Part II: Predicting Performance of DOWEX 21K Resin for Remediation of Comingled Contaminants in Groundwater

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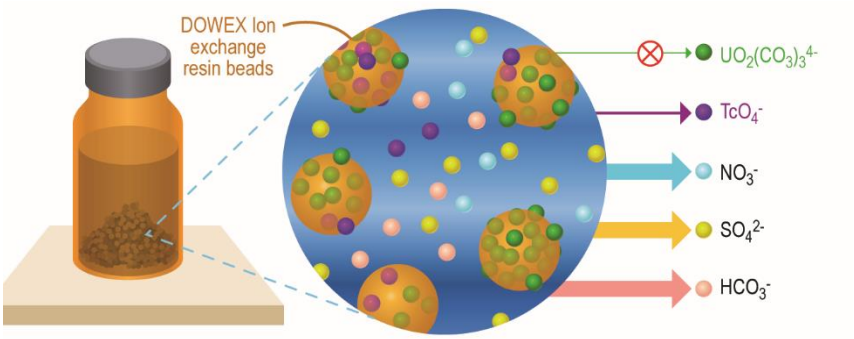
Abstract

The selectivity of ion exchange (IX) resins for aqueous contaminant removal can be impacted by changing concentrations of competing natural groundwater ions. In a two-part investigation, the Hanford Site 200 West Area pump-and-treat (P&T) facility in Washington State, USA is used as a case study to evaluate the performance of two IX resins for groundwater treatment: Purolite® A532E for pertechnetate (TcO_4^-) removal, explored in Part I, and DOWEX 21K (DOWEX) for uranium (U) removal. In Part II, DOWEX selectivity for U, as uranyl carbonate species, and uptake kinetics is quantified in a series of laboratory-scale aqueous batch experiments containing Hanford-relevant concentrations of competing anions nitrate (NO_3^-), sulfate (SO_4^{2-}), chloride (Cl^-), and carbonate (CO_3^{2-}), as well as co-mingled contaminant TcO_4^-. The results demonstrate that DOWEX trimethylammonium functional groups are highly selective for U carbonate species (85% - 100% uptake) under all conditions investigated. Only NO_3^- concentrations of 100 mM were shown to decrease U removal, with the extent (85% – 99%) depending on competing anion concentrations present in solution. However, at the highest NO_3^- concentrations reported for groundwaters treated at the P&T facility (25 mM), the effect on U uptake is minimal. The batch sorption results are modeled to obtain chloride normalized equilibrium exchange coefficients (K) for predicting DOWEX performance: $K_{SO4--/Cl-}$ = 2.0, $K_{NO3-/Cl-}$ = 5.0, $K_{HCO3-/Cl-}$ = 1.5, $K_{TcO4-/Cl-}$ = 2000, and $K_{U/Cl-}$ = 50,000. These K values predict little effect of current and future influent chemistries on U removal by DOWEX, where both uranyl carbonate species and TcO_4^- are removed such that effluent concentrations meet groundwater treatment requirements.

Key words: pump-and-treat; uranium; technetium, anion exchange; Hanford

TOC Graphic:



Highlights:

- **i.** Targeted batch experiments parameterize DOWEX 21K site-specific anion selectivity.
- **ii.** U(VI) uptake by DOWEX unaffected by competing anions TcO_4^-, SO_4^{2-}, CO_3^{2-}, and Cl^-.
- **iii.** U(VI) uptake by DOWEX may be affected by NO_3^- at concentrations > 100 mM.
- **iv.** DOWEX effectively removes TcO_4^- without impacting U uptake in batch experiments.
- **v.** Derived anion equilibrium exchange coefficients for predicting DOWEX performance.

1 Introduction

The primary objective of the 200 West Area pump-and-treat (200W P&T) facility at the U.S. Department of Energy's Hanford Site, a former plutonium production site in southeastern Washington State (USA), is to strip chemical and radiological contaminants from groundwater. The facility treats up to 2500 gallons of contaminated groundwater per minute from multiple extraction wells to remediate groundwater plumes with distinct water chemistry signatures from across the 200 Area (Central Plateau) of the Hanford Site. The primary radioactive contaminants are uranium (U), present as anionic uranyl carbonate complexes (e.g., $U(VI)O_2(CO_3)_3^{4-}$), and technetium-99 (Tc-99), present as anionic pertechnetate (TcO_4^-) [1]. The 200W P&T facility uses two strong base anion styrene-divinylbenzene gel exchange resins: (i) Purolite® A532E (A532E), with bifunctional quaternary amine (triethylammonium and trihexylammonium) functional groups, to selectively remove the large, weakly hydrated TcO_4^- anion [2-8]; and (ii) DOWEX 21K (DOWEX), with trimethylammonium functional groups, to selectively remove the more densely charged U carbonate species (Figure 1 in Part I [9]). In the current configuration of the 200W P&T facility, DOWEX removes U first, then A532E removes Tc-99. The incoming water volume and characteristics are different for the two treatment trains (Figures S1 and S2 in Part I [9]). This study is presented in two parts, with A532E performance for the removal of Tc-99 evaluated in Part I, and the performance of DOWEX for the removal of U evaluated here in Part II. The aim of this work is to reduce the uncertainty associated with the impact of changing groundwater chemistry on ion exchange (IX) resin performance for the removal of radionuclides from contaminated groundwater, and to provide a technical basis to optimize operations for treatment of different groundwater plumes in the future.

Aqueous U concentrations across the Hanford Site can vary from 3.4 – 50,000 µg/L, with some areas exceeding the U.S. Environmental Protection Agency regulated maximum contaminant level of 30 µg/L [10, 11]. DOWEX efficiently removes U from influent groundwater, and analysis of spent DOWEX resin from the lead column after 4 years of service in the U IX treatment train at the 200W P&T facility showed a high U loading of 18,500 µg/g resin [12]. However, DOWEX also has an affinity for common groundwater constituents such as sulfate (SO_4^{2-}) and nitrate (NO_3^-), which are present at concentrations up to three orders greater than the concentration of U in the U IX influent stream (Tank Y10, Table 1). Although the U loading on spent DOWEX resin was high, the measured NO_3^- and SO_4^{2-} loadings were 27,500 ± 3025 µg/g resin and 17,280 ± 2,246 µg/g resin, respectively, and together account for 21.5% of the theoretical capacity [12]. In addition to U, NO_3^-, and SO_4^{2-}, other ions (Fe, Ca, ^{127}I, and ^{129}I) were present on the spent DOWEX resin [13]. Other studies that have observed the removal effects of co-mingled anions include Nur and others, who reported that DOWEX removed 70% of the NO_3^- from a 20-mg/L solution in batch experiments [14]. Mattigod and colleagues found that partitioning coefficients for U were reduced by half (72,830 mL/g vs. 31,670 mL/g) in 306 mg/L NO_3^- solutions [15]. Kalaruban and others found that, in solutions containing NO_3^- (20 mg/L), phosphate (PO_4^{3-}, 0.5 – 30 mg P/L), chloride (Cl^-, 20 – 70 mg Cl/L), and SO_4^{2-} (10 – 70 mg S/L), higher SO_4^{2-} concentrations only reduced NO_3^- adsorption, leading them to conclude that competition between anions usually depends on the concentration of NO_3^- [16]. The removal of U by DOWEX may be further complicated by changes in U speciation, which is highly dependent on groundwater pH and ion concentration (e.g., CO_3^-/HCO_3).

In the future, the 200W P&T facility could accept influent streams from new extraction wells, e.g., wells extracting groundwater from a nitrate plume, and this could change equilibrium uranyl

speciation and impact U removal efficacy by DOWEX [12]. Understanding the potential impact of varying groundwater compositions from current and future influent streams on the performance of IX resins is necessary to sustain maximum operational efficiency, but published Hanford-specific data describing competing anion effects during IX at the 200W P&T facility is limited.

Here, a series of binary and multicomponent batch experiments were conducted to determine the selectivity of DOWEX for different anions, e.g., U(VI) species, TcO_4^-, SO_4^{2-}, NO_3^-, Cl^-, and CO_3^{2-} (known to influence U(VI) speciation), and the potential competitive effects that these species have on U removal by DOWEX. The batch experiments were not designed to replicate the composition of the groundwater influent, but instead to probe the effect of individual anions over a range of concentrations that represent current and future groundwater influent compositions to the 200W P&T facility. The results were used as a training set to generate an initial thermodynamic model for predicting DOWEX resin performance as a function of changes in influent composition. As stated in the Part I [9], the ion removal mechanism is often considered a simple electrostatic interaction in most IX models. With the approach used herein, other factors that impact the thermodynamics of IX reactions, such as (i) anion hydration energy; (ii) the size and nature of counterions; (iii) the resin functional group(s); and (iv) competing sorption reactions are taken into account when calculating anion specific exchange coefficients used as inputs for the thermodynamic model[7]. However, kinetic effects can play an important role in contaminant uptake efficiency under the dynamic conditions in the IX vessels at the 200W P&T facility. Thus, an ongoing study is evaluating IX performance under flow conditions, firstly with a synthetic groundwater containing the anions included in these batch experiments, and secondly with actual groundwater from the 200 Area, with the batch-derived thermodynamic model coefficients used in flow and transport modeling to fit contaminant breakthrough data. These column experiments will allow the model presented in this work to be optimized to account for both thermodynamic and kinetic effects, then ultimately scaled up to provide operational feedback to the 200W P&T facility and inform future resin treatment train design for optimization of both U and Tc-99 removal.

2 Materials and Methods

2.1 Materials

DOWEX is a strong base Type I anion exchange resin used to remove U(VI) from solution [13]. The polystyrene resin crosslinked with divinylbenzene is functionalized with quaternary trimethyl ammonium functional groups. The DOWEX 21K resin has yellow, uniformly sized spherical beads with particles 0.525 – 0.625 mm in diameter and a total capacity >1.4 eq/L in Cl^- form, according to the manufacturer. DOWEX resin beads were pre-conditioned with 1 M NaCl before use to eliminate other anions potentially present on the resin (Part I; [9] unpublished). Preconditioning attempts to maximize the loading capacity of the Cl^- parent anion on the DOWEX resin. The pre-conditioned resin was used in batch experiments as well as to determine the DOWEX resin moisture content (MC) and measure the actual exchange capacity (q_t) since the manufacturer reports a minimum value determined based on the resin manufacturing procedure. The MC for DOWEX resins ranged from 54% – 64% and the q_t value for Cl^-

functionalized DOWEX was determined to be 2.0 meq/g dry resin. When normalized to the mass of wet resin, the q_t value is ~0.9 meq/g wet resin and less than the manufacturer reported value. This could indicate some IX sites are occupied by CO_3^{2-} species that are not displaced by Cl^- during pre-treatment. Procedural details for measuring MC and q_t may be found in the supporting information of Part I [9][unpublished]. The measurements and calculations for determining q_t are provided in the supporting information, Table S1.

2.2 Solution Preparation for Batch Experiments

Solutions for batch experiments were not designed to replicate the composition of the groundwater influent, but instead to probe the effect of individual anions (Cl^-, CO_3^{2-}, NO_3^-, and SO_4^{2-}) over a concentration range that spans the range of blended groundwater compositions in Tank Y10, which is the influent stream to the U IX treatment train (Table 1). The anions were added to double deionized water (DDI) as the sodium salt (NaCl, Na_2CO_3, $NaNO_3$, and $NaSO_4^{2-}$) to make spiking solutions with single or mixed ions. Ammonium pertechnetate (NH_4TcO_4, available in house) and uranyl chloride trihydrate ($UO_2Cl_2 \cdot 3H_2O$, International Bio-Analytical Industries) were added to DDI to make spike solutions of Tc-99 (20 mg/L) and U (11.6 mg/L), respectively. Experiment solutions with U or Tc-99 were spiked with 2 mL of 20 mg/L Tc-99 and/or 2 mL of 11.6 mg/L U for a target concentration of 200 µg/L and/or 116 µg/L, respectively. The concentration of U in Tank Y10 is two orders of magnitude greater than that of Tc-99 (Table 1), but a concentration representative of the U concentration was selected for both Tc-99 and U for comparison in these batch experiments. A total of 17 batch experiments with different combinations of anions (Cl^-, CO_3^{2-}, NO_3^-, SO_4^{2-}, Tc-99, and U) and concentrations, and solution-to-solid ratios, were conducted (Table 2). For Tests A, B, D, E, I, K, and Q (with varied solution:solid ratios), a single stock solution containing the relevant anions was made for each experiment. For all other experiments (with varied [NO_3^-], [SO_4^{2-}], or [Cl^-]), the relevant anions were added as a spike to achieve the target concentrations in Table 2. Prior to adding the DOWEX resin beads to each experiment, the solution pH was adjusted to 7.4 +/- 0.1 (to match that of influent streams) with diluted HCl or NaOH and equilibrated overnight. The solution pH was re-adjusted, if necessary, the next day.

2.3 Batch Sorption and Kinetic Experiments.

Experiments in Table 2 were conducted in duplicate and in 250-mL high-density polyethylene (HDPE) bottles. Since these experiments followed the procedure already reported in Part I [9], the reader is encouraged to reference that text and here only the differences are noted. Following the addition of the DOWEX resins to the required solution volume, the pH of each bottle was immediately measured and then transferred to a bench shaker at 125 rpm for 24 hours (previously 72 hours). At the end of 24 hours, the bottles were removed from the shaker and processed as previously described before analyzing the solutions by inductively coupled plasma-mass spectrometry (ICP-MS, for Tc-99 and U) and ion chromatography (IC, for anions). Carbonate uptake was calculated as the milliequivalent difference in Cl^- released, as measured by IC, also accounting for other measured anions removed from solution of known charge. The carbonate uptake calculation cannot be made for experiments containing U(VI) complexes because the exact charge of the UO_2^{2+} species could not be absolutely determined. The kinetic

batch experiments followed the procedure previously described [9], with aliquot collections for Tc-99 and U measurements and pH measurements occurring at time points 0, 0.5, 1, 2, 4, 8, 24, 48, and 72 hours. No aliquots were collected for IC analysis from the kinetic batch experiments.

The reported ICP-MS method limits of detection for Tc-99 ranged from 0.037 to 0.74 µg/L, and for U from 0.076 to 0.76 µg/L. IC method detection limits for Cl (0.67 – 13.4 mg/L), NO_3^- (0.66 - 23 mg/L), and SO_4^{2-} (0.108 - 50.5 mg/L) ranged according to the dilutions required to analyze the samples. The experimental precision of these DOWEX batch experiments is estimated to be ± 3% and is based on a combination of replicate determinations, volumetric error, and analytical measurement variance. The primary source of error occurs during sample preparation and is reflected in the average solution:solid ratio (mL/g) and standard deviation determined from all A532E experiments with a target solution:solid ratio of 200 mL/g (98 data points), which is 201 ± 7 mL/g of dry resin.

2.4 Adsorption Isotherm Models and Geochemical Modeling

Sorption isotherms from ICP-MS and IC data were initially fit using both Freundlich and Langmuir adsorption models. However, only for Tc-99 in Test M did the Freundlich fit to the data produce an R^2 value greater than the R^2 value for the Langmuir fit, although not within statistical significance (R^2 = 0.911 versus 0.906, respectively). DOWEX has only one active sorption site that is functionalized with trimethylamine groups. Based on the uniformity of available exchange sites, the Langmuir model (Equation 1), which assumes monolayer adsorption onto a surface containing a finite number of identical binding sites, agrees with the observations of the initial fitting exercise and was used to determine the final sorption fit for U, Tc-99, HCO_3, NO_3^-, and SO_4^{2-} isotherms presented herein [17]:

$$q_e = \frac{q_t K_L C_e}{1 + K_L C_e} \qquad \text{Equation 1}$$

Here, q_t is the maximum monolayer coverage capacity (meq/g dry resin), K_L is the Langmuir isotherm constant (L/mmol), q_e is the anion equilibrium sorption capacity (in meq/g dry resin) and C_e is the equilibrium anion concentration in mM .

Geochemical modeling of anion speciation in solution was performed in Part I using Geochemists Workbench (GWB 12.0.7, www.gb.com) [9, 18]. The previously reported methods for calculating anion equilibrium exchange coefficients (K) using HYDROGEOCHEM in Part I is also used here [19]. Again, the K value that minimized the root mean square error (RMSE) of the model fit to the range of experimental data evaluated is reported. The RMSEs reported are not an indication of goodness of fit and for different anions should not be compared as the number of data points and datapoints representing measurable concentrations (those that fall above instrument limits of detection) are often different.

3 Results and Discussion

3.1 Solution speciation modeling

The speciation of NO_3^-, SO_4^{2-}, CO_3^{2-}, Tc-99, and U was modeled in Part I with the GWB

thermodynamic modeling software package using the aqueous conditions of Test G (for the NO_3^- system) and Test N (for the SO_4^{2-} systems) in Table 2 [9, 18]. Based on those results, the loadings of CO_3^{2-}, Tc, and U provided in Table S2 (NO_3^- experiments) and Table S3 (SO_4^{2-} experiments) are calculated assuming HCO_3^-, TcO_4^-, and $UO_2(CO_3)_3^{4-}$ species, respectively.

3.2 Binary sorption isotherms

Sorption isotherms for HCO_3^- (A), and NO_3^- and SO_4^{2-} (C), showing the anion fractional loading q_e/q_t, where anion loading capacity (q_e) in meq/g dry resin is normalized to the experimentally determined total resin capacity for Cl^-, q_t = 2.0 meq/g dry resin, versus the anion equilibrium concentration C_e (mM), were used to assess affinity of DOWEX for these anions (Figure 1). Both DOWEX and A532E resins exhibit similar uptake of carbonate, where DOWEX HCO_3^- q_e values ranged from 0.16 – 0.50 meq/g with no competition anions present (Test A, Table S2) and A532E HCO_3^- q_e values ranged from 0.12 – 0.29 for the same experiment (Part I; [1, 9]). However, DOWEX exhibited significantly greater uptake of SO_4^{2-} (maximum q_e = 3.64 meq/g dry resin) compared to NO_3^- (maximum q_e = 2.86 meq/g dry resin) and Cl^- (q_t = 2.0 meq/g dry resin) when no other anions were present (Figure 1C, Tests B and I in Tables S2 and S3). Indeed q_e/q_t is greater than 1 for SO_4^{2-} and NO_3^- once C_e concentrations exceed ~1.9 and ~0.2 mM for SO_4^{2-} and NO_3^- respectively, which suggests that the total exchange capacity for DOWEX may be anion specific and higher for anions with high selectivity. For SO_4^{2-}, the maximum q_e value reflects DOWEX's higher selectivity for multi-valent, well hydrated anions at the trimethylammonium exchange sites, where SO_4^{2-}has a Gibbs free energy of hydration (ΔG_{hyd}) equal to -1090 kJ/mol compared to Cl^-, -347 kJ/mol [3]. However, the maximum q_e for NO_3^- (ΔG_{hyd} = -306 kJ/mol [3]) also exceeded q_t, despite being a more weakly hydrated anion than Cl^-. The exact cause of this difference between Cl^- and NO_3^- is not known, but may align with the Kalaruban study that reported anion competition for removal by DOWEX depends on the concentration of NO_3^- [16]. The impact of pH was also considered as a potential factor. For Tests B and I the final pH ranged from 6.13 – 6.90 (Tables S2 and S3), whereas in Test A the HCO_3^- buffered the pH between 7.34 – 7.88. The zeta potential for the DOWEX resin is approximately 30 mV from pH 4 – 7, then drops to approximately 22 mV at pH 7.5 [16]. In the pH range of 6.13 – 6.90 observed for Tests B and I, the surface potential would remain at 30 mV; therefore, pH is not expected to contribute significantly to the measured maximum q_e values for NO_3^- and SO_4^{2-}. The best fit to the data for sorption of major anions HCO_3^-, NO_3^-, and SO_4^{2-} on DOWEX was produced with the Langmuir model and is shown in Figure 1B,D.

Given the high exchange capacity of DOWEX, it was necessary to determine a target concentration of Cl^- to use as a background electrolyte, such that changes in uptake would be measurable for the bulk groundwater anions of interest, NO_3^- and SO_4^{2-}. Figure 2 shows the sorption isotherms for NO_3^- (Test C) and SO_4^{2-} (Test J) over a range of Cl concentrations spanning from 0 – 231 mM (Table S1 and S2). The Cl^- concentration chosen from these tests would target NO_3^- and SO_4^{2-} uptake between 20% – 80%. In each experiment, an increase in the Cl^- concentration led to a decrease in NO_3^- (starting concentration of 6 mM) and SO_4^{2-} (starting concentration of 3 mM) sorption onto DOWEX, and thus a decrease in the effective loading (Figure 2). The presence of Cl^- had a significant impact on SO_4^{2-} sorption and, despite its high

charge density and hydrophilic character, the loading of SO_4^{2-} dropped below that of NO_3^- when the concentration of Cl^- was greater than 100 mM. This suggests that, under competitive conditions of high total dissolved solids, DOWEX selectivity is driven by factors other than anion hydration, such as relative anion concentrations and the availability of neighboring binding sites required to accommodate the removal of multivalent anions. In the presence of Cl^- concentrations that increase up to two orders of magnitude greater than SO_4^{2-}, Cl^- occupancy of available anion exchange sites also increase. The presence of Cl^- lowers SO_4^{2-} access to the two neighboring exchange sites required for SO_4^{2-} removal. Yet, in the case of NO_3^-, only one exchange site is needed to remove this anion, so even as the Cl^- concentration increases, NO_3^- access to exchange sites depends mostly on the relative hydration energy of NO_3^- to Cl^-, not on the availability of neighboring exchange sites as influenced by total anions in solution. These factors lead to a more gradual decrease in NO_3^- loading with increased Cl^- C_e than the observed trend for SO_4^{2-} loading shown in Figure 2.

At the conclusion of Tests C and J, a Cl^- concentration of 50 mM (or 1768 mg/L) was selected because NO_3^- and SO_4^{2-} uptake reached 44% and 54%, respectively, and fell within the target range of 20% – 80% (Tables S2 and S3). A Cl^- concentration of 50 mM is close to the maximum total dissolved solids concentration measured for perched water in the 200W P&T remediation area (1873 mg/L).

3.3 Multicomponent sorption isotherms

3.3.1 Multicomponent experiments containing SO_4^{2-}

The primary competing ion of interest for DOWEX is SO_4^{2-}. The effect of SO_4^{2-} on the uptake of HCO_3^-, Tc, and U was systematically investigated in a series of five experiments (Tests K – N and R, Table 2). The results for SO_4^{2-} experiments, including the change in pH relative to a blank solution without resin, contaminant loadings (q_e), final anion aqueous concentration (C_e), and percent uptake, are summarized in Table S3 and Figure 3.

Due to their larger charge density, highly charged species, e.g., $SO_4^{2-}$and $UO_2(CO_3)_3^{4-}$, generally have a higher affinity for the trimethylammonium groups on DOWEX than less highly charged anions, e.g., NO_3^-, Cl^-. The loading capacity of SO_4^{2-} on DOWEX is thus greater than the loading capacity of NO_3^- and Cl^- in the absence of other anions, as shown in Figure 1C. However, as discussed in the last section, the selectivity for the divalent SO_4^{2-} anion is more sensitive to the total concentration of anions in solution compared to monovalent ions like Cl^- and NO_3^-. Therefore, as more anions were added into solution, a decrease in SO_4^{2-} loading (q_e) (Figure 3A,C) was observed in Tests K – N compared to Test Q. Test Q provides the baseline for SO_4^{2-} removal when the uptake of 3 mM SO_4^{2-} in the presence of 53 mM Cl^- is measured as a function of solution:solid ratio (Table S3). In Test K (Figure 3A,C), the addition of 10 mM HCO_3^- resulted in a decrease in maximum q_e from 0.93 meq/g dry resin (Test Q) to 0.71 meq/g dry resin. This suggests that HCO_3^- remains competitive for the IX sites as a monovalent anion, and further hinders the access of SO_4^{2-} to neighboring exchange sites for removal.

Due to the excess of HCO_3^- (10 mM) compared with Tc-99 (2×10^{-3} mM) and U (4×10^{-4} mM), the addition of Tc-99 and U in Tests M, N, and R did not significantly affect SO_4^{2-} q_e values, and

the SO_4^{2-} sorption isotherms for Tests K, M, N, and R (all containing HCO_3^-) overlap for SO_4^{2-} C_e values ≤ 3 mM (Figure 3A). The SO_4^{2-} sorption isotherm for Test L, which evaluated the effect of SO_4^{2-} on TcO_4^- removal in the presence of 52 mM Cl^- and the absence of HCO_3^-, aligns with the isotherm from Test Q (Cl^- only) and produced the highest SO_4^{2-} loading (q_e = 1.36 meq/g dry resin) determined from the multicomponent tests. In the absence of HCO_3^- and in the presence of a comparatively low concentration of TcO_4^-, SO_4^{2-} loadings are unaffected. When HCO_3^- is added (Test R), the maximum q_e for SO_4^{2-} drops to 1.07 meq/g dry resin, but TcO_4^- removal, remains at 99%, despite a small increase in TcO_4^- C_e (Figure 3B, Table S3). The small effect of HCO_3^- on TcO_4^- removal is likely connected to its Gibbs free energy of hydration, ΔG_{hyd} = -340 kJ/mol [20], which makes it more favorable for hydration than TcO_4^- (ΔG_{hyd} = -251 kJ/mol) and facilitates removal by DOWEX.

For trace contaminant concentrations of Tc-99 and U, uptake was 99% and 100%, respectively, under all conditions tested in the presence of SO_4^{2-}. However, for both Tc-99 and U, the concentration remaining in solution was higher when they were present as co-contaminants, especially at the highest SO_4^{2-} concentrations. Under comingled conditions, the presence of HCO_3^- on the resin is favorable for loading of $UO_2(CO_3)_3^{4-}$, as removal of U is facilitated by complexation with carbonate, as well as by enhanced anion exchange due to the large (4-) charge on the complex. However, the presence of HCO_3^- and U on the resin is less favorable for TcO_4^- loading, with uptake remaining at around 99%, but the concentration remaining in solution increasing slightly. For TcO_4^-, the size and hydrophobicity of the anion are likely responsible for the increase in the concentration remaining in solution under the most competitive aqueous environment (Test N). This provides laboratory-based experimental confirmation of the mechanism behind significant uptake of TcO_4^- after DOWEX resin change-out, which has been empirically observed at the 200W P&T facility. The available exchange sites on the fresh DOWEX initially uptake TcO_4^- from solution, but over time the selectivity of U for those sites, enhanced by the presence of HCO_3^-, results in release of TcO_4^- from the resin.

3.3.2 Multicomponent experiments containing NO_3^-

Figure 4A shows the sorption isotherms for NO_3^-, while panels B and D show the final remaining Tc-99 and U concentrations in solution, respectively. A complete summary of the data obtained from the NO_3^- experiments is provided in Table S2. The increasing trend in NO_3^- loading (q_e) as a function of NO_3^- C_e is observed for all multicomponent isotherms. All NO_3^- sorption isotherms overlap up until NO_3^- C_e values of > 50 mM are reached (Figure 4A), demonstrating the limited effect of other anions on NO_3^- uptake by DOWEX. If NO_3^- loading was affected by total dissolved solids, the NO_3^- loading would have decreased in the presence of HCO_3^-, as observed for SO_4^{2-} isotherms containing HCO_3^- (Figure 3A). The increase in NO_3^- loading with increasing concentration also agrees with previous reports that DOWEX exhibits some affinity for NO_3^- anions [13, 16, 21]. Furthermore, competing anion removal by DOWEX may depend on NO_3^- concentration as reported by Kalaruban and coworkers [16]. Here in Test F, an increase in NO_3^- loading (up to 3.06 meq/g, $[NO_3^-]_0$ = 6240 mg/L) on DOWEX resulted in a decrease in TcO_4^- uptake from 99% to 90%. Again, the hydration of the competing anions has a significant influence on anion removal, with the more easily hydrated NO_3^- (ΔG_{hyd} = -306 kJ/mol) more competitive for hydrophilic trimethylammonium groups on DOWEX than hydrophobic TcO_4^-.

The presence of TcO_4^- in solution did not affect U removal, but around NO_3^- concentrations 52 mM (3230 mg/L) and higher, U uptake begins to decrease from 99% to as low as 85% ($[NO_3^-]_0$ = 100 mM, 6220 mg/L). This suggests that NO_3^- may inhibit DOWEX performance for U removal above concentrations of 6220 mg/L. However, the NO_3^- concentrations in Tank Y20 (Table 1) are more than an order of magnitude less than the highest NO_3^- concentration studied here. Thus, NO_3^- will not impede DOWEX performance for U removal at the 200W P&T facility unless influent NO_3^- concentrations exceed 1000 mg/L.

Lastly, TcO_4^- C_e values decreased in the presence of HCO_3^- for the SO_4^{2-} system (Test R) compared to Test L in the absence of HCO_3^-. Here, for the NO_3^- system, this competition between HCO_3^- and TcO_4^- was not observed. Aside from NO_3^-, the presence of U was the next most competitive anion to hinder TcO_4^- removal based on a comparison of C_e values (Table S2).

3.4 HYDROGEOCHEM Modeling

The calculation for determining equilibrium exchange coefficeints (K) using HYDROGEOCHEM is provided in Part I [9]. For the DOWEX resin, HYDROGEOCHEM calculations assume a q_t = 3.64 meq/g dry resin, which is the highest anion loading value measured (Test I, Table S3). The $K_{SO4--/Cl-}$, $K_{NO3-/Cl-}$, $K_{HCO3-/Cl-}$, and $K_{TcO4-/Cl-}$ calibrated from all experiments for DOWEX using HYDROGEOCHEM were determined to be 2.0, 5.0, 1.5, and 2000, respectively. These coefficients were then fixed to estimate $K_{U/Cl-}$ assuming $UO_2(CO_3)_3^{4-}$ as the exchanged anion. The best estimate of $K_{U/Cl-}$ for Test M and Test N combined is >50,000. With such a high selectivity for U species, these K values suggest that U will out-compete Tc-99 for uptake by at least 25:1 ($K_{U/Cl-}/K_{TcO4-/Cl-}$) when both contaminants are present at competing concentrations. The comparison between the observations and the simulated results for SO_4^{2-}, Tc, and U in Tests M and N are shown in Figure 5Figure . In Figure S2, the observations from all DOWEX experiments and the simulated results are shown for all anions, including NO_3^- and HCO_3^-.

3.5 Batch Sorption Kinetics

Kinetic experiments were conducted to confirm that the IX reaction had reached equilibrium over the time of the batch sorption experiments, and to determine the rate of contaminant uptake so that operating conditions for future column experiments could be optimized. Batch sorption experiments were conducted to determine the kinetics of Tc and U uptake by DOWEX from a solution containing NO_3^- (19 mM), SO_4^{2-} (5 mM), Cl^- (50 mM), and HCO_3^- (10 mM) (Test T, Table 2) over 72 hours. In the presence of NO_3^- (0 – 98 mM, Test H), the batch sorption experiments demonstrated removal of both Tc (90% – 99%) and U (85% – 99%) (Table S2). In the presence of SO_4^{2-} (0 – 10 mM, Test N), the uptake was > 99% for Tc-99 and 100% for U (Table S3). The results from the 24-hour sorption experiments agree with the kinetic experiments and, in the presence of both NO_3^- and SO_4^{2-}, the majority of U (97%) and up to 87% Tc-99 were removed from solution within the first 8 hours. A first order rate model provided the best fit (R^2 = 0.800) to the kinetics of Tc-99 uptake by DOWEX and a rate constant (k) of 0.46 hr^{-1} was calculated (Figure S1). However, the best fit (R^2 = 0.816) to the kinetics of U uptake by DOWEX was achieved using a zero-order rate model, with a k = 14.24 μg/(g hr). These results demonstrate that the IX reaction had reached equilibrium within 8 hours, which is well within the

timeframe of the batch sorption experiments. The different kinetic behavior for uptake of U versus Tc-99 by DOWEX may play an important role in determining uptake efficiency of these two contaminants under the high-flow conditions in the IX vessels at the 200W P&T facility.

4 **Conclusions**

The 200W P&T facility at the Hanford Site currently uses DOWEX to specifically target U in influent groundwater. A planned expansion of the 200W P&T facility will introduce additional groundwater contaminated with Tc-99 and U from beneath aging radioactive waste storage tanks. This work assessed the impact of a broader range of influent chemistries on IX resin performance to confirm that DOWEX will continue to remove U to meet groundwater treatment objectives, with a similar assessment of A532E for Tc removal in Part 1 ([9] unpublished). The results of this study also provide a technical basis for future decisions for 200W P&T facility operational configurations, e.g., A532E and DOWEX treatment vessel configuration.

DOWEX has one type of IX site functionalized with trimethylammonium groups. Due to the open structure of the IX site, multivalent species (e.g., SO_4^{2-}, CO_3^{2-}, $UO_2(CO_3)_3^{4-}$) will outcompete monovalent anions (e.g., NO_3^-, Cl^-) based on their larger hydration energy and charge. However, as the concentration of Cl^- and other monovalent species in solution increases, these multi-valent species are at a disadvantage because they require more than one available sorption site to be removed by the resin, a factor that may not be overcome by their larger electrostatic attraction to the resin sorption sites. Hence, DOWEX is more susceptible to competition from high concentrations of monovalent NO_3^-, Cl^-, HCO_3^-, and even TcO_4^- species that only require one sorption site. This competition resulted in the uptake of nearly all (99%) of the TcO_4^- in the presence of SO_4^{2-}, Cl^-, U, and HCO_3^-, whereas SO_4^{2-} uptake decreased. When divalent SO_4^{2-} was replaced with monovalent NO_3^-, the Tc-99 and U uptake levels decreased from 99% to 90% and from 99% to 85%, respectively, with increasing NO_3^- concentration. However, the most drastic decreases in Tc-99 and U uptake occurred around 100 mM NO_3^-, which is outside the NO_3^- concentration range expected in current and future contaminated groundwater influent to the 200W P&T.

Models informed by these batch sorption results predict equilibrium IX coefficients for DOWEX uptake of SO_4^{2-} ($K_{SO4-/Cl-} = 2.0$), NO_3^- ($K_{NO3-/Cl-} = 5.0$), carbonate as HCO_3^- ($K_{HCO3-/Cl-} = 1.5$), Tc-99 as TcO_4^- ($K_{TcO4-/Cl-} = 2000$), and U as $UO_2(CO_3)_3^{4-}$ ($K_{U/Cl-} > 50{,}000$). Thus, these equilibrium IX coefficients predict little effect of influent chemistry on U removal by DOWEX from a thermodynamic perspective, suggesting that DOWEX will remove $UO_2(CO_3)_3^{4-}$ from current and future influent streams such that effluent concentrations will meet groundwater treatment objectives, even in the presence of high concentrations of competing anions, NO_3^-, SO_4^{2-}, Cl^-, and HCO_3^-/CO_3^{2-}, and TcO_4^- as a co-contaminant. Kinetic effects can play an important role in U uptake efficiency under the high-flow conditions in the IX vessels at the 200W P&T facility, and batch experiments showed that both U and Tc-99 were removed within 8 hours. However, further work is required to demonstrate that the batch equilibrium IX coefficients can be used predict uptake and retention of both U and Tc-99 by DOWEX in 1D flow column studies, where dynamics are expected to play a more significant role. The IX coefficients will be optimized to account for both thermodynamic and kinetic effects, and the model will ultimately be scaled up to provide operational feedback to the 200W P&T facility, and to inform future resin treatment train design for optimization of both U and Tc-99 removal.

5 Acknowledgements

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6 Supporting Information

The following has been provided in the supporting information document: additional experimental procedure details, tabulated results from batch studies that support figures presented in the main text, Tc and U plots from kinetic experiments, additional HYDROGEOCHEM modeling plots, and a comparison of DOWEX resin capacity for U to other material technologies.

7 References

[1] C. CH2M Hill Plateau Remediation Company, Draft Report – Technical Evaluation of Ion Exchange Vessels for the BP-5-PO1 System, CHPRC Richland, Washington (2020).
[2] C.D. Williams, P. Carbone, A classical force field for tetrahedral oxyanions developed using hydration properties: The examples of pertechnetate ($TcO4^-$) and sulfate ($SO42^-$), The Journal of Chemical Physics, 143 (2015) 174502.
[3] T.G. Levitskaia, E.L. Campbell, G.B. Hall, S. Chatterjee, D. Boglaienko, D.D. Reilly, M.A. Carlson, Characterization of spent Purolite A530E resin with implications for long-term radioactive contaminant removal, Journal of Environmental Chemical Engineering, 8 (2020) 104155.
[4] T.G. Levitskaia, E.L. Campbell, S. Chatterjee, G.B. Hall, Analysis of Technetium Ion Exchange Resin from the 200 West Pump-and-Treat Facility, PNNL-26933 United States 10.2172/1569474 PNNL English, ; Pacific Northwest National Lab. (PNNL), Richland, WA (United States) (2017).
[5] J.B. Duncan, Removal of Technetium 99 from the Effluent Treatment Facility (ETF) Basin 44 Using Purolite A-530E & Reillex HPQ & Sybron Ionac SR-7 Ion Exchange Resins, RPP-RPT-23199 Rev 0, Hanford Site (HNF) Richland, WA (United States) (2004).
[6] J.B. Duncan, K. Hagerty, W. Moore, J. Johnson, Laboratory Report on the Removal of Pertechnetate from Tank 241-AN-105 Simulant Using Purolite A530E, LAB-RPT-12-00002 Rev 0, Hanford Site Richland, WA (2012).
[7] B. Gu, Y.-K. Ku, G.M. Brown, Sorption and Desorption of Perchlorate and U(VI) by Strong-Base Anion-Exchange Resins, Environmental Science & Technology, 39 (2005) 901-907.
[8] M.M. Valenta, K.E. Parker, E.M. Pierce, Tc-99 Ion exchange resin testing, PNNL-19681, Pacific Northwest National Laboratory Richland, WA (United States) (2010).
[9] S.A. Saslow, Elsa A. Cordova, Nancy M. Avalos, Daria Boglaienko, Yilin Fang, Xuehang Song, Amanda Lawter, Tatiana G. Levitskaia, Hilary Emerson, Jim Szecsody, Christian D. Johnson, Carolyn I. Pearce, Vicky L. Freedman, R.D. Mackley, Part I: Predicting Performance of

Purolite A532E Resins for Remediation of Comingled Contaminants in Groundwater, Chemical Engineering Journal, *Submitted.* (2023).
[10] DOE, 200-BP-5 and 200-PO-1 Groundwater Operable Units Feasibility Study for Interim Action, U.S. Department of Energy (DOE) Richland, WA (2018).
[11] CHPRC, Draft Report – Technical Evaluation of Ion Exchange Vessels for the BP-5-PO1 System, CH2M Hill Plateau Remediation Company (CHPRC) Richland, WA (2020).
[12] E.L. Campbell, T.G. Levitskaia, M.S. Fujimoto, V.E. Holfeltz, S.D. Chatterjee, G.B. Hall, Analysis of Uranium Ion Exchange Resin from the 200 West Pump-and-Treat Facility, Pacific Northwest National Laboratory Richland, Washington 99352 (2018).
[13] E.L. Campbell, T.G. Levitskaia, M.S. Fujimoto, V.E. Holfeltz, S. Chatterjee, G.B. Hall, Analysis of Uranium Ion Exchange Resin from the 200 West Pump-and-Treat Facility, PNNL-28062 United States 10.2172/1488863 PNNL English, ; Pacific Northwest National Lab. (PNNL), Richland, WA (United States) (2018).
[14] T. Nur, W.G. Shim, P. Loganathan, S. Vigneswaran, J. Kandasamy, Nitrate removal using Purolite A520E ion exchange resin: batch and fixed-bed column adsorption modelling, International Journal of Environmental Science and Technology, 12 (2015) 1311-1320.
[15] S.V. Mattigold, G.E. C., D.M. Wellman, E.A. Cordova, R.M. Smith, Uranium Adsorption on Ion-Exchange Resins – Batch Testing, Pacific Northwest National Laboratory Richland, WA (2010).
[16] M. Kalaruban, P. Loganathan, W.G. Shim, J. Kandasamy, G. Naidu, T.V. Nguyen, S. Vigneswaran, Removing nitrate from water using iron-modified Dowex 21K XLT ion exchange resin: Batch and fluidised-bed adsorption studies, Sep Purif Technol, 158 (2016) 62-70.
[17] D. A.O., Langmuir, Freundlich, Temkin and DubiniŽ Radushkevich Isotherms Studies of Equilibrium Sorption of Zn 2+ Unto Phosphoric Acid Modified Rice Husk, IOSR Journal of Applied Chemistry, 3 (2012) 38-45.
[18] C. Bethke, S. Yeakel, The Geochemist's Workbench, in, Urbana, Illinois, 2009.
[19] G.-T. Yeh, Y. Fang, F. Zhang, J. Sun, Y. Li, M.-H. Li, M.D. Siegel, Numerical modeling of coupled fluid flow and thermal and reactive biogeochemical transport in porous and fractured media, Computational Geosciences, 14 (2010) 149-170.
[20] Y. Marcus, Thermodynamics of solvation of ions. Part 5.—Gibbs free energy of hydration at 298.15 K, J. Chem. Soc., Faraday Trans., 87 (1991) 2995-2999.
[21] S.V. Mattigod, E.C. Golovich, D.M. Wellman, E.A. Cordova, R.M. Smith, Uranium Adsorption on Ion-Exchange Resins - Batch Testing, PNNL-20135; Other: 830403000; TRN: US1101909 United States 10.2172/1009765 Other: 830403000; TRN: US1101909 PNNL English, ; Pacific Northwest National Lab. (PNNL), Richland, WA (United States) (2010).
[22] P.D. Royer, T.P. Franklin, J.J. Garza, C.D. Johnson, N.J. Huerta, J.Q. Wassing, e.a. C.B. Woodford, SOCRATES software release 2.0, Pacific Northwest National Laboratory, Richland, WA., PNNL-SA-167052 (2021).

Table 1. Composition of U ion exchange (IX) influent streams (Tank Y10) [22].

Parameter/Type	Units	Average	Std. Dev.	Number of Measurements
From 6/1/2020 through 5/30/2021		**Y10 (U Influent)**		
Technetium-99	**pCi/L**	**2,130**	**170**	**11**
Uranium	**µg/L**	**173**	**41**	**22**
Nitrate	µg/L	129,000	38,000	11
Sulfate	µg/L	94,000	33,000	11
Chloride	µg/L	22,000	8,000	11
From 6/1/2021 through 5/30/2022		**Y10 (U Influent)**		
Technetium-99	**pCi/L**	**1620**	**470**	**12**
Uranium	**µg/L**	**131**	**74**	**24**
Nitrate	µg/L	109,000	18,000	11
Sulfate	µg/L	78,000	15,000	11
Chloride	µg/L	14,900	4,500	11

Table 2. Experiment matrix with target Cl^-, CO_3^{2-}, NO_3^-, SO_4^{2-}, Tc-99, and U concentrations used in Cl^-treated DOWEX resin batch sorption experiments. The starting solution pH before DOWEX addition was 7.4 ± 0.1.

Test	Solution:Solid Ratio (mL/g dry resin)[*]	Cl^- mM (ppm)[&]	CO_3^{2-} mM (ppm)	NO_3^- or SO_4^{2-} mM (ppm)[%,$]	Tc-99 (ppb)	U (ppb)	Test Objective
A	52 – 1005	15 (520)[**]	10 (600)	-	-	-	Quantify only CO_3^{2-} uptake
NO_3^- Experiments							
B	52 – 1007	-	-	6.0 (375)	-	-	Quantify only NO_3^- uptake
C	201 – 203	1 – 203 (34 – 7180)	-	5.9 – 6.1 (366 – 379)	-	-	Evaluate NO_3^- uptake as a function of $[Cl^-]$
D	51 – 981	50 – 65 (1780 – 2300)	-	6.2 (384)	-	-	Quantify NO_3^- uptake in the presence of optimal $[Cl^-]$
E	51 – 998		10 (600)	6.2 (383)	-	-	Quantify NO_3^- and CO_3^{2-} uptake in the presence of optimal $[Cl^-]$
F	201 – 203		-	<0.37 – 101 (<23 – 6240)	200	-	Determine the effect of $[NO_3^-]$ on Tc-99 uptake in the presence of optimal $[Cl^-]$
G	201 – 202		10 (600)	<0.37 – 101 (<23 – 6240)	-	116	Determine the effect of $[NO_3^-]$ on U uptake in the presence of 10 mM CO_3^{2-} and optimal $[Cl^-]$
H	200 – 201		10 (600)	<0.37 – 104 (<23 – 6460)	200	116	Determine the effect of $[NO_3^-]$ on U and Tc-99 uptake in the presence of 10 mM CO_3^{2-} and optimal $[Cl^-]$
S	202 – 203		10 (600)	<0.37 – 100 (<23 – 6170)	200		Determine the effect of $[NO_3^-]$ on Tc-99 uptake in the presence of 10 mM CO_3^{2-} and optimal $[Cl^-]$
SO_4^{2-} Experiments							
I	58 – 1121	0.18 (7)[**]	-	2.9 (283)	-	-	Quantify only SO_4^{2-} uptake
J	199 – 200	0.15 – 231 (5 – 8200)	-	2.9 – 3.0 (278 – 289)	-	-	Evaluate SO_4^{2-} uptake as a function of $[Cl^-]$
K	51 – 997	51 – 65 (1820 – 2300)	10 (600)	2.9 (283)	-	-	Quantify SO_4^{2-} uptake in the presence of 10 mM CO_3^{2-} and optimal $[Cl^-]$
L	200 – 201		-	<0.02 – 9.8 (<2.16 – 937)	200	-	Determine the effect of $[SO_4^{2-}]$ on Tc-99 uptake in the presence of optimal $[Cl^-]$
M	201		10 (600)	<0.02 – 9.9 (<2.16 – 953)	-	116	Determine the effect of $[SO_4^{2-}]$ on U uptake in the presence of 10 mM CO_3^{2-} and optimal $[Cl^-]$
N	201		10 (600)	<0.02 – 9.8 (<2.16 – 946)	200	116	Determine the effect of $[SO_4^{2-}]$ on U and Tc-99 uptake in the presence of 10 mM CO_3^{2-} and optimal $[Cl^-]$

Test	Solution:Solid Ratio (mL/g dry resin)[*]	Cl^- mM (ppm)[&]	CO_3^{2-} mM (ppm)	NO_3^- or SO_4^{2-} mM (ppm)[%,$]	Tc-99 (ppb)	U (ppb)	Test Objective
Q	51 - 1006		-	3.1 (298)	-	-	Quantify SO_4^{2-} uptake in the presence of optimal [Cl^-]
R	162 – 204		10 (600)	<0.05 – 9.8 (<5 – 941)	200	-	Determine the effect of [SO_4^{2-}] on Tc-99 uptake in the presence of 10 mM CO_3^{2-} and optimal [Cl^-]
Kinetic Experiments							
T	1000	50 (1768)	10 (600)	19 (1190) for NO_3^- and 5 (500) for SO_4^{2-}	200	116	Determine the kinetics of U and Tc uptake in the presence of all anions

Legend:

[*]Ratio [**50 – 1000**]: 50, 100, 200, 500, and 1000 mL/g

[&]Cl^- [**0 to 200 (7072**)]: 0, 10 (354), 50 (1768), 100 (3536), and 200 (7072) mmol/L (ppm)

[%]NO_3^- [**0 to 98 (6040**)]: 0, 6 (372), 20 (744), 38 (2380), 50 (3040), 98 (6040) mmol/ L (ppm)

[$]$SO_4^{2-}$ [**0 to 10 (1000**)]: 0, 0.5 (50), 2 (150), 5 (500), 10 (1000) mmol/ L (ppm)

[**] Presence of Cl^- due to pH adjustment.

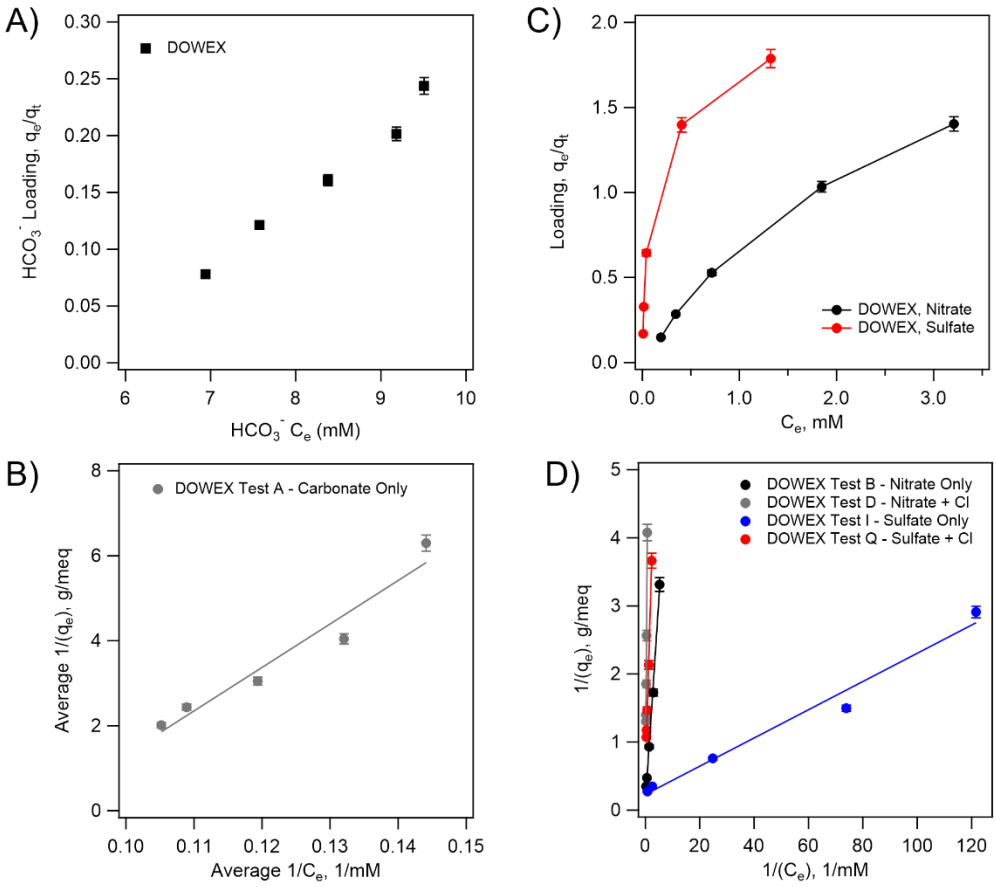

Figure 1. Sorption isotherms for DOWEX with HCO_3^- (A) and Langmuir fit (B). Sorption isotherms for DOWEX with NO_3^- and SO_4^{2-} (C) and Langmuir fit (D). In A and C, uptake by DOWEX resins is presented as a fractional loading q_e/q_t of the target anion, where q_e is the equilibrium loading for this anion and q_t is the total ion exchange capacity of the resin (q_t = 2.0 meq/g dry resin). Initial concentrations of CO_3^{2-}, NO_3^- or SO_4^{2-} were 10 mM, 6 mM, and 3 mM, respectively. The solution-to-dry-resin mass ratio varied from 50 to 1000 mL/g. Testing was conducted at ambient temperature. Error bars indicate the experimental error of ± 3%.

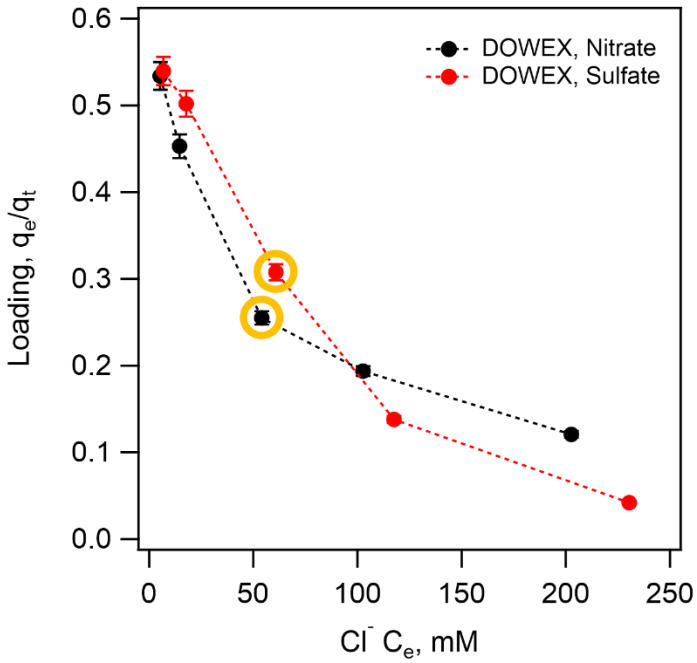

Figure 2. Sorption isotherms for NO_3^- and SO_4^{2-} uptake at different Cl^- concentrations for DOWEX resins, presented as a fractional loading q_e/q_t of the target anion, where q_e is the equilibrium loading for this anion and q_t is the total ion exchange capacity of the resin (q_t = 2.0 meq/g dry resin). Concentrations of NO_3^-, SO_4^{2-}, and Cl^- were 6 mM, 3 mM, and a range from 0 – 200 mM, respectively. Testing was conducted at ambient temperature. The optimal Cl^- concentration point chosen, 50 mM, is identified by a gold open circle. Error bars indicate the experimental error of ± 3%.

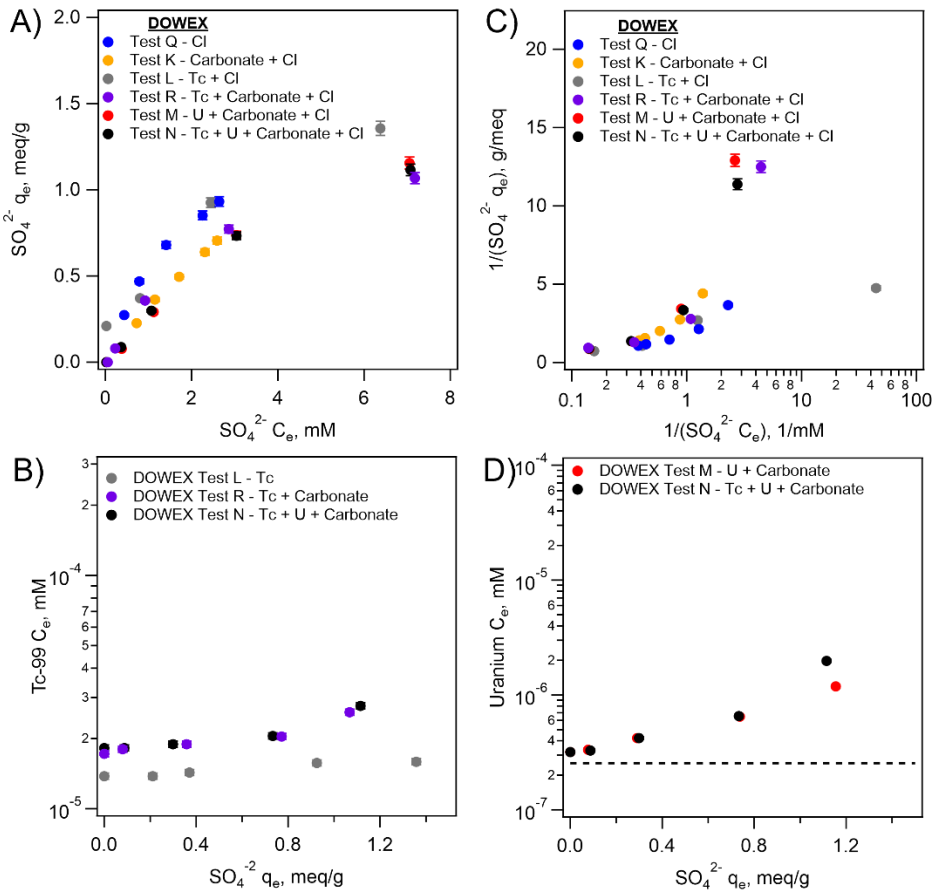

Figure 3. DOWEX SO_4^{2-} sorption (A) and Langmuir (C) isotherms for experiments with multiple anions present. The effect of SO_4^{2-} loading on the final aqueous concentrations of Tc-99 and U is shown in panels (B) and (D), respectively. Note that Test K was performed under variable solution:solid ratio rather than a function of SO_4^{2-} concentration; therefore, a direct comparison should not be made. The dashed line in (D) indicates the ICP-MS limit of detection for U (2.55×10^{-7} mM). The ICP-MS limit of detection for Tc-99 is 3.74×10^{-7} mM for tests L and N, and 3.74×10^{-6} mM for test R. Error bars indicate the experimental error of ± 3%.

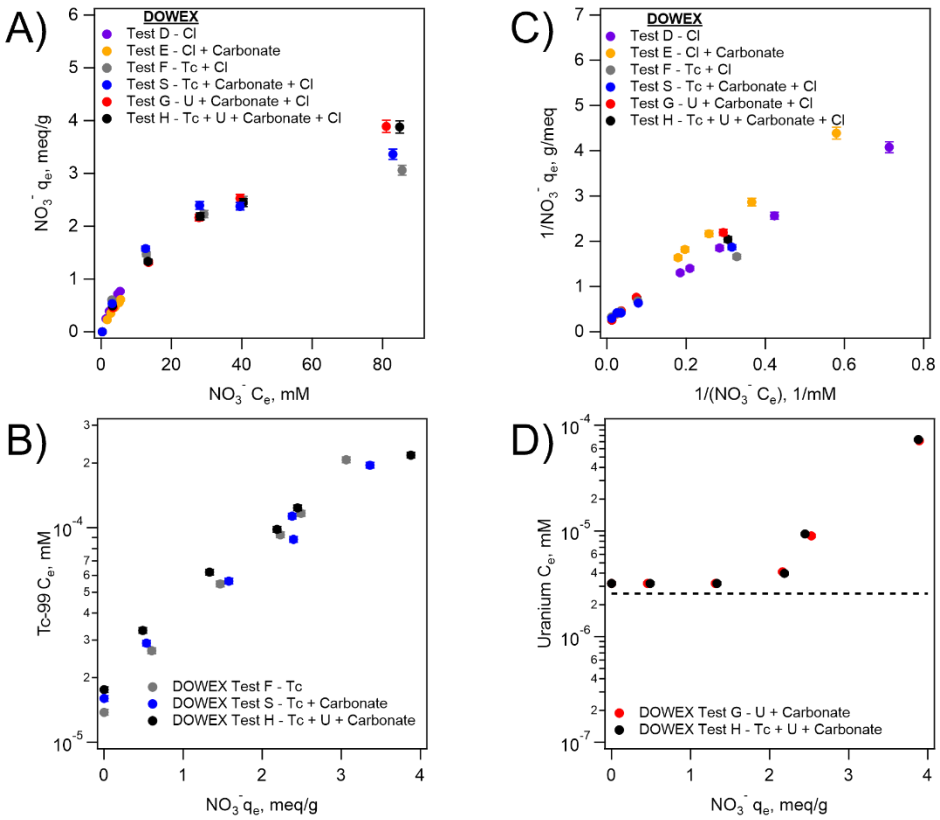

Figure 4. DOWEX NO_3^- sorption (A) and Langmuir (C) isotherms for experiments with multiple anions present. The effect of NO_3^- loading on the final aqueous concentrations of Tc-99 and U is shown in panels (B) and (D), respectively. The dashed line in (D) indicates the ICP-MS limit of detection for U (2.55×10^{-6} mM). The ICP-MS limit of detection for Tc-99 is 3.74×10^{-6} mM for tests S and H, and 7.48×10^{-6} mM for test F. Error bars indicate the experimental error of ± 3%.

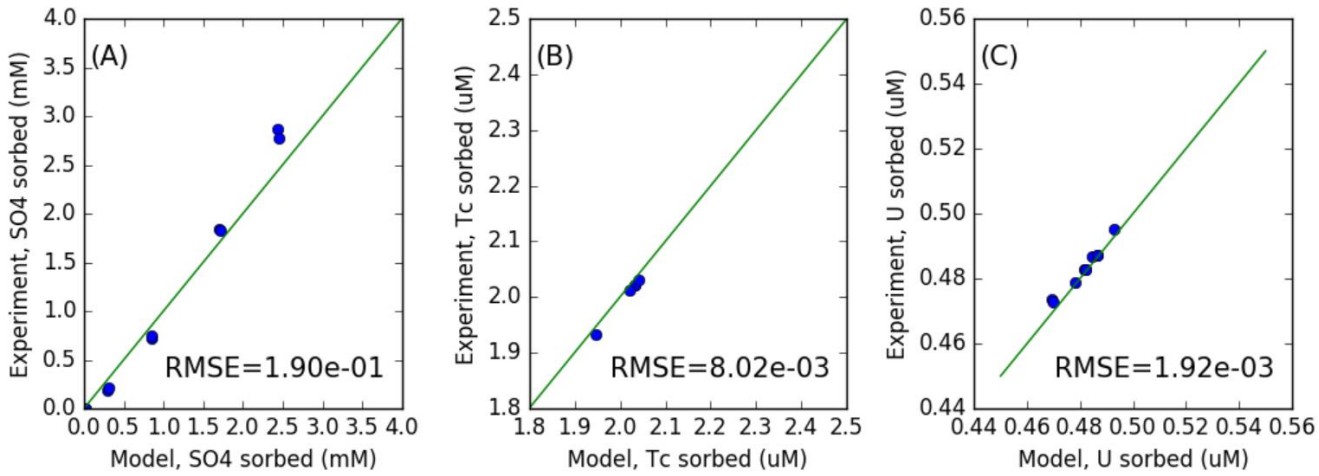

Figure 5. Comparison between measured values and HYDROGEOCHEM model results for (A) SO_4^{2-}, (B) Tc-99, and (C) U in DOWEX Test M and Test N. Reported values for $K_{SO4-/Cl-}$ (2.0), $K_{TcO4-/Cl-}$ (2000), and $K_{U/Cl-}$ (50,000) represent the K values where the root mean square error (RMSE) value was minimized for the specific anion and dataset used for fitting.