)_3(OH)_5^+ + 5H^+$	-15.55 ± 0.12	(a)
$(UO_2)_3(OH)_7^-$	$3UO_2^{2+} + 7H_2O\ (l) \leftrightarrow (UO_2)_3(OH)_7^- + 7H^+$	-32.20 ± 0.80	(a)
$(UO_2)_4(OH)_7^+$	$4UO_2^{2+} + 7H_2O\ (l) \leftrightarrow (UO_2)_4(OH)_7^+ + 7H^+$	-21.90 ± 1.00	(a)
$UO_2\ CO_3$ (aq)	$UO_2^{2+} + CO_3^{2-} \leftrightarrow UO_2\ CO_3$ (aq)	9.94 ± 0.03	(a)
$UO_2\ CO_3$ (s)	$UO_2^{2+} + CO_3^{2-} \leftrightarrow UO_2\ CO_3$ (cr)	14.760 ± 0.02	(a)
$UO_2\ (CO_3)_2^{2-}$	$UO_2^{2+} + 2CO_3^{2-} \leftrightarrow UO_2\ (CO_3)_2^{2-}$	16.61 ± 0.09	(a)
$UO_2\ (CO_3)_3^{4-}$	$UO_2^{2+} + 3CO_3^{2-} \leftrightarrow UO_2\ (CO_3)_3^{4-}$	21.84 ± 0.04	(a)
$(UO_2)_3(CO_3)_6^{6-}$	$3UO_2^{2+} + 6CO_3^{2-} \leftrightarrow (UO_2)_3(CO_3)_6^{6-}$	54.00 ± 1.00	(a)
$UO_2\ NO_3^+$	$UO_2^{2+} + NO_3^- \leftrightarrow UO_2\ NO_3^+$	0.300 ± 0.150	(a)
$UO_2\ Cl^+$	$UO_2^{2+} + Cl^- \leftrightarrow UO_2\ Cl^+$	0.170 ± 0.020	(a)
$UO_2\ Cl_2$ (aq)	$UO_2^{2+} + 2Cl^- \leftrightarrow UO_2\ Cl_2$ (aq)	-1.10 ± 0.400	(a)
$UO_2\ SO_4$ (aq)	$UO_2^{2+} + SO_4^{2-} \leftrightarrow UO_2\ SO_4$ (aq)	3.15 ± 0.020	(a)
$UO_2\ (SO_4)_2^{2-}$	$UO_2^{2+} + 2SO_4^{2-} \leftrightarrow UO_2\ (SO_4)_2^{2-}$	4.14 ± 0.070	(a)
$UO_2\ (SO_4)_3^{4-}$	$UO_2^{2+} + 3SO_4^{2-} \leftrightarrow UO_2\ (SO_4)_3^{4-}$	3.02 ± 0.380	(a)
$CaUO_2\ (CO_3)_3^{2-}$	$UO_2^{2+} + Ca^{2+} + 3CO_3^{2-} \leftrightarrow CaUO_2\ (CO_3)_3^{2-}$	27.18 ± 0.06	(b)
$Ca_2UO_2\ (CO_3)_3$ (aq)	$UO_2^{2+} + 2Ca^{2+} + 3CO_3^{2-} \leftrightarrow Ca_2UO_2\ (CO_3)_3$ (aq)	30.70 ± 0.05	(b)
$MgUO_2\ (CO_3)_3^{2-}$	$UO_2^{2+} + Mg^{2+} + 3CO_3^{2-} \leftrightarrow MgUO_2\ (CO_3)_3^{2-}$	26.11 ± 0.04	(b)
H_2CO_3	$2H^+ + CO_3^{2-} \leftrightarrow H_2CO_3$	16.681 ± 0.02	(c)
HCO_3	$H^+ + CO_3^{2-} \leftrightarrow HCO_3$	10.329 ± 0.01	(c)
H_2O	$H^+ + OH^- \leftrightarrow H_2O$	-13.997 ± 0.003	(c)

(a) Data from OECD-NEA thermodynamic database (Guillaumont et al. 2003)
(b) Data from reference (Dong and Brooks 2006)
(c) Data from reference (Martell and Smith 1976)

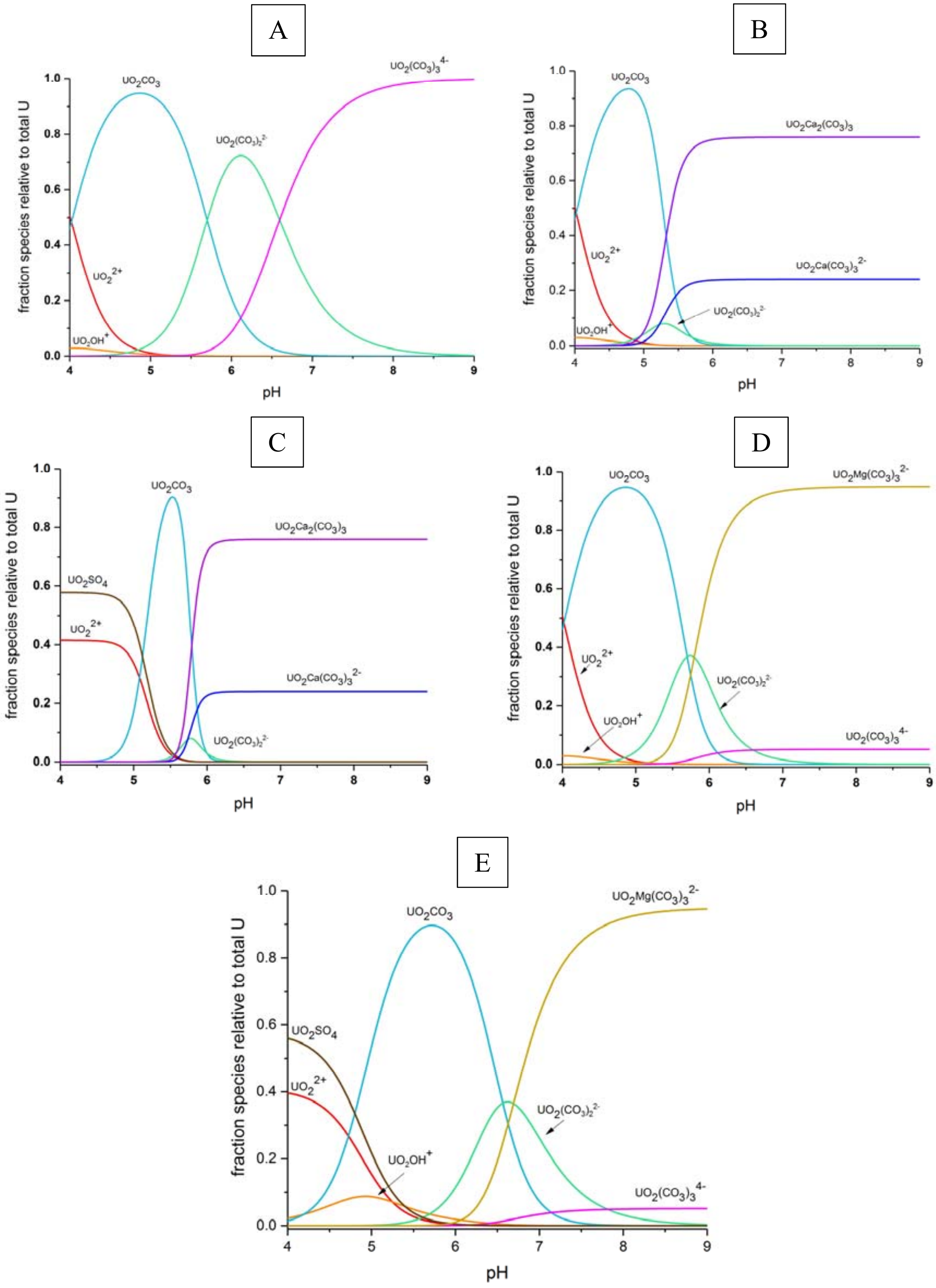

Figure 13. Speciation of 25 µM Uranyl in (A) 50 mM CO_3^{2-}, (B) 50 mM CO_3^{2-} + 1 mM $CaCl_2$, (C) 50 mM CO_3^{2-},1 mM $CaCl_2$ and 1 mM Na_2SO_4, (D) 50 mM CO_3^{2-} + 1 mM $MgCl_2$, and (E) the Simple Groundwater Simulant with 2 mM CO_3^{2-}, 0.75 mM NO_3^-, 1 mM Mg^{2+}, 1 mM SO_4^{2-}, and 1 mM Cl^-. FIO

4.2.2 Uranium Sorption onto Dowex 21K XLT Anion Exchange Resin

To evaluate the affinity of the resin for particular uranyl species, batch contact sorption experiments were performed to determine sorption isotherms, loading capacity, and K_d values under a variety of conditions. Contacting solutions containing uranyl were prepared to carefully maintain the speciation of uranyl complexes (anionic and/or neutral) to determine the affinity of particular uranyl species. As the uranyl speciation is strongly dependent upon the concentration of U, in each sorption experiment, the concentration of U was kept constant and mass of resin was varied instead to achieve different loading ratios.

Results from the 14 uranium sorption experiments listed above are summarized in Table 13. This table compares the loading capacity, K_d, and percent uptake of the resin under the loading condition listed above for corresponding batch IDs. Overall, all sample matrices tested at pH 6 and 8, regardless of dominant U species, showed U sorption > 99.2%, or nearly complete quantitative uptake. Obtained analytical results for U were too close to the limit of quantification to draw definitive conclusions, and analyses of these samples using a different analytical method are currently in progress to improve analytical statistics.

Table 13. Resin Loading, K_d, and % Uptake for Uranium Sorption Experiments with the Respective Dominant Uranium Species Expected in the Solution Matrix.

Batch ID	Dominant Species	Volume:Mass Ratio (mL solution/g resin), range	Resin Loading (mg U/g resin)	K_d (mL/g)	% Uptake	Notes
pH 5						
1	UO_2CO_3	67 – 7.1	0.038 – 0.33	960 – 2,450	93.6 – 99.7	[b] [c]
9	UO_2CO_3	526 – 17	ND	ND	ND	[a], [b]
12	UO_2CO_3	588 – 17	0.085 – 3.28	74 – 6,110	77.9 – 91.0	
pH 6						
2	$UO_2(CO_3)_2^{2-}$	67 – 3.4	0.019 – 0.37	33,600 – 169,000	99.9	[c]
4	$UO_2Ca_2(CO_3)_3$	67 – 3.4	0.026 – 0.38	8,510 – 34,700	99.2 – 99.9	
5	$UO_2Ca_2(CO_3)_3$	278 – 59	0.33 – 2.6	13,600 – 64,800	99.9	[a], [b]
10	$UO_2Ca_2(CO_3)_3$	556 – 278	1.4 – 3.0	55,900 – 62,800	99.9	[a], [b]
13	UO_2CO_3	286 –17	0.10 – 1.7	20,900 – 888,000	99.8 – 99.9	[a]
pH 8						
3	$UO_2(CO_3)_3^{4-}$	67 – 4.0	0.044 – 0.74	49,200 – 232,000	99.8 – 99.9	[c]
6	$UO_2Ca_2(CO_3)_3$	67 – 27	0.15 0.37	326,000 –350,000	99.9	[b]
7	$UO_2Ca_2(CO_3)_3$	370 – 15	0.085 – 2.1	6,420 – 402,000	99.9	[a]
8	$UO_2Mg(CO_3)_3^{2-}$	588 – 17	0.089 –3.2	177,000 – 5,170,000	99.9	[a]
11	$UO_2Ca_2(CO_3)_3$	526 – 17	0.19 – 2.9	52,900 – 266,000	99.9	[a]
14	$UO_2Mg(CO_3)_3^{2-}$	588 – 17	0.10 – 3.5	35,200 – 8,680,000	99.3 – 99.9	[a]

(a) Analytical concentration less than 2x EQL for majority of samples; samples in process of re-analysis with lower EQL

(b) Reported range limited to samples greater than 2x EQL

(c) Isotherm shown in Figure 14

The tests performed at pH 5 included three samples with matrices of 50 mM carbonate (sample 1), 50 mM carbonate – 1 mM Ca^{2+} – 1 mM sulfate (sample 9), and groundwater simulant reported in Table 4 (sample 12). Under these conditions, neutral uranyl species UO_2CO_3 are expected to dominate in the initial solution. However, even in the worst performing matrix, nearly 78% to 91% of uranyl is removed from solution. This indicates that even when the neutral uranyl species is present in the solution, sorption of U(VI) is facilitated by the formation of the anionic U species in the resin. For samples 1 and 9, contact resin was re-equilibrated with the corresponding solution matrices. For sample 1, native Cl^- anion is partly exchanged for HCO_3^-, and U(VI) sorption is driven by the formation of the $UO_2(CO_3)_2^{2-}$ complex resulting in 93.6% to 99.7 % uptake. Addition of even small concentration of sulfate in the solution matrix significantly enhances U(VI) sorption, which could be explained by the quantitative uptake of the sulfate by the resin leading to the formation of the $UO_2(SO_4)_2^{2-}$ or mixed $UO_2(CO_3)(SO_4)^{2-}$ complex. For the sample 12, no resin pre-equilibration with the solution matrix was performed, resulting in the reduced U(VI) uptake, which is presumably due to the low concentrations of the carbonate and sulfate on the resin controlling formation of the negatively charged U(VI) complexes.

Comparisons between U(VI) sorption isotherms using the 50 mM $NaHCO_3$ matrix at pH 5, 6, and 8 illustrate the relative affinity of the resin toward various uranium species. Figure 14 shows that a similar loading capacity (ca. 0.35 mg U/g resin) achieved under these conditions corresponds to the vastly different equilibrium aqueous uranyl concentrations so that the sorption efficiency increases in the order pH 5 << pH 6 < pH 8. At pH 5, the dominant species is predicted to be the neutral UO_2CO_3 (Figure 13), which must first form an anionic complex in order to sorb onto the resin, thereby introducing an additional energy barrier to the IX process. However, at pH 6 and 8, the anionic species, $UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$, respectively, are dominant in solution, thus facilitating their preferential sorption to the resin. As a result, the loading of uranyl onto the resin is significantly higher from the pH 6 and 8 relative to the pH 5 matrix as indicated in Figure 14 and Table 13.

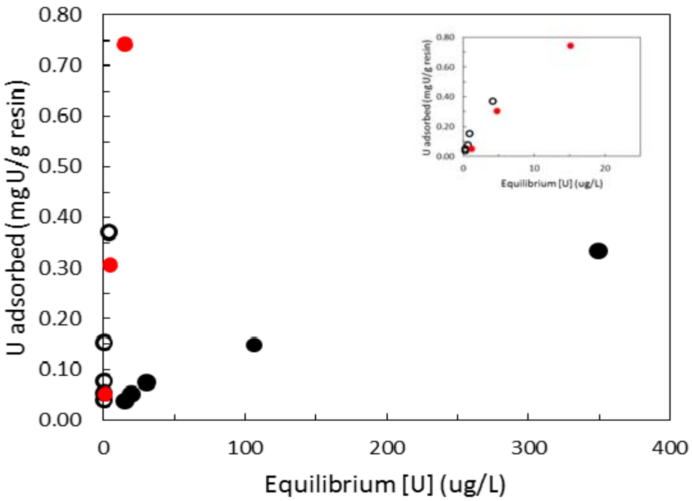

Figure 14. Sorption Isotherm of Uranyl from a Matrix of 50 mM $NaHCO_3$ at pH 5 (black), pH 6 (open) and pH 8 (red) onto Dowex 21K XLT Resin. Inset highlights the 50 mM $NaHCO_3$ at pH 6 (open) and pH 8 (red) isotherm over the range of equilibrium U 0-20 µg/L.

4.2.3 Sulfate Affinity toward Dowex 21K XLT

Wet oxidation and stripping studies have indicated the second highest concentration on the P&T resin is sulfur existing in the chemical form of sulfate. Raman spectroscopy was utilized to monitor the concentration of SO_4^{2-} in solution after contact with conditioned Dowex 21K XLT resin to investigate the sorption capacity of sulfate. The concentration of sulfate sorbed to the resin was calculated using a calibration curve and results are shown in Figure 15.

$$\%\, uptake = 1 - \frac{(Intensity\ of\ Raman\ band\ in\ solution\ after\ contact)}{(Intensity\ of Raman\ band\ in\ initial\ solution)}\ x\ 100 \qquad (1)$$

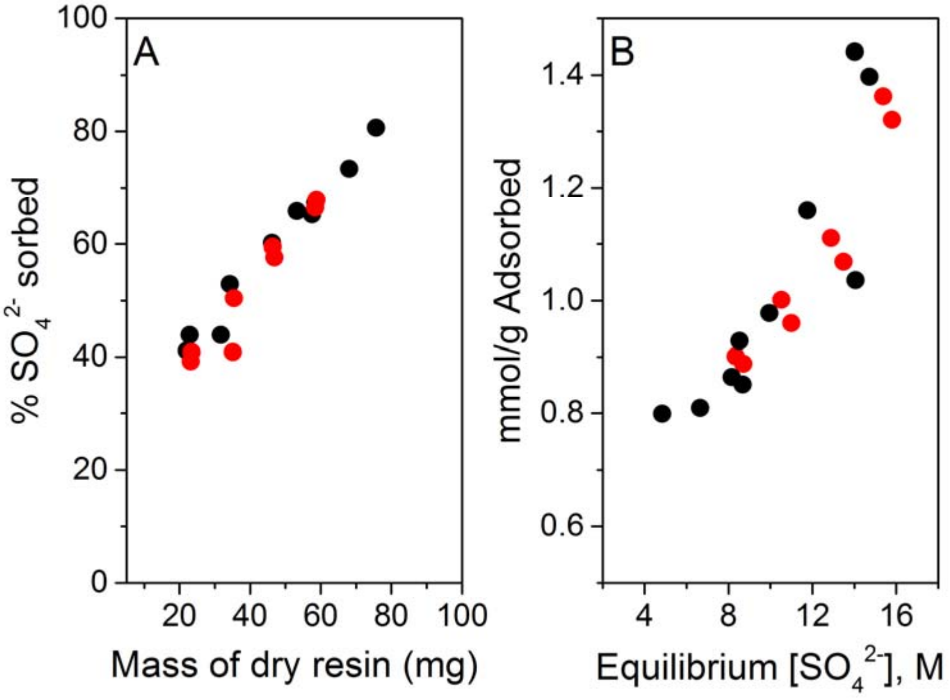

Figure 15. (A) Sulfate Sorption from (black) DI Water and (red) Groundwater Simulant, and (B) Corresponding Isotherm.

The sorption isotherms in Figure 15B indicate no difference in the sorption uptake from DI water and the groundwater matrix. Both DI water and groundwater show high sorption capacity for sulfate with sorption ranging from 0.8-1.4 mmol/g resin.

4.3 Quantification Method for Ferrocyanide $Fe(CN)_6^{4-}$

In 1950s, ferrocyanide and nickel sulfate were used to in situ precipitate Cs-137 inside Hanford storage tanks. After precipitate settled, the liquid waste fraction was discharged to cribs and trenches. Since precipitation requires excess of reagents that remained in the liquid fraction, this resulted in the release of various alkali salts of ferrocyanide $Fe(CN)_6^{4-}$ and nickel ferrocyanide $NiFe(CN)_6^{2-}$ in the environment.

Negatively charged ferrocyanide, other cyanide-transition metal complexes, and free cyanide are expected to retain by DOWEX 21K resin. While strongly bound cyanide-transition metal complexes are considered non-toxic, free cyanide and weak cyanide complexes, which can dissociate under mild conditions and release free cyanide, may affect the performance of the 200 West P&T fluidized bed reactor. Since the strong cyanide-transition metal complexes are typically inert and non-reactive under wide range of pH/Eh conditions and resistant to the microbial degradation, ferrocyanide and its oxidized couple ferricyanide $Fe(CN)_6^{3-}$ are of most interest.

The analytical method developed here is capable of differentiating and quantifying ferrocyanide retained on the DOWEX 21K resin. An analytical method for the selective and rapid determination of ferrocyanide in solution was first developed. The proposed method is based on the initial oxidation of ferrocyanide to ferricyanide followed by the measurement of the ferricyanide aqueous concentrations before and after oxidation using UV-vis absorbance.

The UV-vis spectra of $Fe(CN)_6^{4-}$ and $Fe(CN)_6^{3-}$ contain two primary regions of interest. The ultraviolet region exhibits an intense absorbance band with a high molar extinction coefficient for both molecules corresponding to the ligand to metal charge transfer. The visible region captures the d→d transition of both molecules. The use of the ultraviolet region for analytical measurements of ferro/ferricyanide presents multiple challenges. First, the signals of the $Fe(CN)_6^{4-}$ and $Fe(CN)_6^{3-}$ signal overlap, which causes interfering signals if both oxidation states are present. Second, the signal position and intensity are sensitive to even small changes in the solution composition (i.e., presence of other ions and ionic strength). Third, this region exhibits the signal for many environmentally present salts including nitrate, which can interfere with the ferro/ferricyanide signal.

The visible region is very different in nature. Ferrocyanide has O_h symmetry, which displays a weak and poorly suited quantification purposes signal, whereas ferricyanide exhibits much stronger absorbance due to the distortion in the molecular symmetry and greatly increased molar extinction coefficient at 420 nm to 1.04×10^3 (Appleby and Morton 1959; Cohen and Plane 1957). Additionally, changes in the solution composition have little effect on the molar absorptivity, or peak position of this electronic transition. This enables a pathway to determine the concentration of both ferro and ferricyanide in solution, by first measuring the absorbance at 420 nm to determine ferricyanide concentration, oxidizing all ferrocyanide, once again measuring the absorbance at 420 nm and determining the concentration of ferrocyanide by difference. The standard reduction potential of ferricyanide to ferrocyanide is considered to be 0.43 V (Clark et al. 1925), although the redox couple is known to vary due to ionic strength and matrix variations; thus, a value of 0.41 to 0.43 V should be considered (O'Reilly 1973). For this study, sodium hypochlorite was selected as the oxidant, as it is readily available, will not optically interfere in the visible region, and has a sufficient standard reduction potential of 1.63 V under acidic conditions, and 0.89 V under basic conditions (Cotton and Wilkinson 1972). This allows for the oxidation of ferrocyanide to ferricyanide without an interfering spectroscopic signal.

The second step in the method development is focused on developing a selective quantitative method for stripping ferrocyanide, which is needed to eliminate optical interferences such as uranyl, which would hamper quantification of the ferrocyanide in solution. To this end, ferrocyanide retention on the pristine Dowex 21K resin was measured, allowing monitoring of the recovery of ferrocyanide. A wide range of eluents were tested to identify the right composition for its selective stripping. The developed protocol is was tested using spent P&T resin and verified using independent measurement.

4.3.1 Stripping of Ferrocyanide-Loaded Dowex 21K XLT Resin

To develop a method for the quantification of ferrocyanide in aqueous solution, a series of calibration curves were generated using $K_4Fe(CN)_6$ in the appropriate stripping matrix treated with NaOCl. Representative spectral overlays collected from 0.03 to 1 mM $Fe(CN)_6^{3-}$ calibration solutions are shown in Figure 16, along with a calibration curve plotted from absorbance intensities at 420 nm.

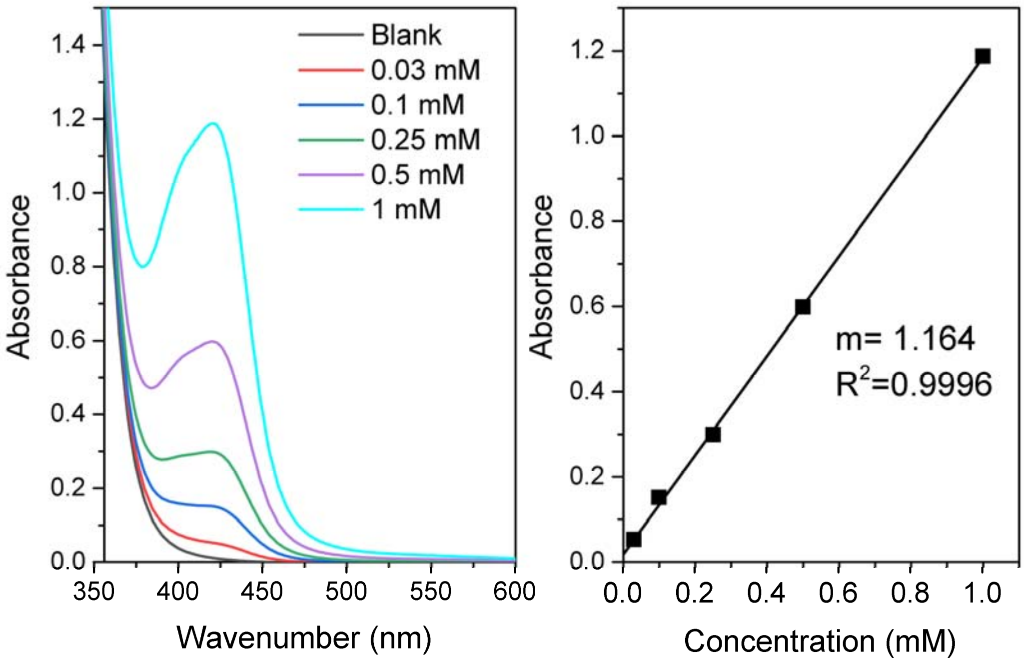

Figure 16. (left) Absorbance Spectra of 0.03 – 1 mM $Fe(CN)_6^{3-}$ in 0.5 M NaCl Collected after Quantitative Oxidation of the $Fe(CN)_6^{4-}$ with NaOCl and (right) Corresponding Calibration Curve Using Intensities at 420 nm.

Extinction coefficients, R^2, detection limits, and concentration of $Fe(CN)_6^{4-}$ in the various stripping solutions are shown in Table 14. The average extinction coefficient for $Fe(CN)_6^{3-}$ by this method, can be determined using the Beer-Lambert law:

$$A = \varepsilon b c \tag{2}$$

where *A* is absorbance, *b* is the cell pathlength (10 mm), and *c* is the concentration. Using the calibration curves in the different matrices and plotting the concentration vs. the absorbance, the molar absorptivity of ferricyanide can be calculated from the slope. With exclusion of the Na_2SO_4 matrix, the molar absorptivity for ferricyanide was found to be 1119(±48) cm^{-1} M^{-1}, in agreement with the literature value of 1040 cm^{-1} M^{-1} (Appleby and Morton 1959; Cohen and Plane 1957).

Table 14. Extinction Coefficients, R^2 Values of Calibration Plots, and Detection Limits Corresponding to the Various Solution Matrices Used to Strip Ferrocyanide from Dowex 21K Resin. The average concentration of ferrocyanide (mM) in the supernatant and percent recovery are also provided.

Stripping Matrix	Extinction Coefficient cm^{-1} M^{-1}	Detection Limit (mM) at Confidence Interval of		R^2	Avg. Concentration		% recovery
		95%	99.9%		mM	µg/g	
2 M $CaCl_2$$^{(a)}$	1.139	0.001	0.23	0.9982	1.993	12419	90(±0.6)
0.1 M NaOAc pH 5	(d)	NM	NM	(d)	ND	NA	N/A
1 M $NaHCO_3$$^{(a)}$	1.197	0.006	0.32	0.9985	0.010	65	0.5(±0.1)
0.9 M $Na_2SO_4$$^{(a)}$	0.615	0.02	0.07	0.9917	0.0148	90	0.7(±0.0)
0.05 M KCl$^{(a)}$	1.0945	NM	NM	0.9992	ND	NA	N/A
0.5 M KCl$^{(a)}$	1.0593	NM	NM	0.9983	-	NA	4.0(±0.1)
2 M KCl$^{(a)}$	(c)	(c)	(c)	(c)	-	NA	59(±3)
0.5 M NaCl$^{(b)}$	1.164	0.008	0.01	0.9996	0.0692	443	47.2(±0.2)
1 M NaCl$^{(b)}$	1.083	0.009	0.02	0.9979	0.7935	5193	48(±1)
2 M NaCl$^{(b)}$	1.098	0.008	0.01	0.9989	1.3953	8819	80(±2)
3 M NaCl$^{(b)}$	1.091	0.008	0.02	0.9976	1.3802	8440	77(±3)
4 M NaCl$^{(b)}$	1.135	0.008	0.02	0.9991	1.3596	8351	76(±9)
4 M NaCl$^{(a)}$	1.135	0.008	0.02		1.8059	11330	83
5 M NaCl$^{(a)}$	1.048	0.005	0.01	0.9960	2.171	13165	96(±6)

(a) K4Fe(CN)6 loaded from 50 mM NaHCO3 solution at pH 8.1
(b) K4Fe(CN)6 loaded from 10 mM MgCl2 solution with resin pre-equilibrated with concentrated (10x) GW simulant
(c) Measured on 0.5 M KCl calibration curve based on the assumption the change in extinction coefficient is minimal
(d) No absorbance observed from supernatant; not quantified by calibration curve
ND = not detected
NM = not measured

Ferrocyanide detection limits using UV-vis measurements were determined using the graphical approach at 99.9% confidence level using the following equation:

$$C_L = \frac{k s_B}{m \pm t_{\propto} s_m} \qquad (3)$$

where k=3 corresponding for 99.9% confidence interval, s_B is the standard deviation of blank measurements, m is the slope, t_α is the value from the student t table for 99.9% confidence, and s_m is the standard deviation of the slope (Long 1983). The t_α value for n-2 degrees of freedom was used for linear regression analysis. The detection limit for 95% confidence can be calculated using k=2 and the student t values for the 95% confidence interval. Detection limits for 95% confidence are listed in Table 14 for comparison and the detection limits decrease by at least an order of two for all matrices studied.

No observable stripping is seen within the detection limits of the technique (DL < 0.02 mM) for all solutions of low ionic strength, and the 1 M $NaHCO_3$ solution, demonstrating a high retention of $Fe(CN)_6^{4-}$ for Dowex 21K. Transitioning to higher ionic strength strip solutions, the $Fe(CN)_6^{4-}$ resin loaded from the carbonate matrix showed improved stripping, with 6.2% of the ferrocyanide stripped from the resin by 0.5 M KCl, 59% stripped by 2.0 M KCl, 83% stripped by 4 M NaCl, and near quantitative stripping observed for 5 M NaCl.

The dependence of NaCl solution on the stripping of $Fe(CN)_6^{4-}$ was explored using the resin first saturated with groundwater simulant, followed by loading with nominally 2.75 mM $Fe(CN)_6^{4-}$ in 10 mM $MgCl_2$. The percent $Fe(CN)_6^{4-}$ stripped with respect to concentration of NaCl up to concentrations of 4 M is plotted in Figure 17. The results indicate that the stripping plateaus around 80% for 2 to 4 M. The 4 M

NaCl strip of $Fe(CN)_6^{4-}$ loaded from carbonate and $MgCl_2$ matrices are within error of one another, suggesting minimal impact of loading matrix for analysis of the stripping solution using this method. These NaCl strips were also analyzed for total cyanide and the results are discussed below.

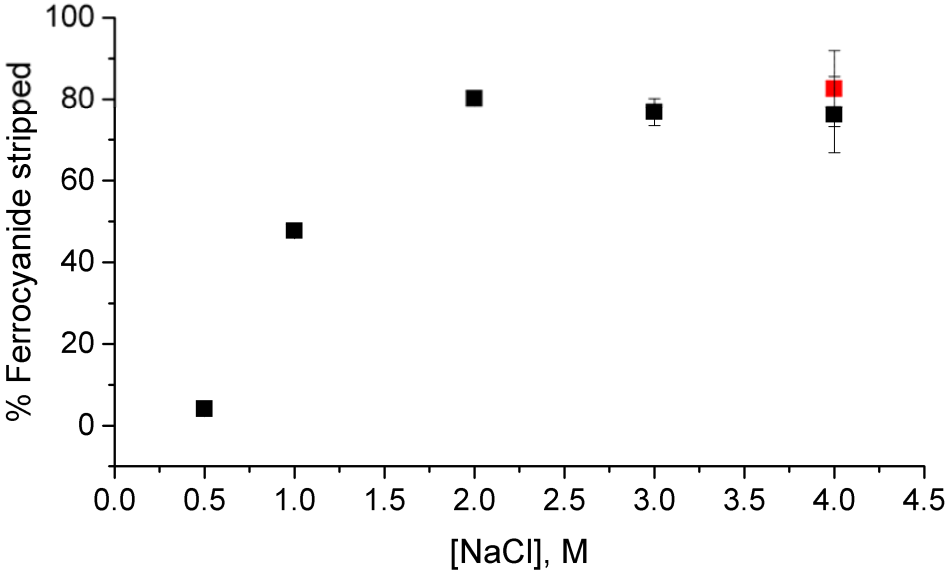

Figure 17. The Effect of NaCl Concentration on the Stripping Efficiency of $Fe(CN)_6^{4-}$ Loaded on Dowex21K from the $MgCl_2$ Matrix and (red) $Fe(CN)_6^{4-}$ Loaded from 50 mM Carbonate.

It is important to note that Mg^{2+} is a problematic constituent for this analytical technique, when present in excessive concentrations. For example, an attempt to quantify the 2.75 mM $Fe(CN)_6^{4-}$ in 10 mM $MgCl_2$ stock solution resulted in precipitation after addition of the NaOCl. The same precipitation was observed when attempting to strip both loaded resin as well as the actual P&T resin sample with 2 M $MgCl_2$, indicating the problem is indeed derived from the presence of Mg^{2+}.

The total cyanide analysis was also performed on the laboratory-loaded resin samples. The results from spectrophotometric analysis for the resin loaded from the $MgCl_2$ matrix created unreliable data for any NaCl concentrations > 0.5 M. The sample formed a dark purple precipitate upon color development in the spectrophotometric step. The precipitate was filtered before quantification of total CN^-, but resulted in poor recovery of CN^- in the stripping solutions. The same precipitate was formed for the stripping of the P&T resin sample with $MgCl_2$. That information, coupled with the significantly low concentration of CN^- measured in the strip solutions, indicates that the precipitate is likely $MgFe(CN)_6^{2-}$ species.

The total cyanide analysis of 0.5 M NaCl eluent, where no precipitate was formed during color development, is in excellent agreement with the concentration of CN^- determined from the UV-vis NaOCl method with concentrations of 65.6 and 67.1 µg CN^-/g resin, respectively. However, this only equates to approximately 4% stripping, and thus a minimal impact of Mg^{2+} on the quantification of CN^-.

Near quantitative stripping of $Fe(CN)_6^{4-}$ was achieved with 2 M $CaCl_2$ and 5 M NaCl. Moreover, 5 M NaCl also quantitatively stripped the U from the U-loaded resin, but the same was not observed for $CaCl_2$. The fact that the $CaCl_2$ efficiently strips both I-127 and $Fe(CN)_6^{4-}$ supports the hypothesis for precipitation of the $Ca/U/CO_3$ species, resulting in poor recovery of U for that stripping matrix.

Based on this information, a protocol for the sequential stripping of the loaded DOWEX 21K resin has been developed. First, U(VI) can be selectively stripped using 1 M $NaHCO_3$ which does not remove

$Fe(CN)_6^{4-}$ from the resin followed by the chloride strip to elute $Fe(CN)_6^{4-}$. This eliminates U(VI) spectral interference.

4.3.2 Stripping of 200 West P&T Resin

The total cyanide was quantified in the strips of P&T resin, and the results are shown in Table 15. Note that the total cyanide was measured in these samples, whereas method development listed above is for the detection and quantification of $Fe(CN)_6^{4-}$; thus, the results cannot be directly correlated to the stripping efficiencies mentioned above.

Table 15. Total CN^- Concentration in the Stripping Solutions of 200 West P&T resin B3FM14 as Determined by Spectrophotometric Analysis.

Stripping Solution	CN^-			Fe		Mole Ratio CN:Fe
	µg/g	mol/g	%RSD	µg/g[(a)]	mol/g	
5 M NaCl	98	3.8E-06	12	539	9.7E-06	0.4
0.9 M $MgSO_4$	21	7.9E-07	11	5.4	9.7E-08	8
2 M $CaCl_2$	82	3.2E-06	6	456	8.2E-06	0.4
2 M $MgCl_2$[(b)]	77	2.9E-06	43	274	4.9E-06	0.6
0.9 M Na_2SO_4	13	5.1E-07	1	5.2	9.4E-08	5.4
1 M NaCl	90	3.4E-06	1	118	2.1E-06	1.6
0.1 M NaOAc pH 5	ND	NA	NA	ND	NA	-

(a) Quantified by ICP-OES

(b) Sample formed a very dark purple/black color once the PBA reagent was added. Precipitate formed during color development. Filtered sample with a 0.45µm PVDF filter before reading in spectrophotometer.

Results indicate that chloride matrices strip the highest concentration of total cyanide, resulting in the order of stripping efficiency of 5 M NaCl >1 M NaCl > 2 M $CaCl_2$. Both sulfate stripping solutions poorly strip cyanide, judging by the significantly lower concentrations observed for those two strip solutions tested. This is consistent with the poor U(VI) stripping by the sulfate solutions as well.

The mole ratio of CN:Fe is 0.4 for both 5 M NaCl and 2 M $CaCL_2$ stripping solutions, whereas the expected mole ratio would be 6 if all the CN^- were present as $Fe(CN)_6^{4-}$. This indicates that the vast majority of Fe originates from the other Fe species on the 200 West P&T resin. This is consistent with previous work, where high concentrations of Fe were identified on the TcO_4^- IX resin (Levitskaia et al. 2017).

To apply the UV-vis method to the actual P&T samples, selective stripping is necessary to remove the U(VI), which absorbs in the 420 nm range. The 1 M $NaHCO_3$ strips uranium quantitatively, but does not strip $Fe(CN)_6^{4-}$ from the resin. This is advantageous in quantifying $Fe(CN)_6^{4-}$ on the spent P&T resin because U can be selectively stripped first, so U(VI) does not interfere with quantification by UV-vis.

The two eluents with the best performance for stripping ferrocyanide, 2 M $CaCl_2$ and 5 M NaCl, were tested in the stripping of the actual P&T resins. First, the uranium was removed using 1 M $NaHCO_3$, which was shown to exhibit very poor stripping of $Fe(CN)_6^{4-}$, but quantitative stripping of uranium. The resin was contacted with fresh 1 M $NaHCO_3$ three times and the sequential supernatants were progressively less yellow in color. The resin was then subjected to the $Fe(CN)_6^{4-}$ and the resulting supernatant was dark yellow for the 5 M NaCl strip and lighter yellow for the 2 M $CaCl_2$ strip. Two dilutions (2x and 20x) of each strip were performed in the corresponding matrix and treated with NaOCl. The UV-vis of the two P&T strip samples are shown in Figure 18.

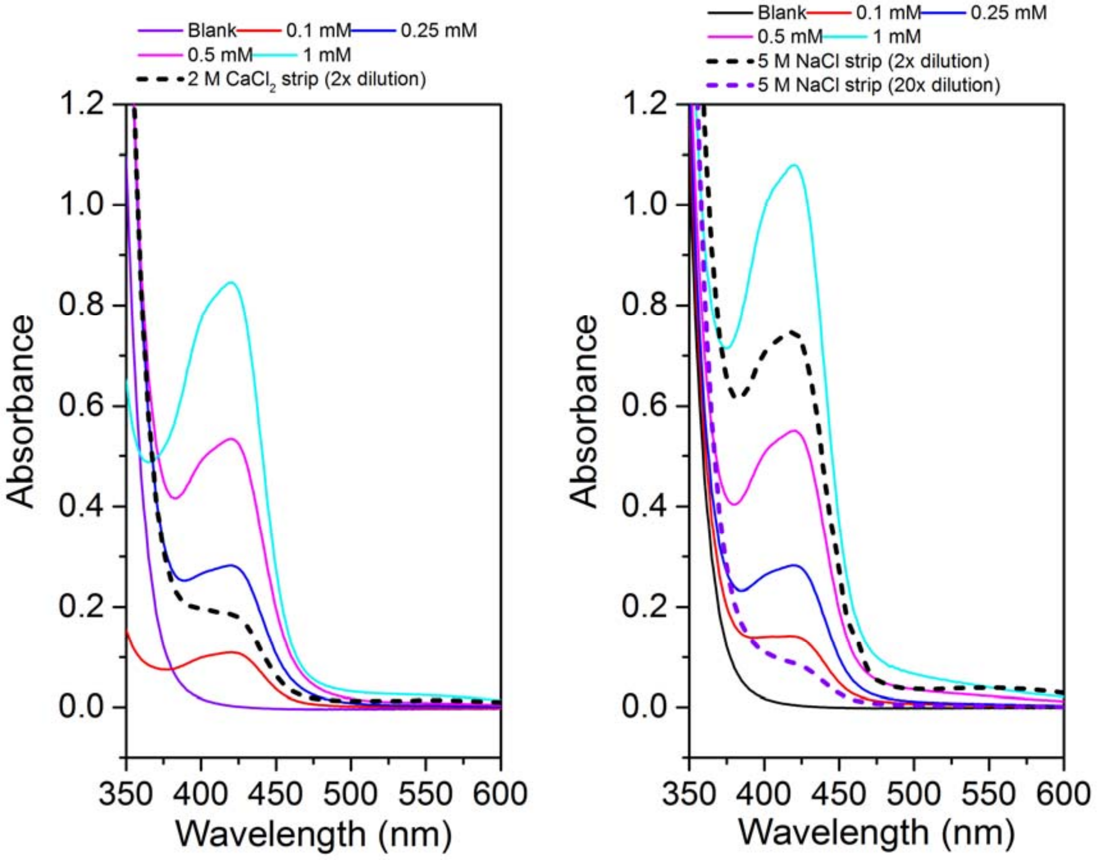

Figure 18. UV-vis Spectra of 200 W P&T Resin Stripped with 1 M $NaHCO_3$ to Remove Uranium, followed by Stripping with (left) 2 M $CaCl_2$ and (right) 5 M NaCl to Determine the Concentration of $Fe(CN)_6^{4-}$ Retained by the Resin.

The absorbance of the stripping solutions before oxidation was subtracted from the corresponding solution absorbance after NaOCl treatment, and the concentration of CN^- calculated from the $Fe(CN)_6^{4-}$ retained by the resin was found to be 86 µg/g and 1117 µg/g from 2 M $CaCl_2$ and 5 M NaCl stripping matrices, respectively. The corresponding concentrations obtained independently from the total CN^- method were 82 and 98 µg/g for $CaCl_2$ and NaCl. This suggests that while agreement of the developed method was observed using 2 M $CaCl_2$ eluent (assuming that ferrocyanide is the dominant cyanide species on the resin), the NaCl strip contained constituents presenting optical interference after oxidation with NaOCl.

Further method development is warranted to refine selective stripping parameters as other contaminants, such as minute concentrations of uranium remaining on the resin, as well as chromium, are likely to interfere in quantification of $Fe(CN)_6^{4-}$. The contribution of these absorbing species would lead to artificially high concentrations of $Fe(CN)_6^{4-}$ retained by the resin. Additionally, the total CN^- method formed a white precipitate during analysis for both of these eluates, which solidifies the need for an additional method development for cyanide in general in the groundwater matrix. The method for quantifying ferro/ferricyanide presented here has proven quantitative stripping in control samples, but optimization is necessary to quantify ferro/ferricyanide in a complex matrix, such as that present from co-contaminants in the groundwater.

5.0 Quality Assurance

The results presented in this report originate from work governed by the PNNL Nuclear Quality Assurance Program (NQAP). The NQAP implements the requirements of U.S. Department of Energy Order 414.1D, *Quality Assurance*, and 10 CFR 830 Subpart A, *Quality Assurance Requirements*. The NQAP uses ASME NQA-1-2012, *Quality Assurance Requirements for Nuclear Facility Applications*, as its consensus standard and NQA-1-2012 Subpart 4.2.1 as the basis for its graded approach to quality.

Two quality grading levels are defined by the NQAP:

Basic Research - The required degree of formality and level of work control is limited. However, sufficient documentation is retained to allow the research to be performed again without recourse to the original researcher(s). The documentation is also reviewed by a technically competent individual other than the originator.

Not Basic Research - The level of work control is greater than basic research. Approved plans and procedures govern the research, software is qualified, calculations are documented and reviewed, externally sourced data is evaluated, and measuring instrumentation is calibrated. Sufficient documentation is retained to allow the research to be performed again without recourse to the original researcher(s). The documentation is also reviewed by a technically competent individual other than the originator.

The work supporting the results presented in this report was performed in accordance with the Not Basic Research grading level controls.

A portion of this work (e.g., the chemical analyses of the liquid samples from the batch and column experiments) used PNNL’s Environmental Sciences Laboratory (ESL). The ESL operates under a dedicated QA plan that complies with the HASQARD (DOE/RL-96-68), Rev. 3. The ESL implements HASQARD through CAWSRP. Data Quality Objectives established in CAWSRP were generated in accordance with HASQARD requirements.

6.0 Conclusions

After processing 5 million gallons of contaminated groundwater, equating to nearly 20 kg of uranium, the lead column for the uranium removal IX treatment train was removed from service and analyzed using destructive and nondestructive techniques. Wet oxidation was used to destroy the resin framework and quantify uranium and co-contaminants sorbed to the resin by ICP-OES and MS. Analysis of uranium-loaded Dowex 21K as a control indicated quantitative (99±1%) recovery of uranium upon two sequential digestions. By this method, the average U-238 loading for the three P&T samples (B3FM14, B3FM23, and B3FM32) was found to be 18.5 mg U/g of resin.

Appreciable concentrations of calcium, sulfur, sodium, and iron were also found on the spent P&T resin. The concentration of sodium and boron quantified in the dissolution of conditioned Dowex 21K was consistent with the values reported for the P&T samples, indicating Na and B are either from dissolution of the resin itself or potentially the glassware used in the digestions. Calcium is reported for dissolution of conditioned Dowex 21K, the U-loaded control, as well as the P&T samples. The calcium concentration reported for the P&T samples is slightly elevated in comparison to the control dissolutions, but reproducibility of replicate measurements is poor, with a range of 6.2 to 16.3 mg Ca/g resin.

Significant quantities of sulfur and iron were retained by the resin at 7.7 mg S/g resin and 3.1 mg Fe/g resin. The sulfur exists as the inorganic sulfate anion, which was found to have strong affinity towards DOWEX 21K. Additionally, the P&T resin was found to retain small quantities of iodine and chromium. However, there was no detectable concentration of Tc-99 on the spent P&T resin by ICP-MS.

Stripping studies with uranium-loaded Dowex 21K resin, as a control, indicated that 1 M HCl and 1 M $NaHCO_3$ stripped the uranium quantitatively. Comparing the concentration of U from stripping the spent P&T samples to the U concentration determined from wet-oxidation experiments can provide stripping efficiencies for different eluents. For the spent P&T, 1 M HCl, 1 M $NaHCO_3$, *and* 5 M NaCl have the highest concentrations of uranium in the strip solution. The uranium on the control resin was loaded as a uranium carbonate complex; thus, one explanation for the enhanced stripping of U on the spent P&T resins with 5 M NaCl is a difference in uranium speciation on the P&T resin, which forms a weaker complex than the U-carbonate species (such as a uranium-sulfate complex) and is more readily stripped.

Other constituents quantified in strip solutions include chromium, cobalt, I-127, and sulfur. Strip solutions were analyzed by IC for inorganic anions and a significant concentration of sulfate and nitrate was measured. The sulfate concentration in chloride eluates was 26.4 mg/g resin, which equates to approximately 8.8 mg S/g resin in agreement with the value of 7.7 mg S/g resin obtained by the wet oxidation method.

The concentration of I-127 from chloride stripping solutions remained fairly constant at 45 ± 3 μg/g resin. This was the highest concentration of I-127 of all analysis.

GEA is a nondestructive technique that is useful for quantifying radionuclides retained by Dowex 21K. Results indicate that Co-60, U-235, U-238, and I-129 were the primary isotopes identified in all three resin samples. The activities of U-235 and U-238 averaged 11.9 and 264 Bq/g, which translates to 149 μg U-235/g and 21210 μg U-238/g resin, respectively. The total U concentration determined from GEA analysis was 21.1 mg U/gram resin, which is in good agreement with uranium concentrations quantified by wet-oxidation and stripping studies on spent P&T resin samples.

Quantification of I-129 by GEA analysis indicated 0.11 μg I-129/g resin. Comparing the I-127 concentrations from ICP-MS to the I-129 concentration from nondestructive GEA analysis gives a ratio of

I-127/I-129 of approximately 400, which is 2.5 lower relative to the ratio calculated on the Purolite IX train at the 200 West P&T Facility (Levitskaia et al. 2017).

Speciation diagrams were created from stability constants reported in the literature to target sorption behavior of different uranium species. Anionic uranium/calcium species are reported in the literature and those values were included in the speciation model. However, only a few reports are available regarding formation of the complexes of the uranyl carbonates with Mg^{2+}, and only single species $MgUO_2(CO_3)_3^{2-}$ have been reported in the literature at pH 8 along with the corresponding association constant (Dong and Brooks 2006, 2008). It is not clear whether other magnesium-uranyl complexes can be formed under different conditions, and they could potentially impact IX treatment.

Uranium speciation is highly sensitive to carbonate concentrations; however, uranium sorption onto DOWEX 21K resin at $pH > 6$ was quantitatively complete in all matrices tested. At $pH < 6$, the sorption is reduced due to the dominance of the neutral UO_2CO_3 species in the solution. The formation of the anionic $UO_2(CO_3)_2^{2-}$ and $UO_2(SO_4)_2^{2-}$ complexes on the resin drives U(VI) sorption from these solutions. Uranium was found to be in the +6 oxidation state when the resin was analyzed by XAS and XPS. The XPS data indicate two environments for U, as well as two sulfur environments, which is consistent with sulfate bound to either alkyl ammonium sites of the resin or uranyl. This accounts for the formation of uranium sulfate species on the resin.

Ferrocyanide, which entered the groundwater as secondary waste from in situ Cs-137 sequestration in Hanford storage tanks, was shown to sorb quantitatively to Dowex 21K from both HCO_3^- and $MgCl_2$ matrices tested. This work focused on designing a method to quantify ferrocyanide sorbed on Dowex 21K resin by stripping the ferrocyanide, oxidizing the iron center to ferricyanide, and quantifying using UV-vis spectroscopy. A variety of different matrices were investigated for stripping a ferrocyanide-loaded control sample. Matrices with the best stripping efficiency included 2 M $CaCl_2$ and 5 M NaCl with recoveries of 93 and 97%, respectively. The detection limit for 5 M NaCl strips using this method was found to be 0.01 mM at 99.9% confidence as compared to 0.23 mM for $CaCl_2$.

Independent measurements of total cyanide were performed and preliminary results verify that the UV-vis method of oxidizing ferrocyanide using select stripping solutions is a valid approach. One problem that was encountered with independent total cyanide quantification, derived from the EPA Methods 9010B and 9014, is related to magnesium that appeared to interfere with the measurements by causing a stark color-change followed by a white precipitate. Magnesium did not pose interference to the UV-vis method to quantify ferro/ferricyanide.

Finally, selective stripping of uranium from ferrocyanide is advantageous when applying this method to the spent P&T samples. Uranium absorbs in the same spectral region as ferrocyanide; thus, the presence of uranium in the strip solution will be detrimental to detection/quantification of ferrocyanide. Stripping uranium from the P&T samples using 1 M $NaHCO_3$, followed by stripping with 2 M $CaCl_2$ or 5 M NaCl, was demonstrated for stripping and quantifying ferrocyanide.

7.0 References

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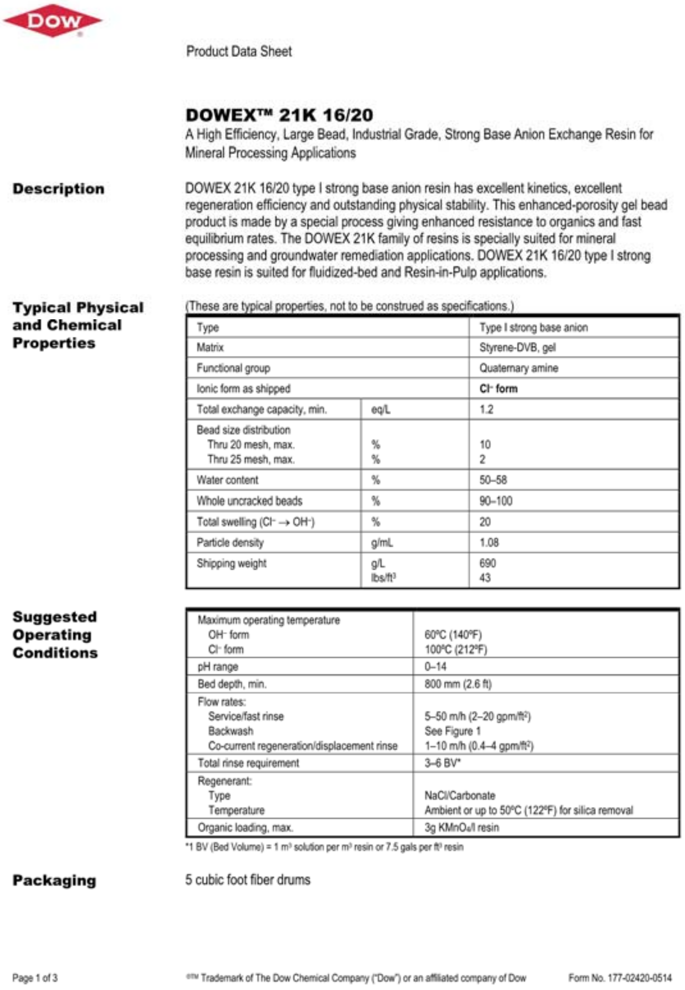
Appendix A

Dowex 21K 16/20 Product Sheet

Appendix A

Dowex 21K 16/20 Product Sheet



Product Data Sheet

DOWEX™ 21K 16/20

A High Efficiency, Large Bead, Industrial Grade, Strong Base Anion Exchange Resin for Mineral Processing Applications

Description

DOWEX 21K 16/20 type I strong base anion resin has excellent kinetics, excellent regeneration efficiency and outstanding physical stability. This enhanced-porosity gel bead product is made by a special process giving enhanced resistance to organics and fast equilibrium rates. The DOWEX 21K family of resins is specially suited for mineral processing and groundwater remediation applications. DOWEX 21K 16/20 type I strong base resin is suited for fluidized-bed and Resin-in-Pulp applications.

Typical Physical and Chemical Properties

(These are typical properties, not to be construed as specifications.)

Type		Type I strong base anion
Matrix		Styrene-DVB, gel
Functional group		Quaternary amine
Ionic form as shipped		**Cl^- form**
Total exchange capacity, min.	eq/L	1.2
Bead size distribution Thru 20 mesh, max. Thru 25 mesh, max.	 % %	 10 2
Water content	%	50–58
Whole uncracked beads	%	90–100
Total swelling ($Cl^- \rightarrow OH^-$)	%	20
Particle density	g/mL	1.08
Shipping weight	g/L lbs/ft^3	690 43

Suggested Operating Conditions

Maximum operating temperature OH^- form Cl^- form	 60ºC (140ºF) 100ºC (212ºF)
pH range	0–14
Bed depth, min.	800 mm (2.6 ft)
Flow rates: Service/fast rinse Backwash Co-current regeneration/displacement rinse	 5–50 m/h (2–20 gpm/ft^2) See Figure 1 1–10 m/h (0.4–4 gpm/ft^2)
Total rinse requirement	3–6 BV*
Regenerant: Type Temperature	 NaCl/Carbonate Ambient or up to 50ºC (122ºF) for silica removal
Organic loading, max.	3g $KMnO_4$/l resin

*1 BV (Bed Volume) = 1 m^3 solution per m^3 resin or 7.5 gals per ft^3 resin

Packaging

5 cubic foot fiber drums

Page 1 of 3

®™ Trademark of The Dow Chemical Company ("Dow") or an affiliated company of Dow

Form No. 177-02420-0514

Appendix B

Dowex 21K XLT Product Sheet

Appendix B

Dowex 21K XLT Product Sheet

Product Information

DOWEX 21K XLT

A Uniform Particle Size, High Capacity, Strong Base Anion Exchange Resin for Mineral Processing Applications

Product	Type	Matrix	Functional group
DOWEX* 21K XLT	Type I strong base anion	Styrene-DVB, gel	Quaternary amine

Guaranteed Sales Specifications		
Total exchange capacity, min.	eq/L	1.4
Water content	%	50 - 60
Bead size distribution		
Volume median diameter	µm	525 - 625
Uniformity coefficient, max.	%	1.1

Typical Physical and Chemical Properties		
Ionic form as delivered		Cl^-
Total swelling (Cl ☐ OH), approx.	%	18 - 20
Whole uncracked beads, min.	%	90
Particle density, approx.	g/mL	1.08
Shipping weight, approx.	g/L lbs/ft^3	670 42

Recommended Operating Conditions

☐ Maximum operating temperature:	
OH^- form	60°C (140°F)
Cl^- form	100°C (212°F)
☐ pH range	0 - 14
☐ Bed depth, min.	800 mm (2.6 ft)
☐ Flow rates:	
Service/fast rinse	5 - 60 m/h (2 - 24 gpm/ft^2)
Backwash	See figure 1
Co-current regeneration/displacement rinse	1 - 10 m/h (0.4 - 4 gpm/ft^2)
Counter-current regeneration/displacement rinse	5 - 20 m/h (2 - 8 gpm/ft^2)
☐ Total rinse requirement	3 - 6 Bed volumes
☐ Regenerant:	
Type	NaCl/Carbonate
Temperature	Ambient or up to 50°C (122°F) for silica removal
☐ Organic loading, max.	3g $KMnO_4$/L resin

* Trademark of The Dow Chemical Company
DOWEX Ion Exchange Resins

Appendix C

Complete ICP-MS and OES analytical results for B3FM14, B3FM23, and B3FM32 resin strips

Appendix C

Complete ICP-MS and OES analytical results for B3FM14, B3FM23, and B3FM32 resin strips

Table C.1. Analytical ICP-OES and MS results for stripping of P&T resins B3FM14, B3FM23, and B3FM32 with 1 M HCl, 1 M $NaHCO_3$, and 1.5 M NaOH. Nominally 0.1 g of resin to 6 mL of solution.

	B3FM14						B3FM23						B3FM32					
	1 M HCl		1 M $NaHCO_3$		1.5 M NaOH		1 M HCl		1 M $NaHCO_3$		1.5 M NaOH		1 M HCl		1 M $NaHCO_3$		1.5 M NaOH	
	µg/g	RSD	µg/g	RSD	µg/g	RSD	µg/g	RSD	µg/g	RSD	µg/g	RSD	µg/g)	RSD	µg/g	RSD	µg/g	RSD
Aluminum	ND	NA	596	NA	667	3	ND	NA	297	17	475	26	ND	NA	314	26	408	17
Barium	ND	NA	5.7	NA	ND	NA	ND	NA	ND	NA	ND	NA	ND	NA	ND	NA	ND	NA
Barium 138	ND	NA	4.3	3	ND	NA	ND	NA	5.1	8	ND	NA	ND	NA	4.3	16	ND	NA
Cadmium 114	ND	NA	ND	NA	ND	NA	ND	NA	ND	NA	ND	NA	ND	NA	ND	NA	ND	NA
Calcium	ND	NA	193	NA	ND	NA	ND	NA	ND	NA	ND	NA	ND	NA	208	NA	ND	NA
Chromium	45	6	26	4	26	3	49	6	29	1	29	6	51	13	26	4	31	6
Chromium 52	42	7	29	7	26	12	46	6	30	1	28	8	48	14	27	3	29	1
Cobalt	ND	NA	2.6	NA	ND	NA	ND	NA	ND	NA	ND	NA	ND	NA	ND	NA	ND	NA
Copper 63	ND	NA	13	3	16	4	ND	NA	12.6	25	17	13	ND	NA	11	4	17	3
Iodine 127	16	13	31	9	7.0	5	19	1	31.8	0	7.7	8	19	9	31	4	8.0	4
Iron	337	77	70	22	79	NA	160	2	65	NA	ND	NA	240	46	60	19	ND	NA
Lead	ND	NA	17	NA	ND	NA	ND	NA	ND	NA	ND	NA	ND	NA	ND	NA	ND	NA
Lead 208	ND	NA	ND	NA	ND	NA	ND	NA	ND	NA	ND	NA	ND	NA	ND	NA	ND	NA
Magnesium	ND	NA	52	16	ND	NA	ND	NA	48	1	ND	NA	ND	NA	48.1	13	ND	NA
Manganese	ND	NA	2.7	NA	ND	NA	ND	NA	ND	NA	ND	NA	ND	NA	ND	NA	ND	NA

Molybdenum 98	4.2	53	4.9	0	4.0	9	3.8	40	4.8	12	2.8	13	2.7	NA	3.6	3	3.0	11
Potassium	ND	NA	ND	NA	ND	NA	ND	NA	ND	NA	ND	NA	ND	NA	ND	NA	ND	NA
Ruthenium 104	ND	NA	ND	NA	ND	NA	ND	NA	ND	NA	ND	NA	ND	NA	ND	NA	ND	NA
Sodium	1692	24	1250847	15	1859355	6	669	NA	1308134	4	1793537	5	626	NA	1210559	13	1930042	4
Sulfur	8259	5	9132	7	7838	2	8544	2	9320	1	8150	7	8387	3	8449	3	8517	2
Titanium	ND	NA	8.4	NA	ND	NA	ND	NA	ND	NA	ND	NA	ND	NA	ND	NA	ND	NA
Zinc	ND	NA	ND	NA	ND	NA	ND	NA	ND	NA	ND	NA	ND	NA	ND	NA	ND	NA
Uranium 238	19148	5	17372	2	2009	1	20640	2	19487	4	1902	10	19843	4	18041	1	1952	3

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