

Regeneration of pilot-scale ion exchange columns for hexavalent chromium removal

Julie A. Korak^{*}, Richard Huggins, Miguel Arias-Paic

Bureau of Reclamation, U.S. Department of the Interior, PO Box 25007, Denver, CO 80225, USA

A B S T R A C T

Due to stricter regulations, some drinking water utilities must implement additional treatment processes to meet potable water standards for hexavalent chromium (Cr(VI)), such as the California limit of 10 µg/L. Strong base anion exchange is effective for Cr(VI) removal, but efficient resin regeneration and waste minimization are important for operational, economic and environmental considerations. This study compared multiple regeneration methods on pilot-scale columns on the basis of regeneration efficiency, waste production and salt usage. A conventional 1-Stage regeneration using 2 N sodium chloride (NaCl) was compared to 1) a 2-Stage process with 0.2 N NaCl followed by 2 N NaCl and 2) a mixed regenerant solution with 2 N NaCl and 0.2 N sodium bicarbonate. All methods eluted similar cumulative amounts of chromium with 2 N NaCl. The 2-Stage process eluted an additional 20–30% of chromium in the 0.2 N fraction, but total resin capacity is unaffected if this fraction is recycled to the ion exchange headworks. The 2-Stage approach selectively eluted bicarbonate and sulfate with 0.2 N NaCl before regeneration using 2 N NaCl. Regeneration approach impacted the elution efficiency of both uranium and vanadium. Regeneration without co-eluting sulfate and bicarbonate led to incomplete uranium elution and potential formation of insoluble uranium hydroxides that could lead to long-term resin fouling, decreased capacity and render the resin a low-level radioactive solid waste. Partial vanadium elution occurred during regeneration due to co-eluting sulfate suppressing vanadium release. Waste production and salt usage were comparable for the 1- and 2-Stage regeneration processes with similar operational setpoints with respect to chromium or nitrate elution.

1. Introduction

Hexavalent chromium (Cr(VI)) is present in many groundwater aquifers used as drinking water sources and may be naturally occurring or due to anthropogenic sources (Ball and Izbicki, 2004; Seidel and Corwin, 2013). While the US Environmental Protection Agency (USEPA) regulates total chromium (trivalent and hexavalent) concentrations at 100 µg/L, the State of California has set a maximum contaminant level (MCL) for Cr(VI) in drinking water at 10 µg/L. As a result of this new regulation, many drinking water utilities in California now require expanded treatment operations to meet the California MCL (California Environmental Protection Agency, 2014). If a nationwide regulation is implemented, it is anticipated that thousands of entry points in public water systems

would require additional treatment (Seidel and Corwin, 2013) at a cost of \$0.5–\$5.1 billion per year (Seidel et al., 2013).

Strong base anion exchange (SBA) is one treatment technology that is effective for removing Cr(VI) (Gorman et al., 2016; Li et al., 2016a; McGuire et al., 2006; Seidel et al., 2013; Sengupta and Clifford, 1986a, 1986b). SBA uses an inert polymeric resin activated with surface and interstitial exchangeable functional groups, such as quaternary amines. For a chloride regenerated SBA resin, sulfate, bicarbonate, nitrate, and other anions with greater affinity for the resin functional groups exchange with chloride based on ion selectivity in ratios that maintain charge balance in the system. Divalent anions are generally more selective than monovalent anions (Clifford and Weber, 1983; Subramonian and Clifford, 1988). Additional transformations can occur within the pore structure; weak acids, such as bicarbonate (HCO_3^-), can deprotonate to form a more selective multivalent anion (Horng and Clifford, 1997; Zhang and Clifford, 1994).

Resin exhaustion is operationally-defined based on contaminants of concern and process configuration. In a single pass system,

the threshold for Cr(VI) exhaustion may occur when the effluent concentration exceeds a pre-defined concentration either from an individual contactor or the blended effluent from several contactors (e.g., 8 µg/L or 80% of the California MCL). In a lead-lag configuration, the lead (i.e., first) contactor is fully loaded with Cr(VI) at exhaustion, and a second contactor in series (i.e., lag) captures Cr(VI) in the effluent of the lead unit. Upon exhaustion, SBA resin can be regenerated using a concentrated salt solution. In the case of Cr(VI) processes, this waste brine is hazardous, and disposal represents a major operating cost.

Currently, there are two regeneration approaches implemented at full-scale plants. One approach uses a single regenerant solution concentration, while the second uses a staged approach with multiple regenerant solution concentrations. The multi-stage approach includes strategically increasing the regenerant concentration to first elute sulfate and bicarbonate followed by chromium and nitrate (Waite, 2015). While implemented at the full-scale, little information exists to objectively compare the regeneration approaches to make informed decisions about optimal process operation. At the bench- and pilot-scale, previous work has investigated using sodium bicarbonate in lieu of sodium chloride as an alternative regeneration approach (Li et al., 2016b), but mixed regenerant solutions have not been investigated.

Regeneration efficiency, waste production and salt usage are primary factors governing SBA selection for full-scale treatment of drinking water, but little research has focused on the regeneration efficiency of chromium treatment. In most studies, only chromate, sulfate and/or nitrate data is presented (Li et al., 2016a; Sengupta et al., 1988). The impacts of treatment and regeneration on other trace metals (e.g., uranium, vanadium, arsenic, molybdenum) has not been investigated. An evaluation of regeneration efficiency for chromium and other trace metals, waste production and salt usage is needed to evaluate current approaches and provide a basis for future innovation.

The objective of this study was to regenerate parallel loaded pilot-scale SBA columns for drinking water Cr(VI) removal using different regeneration approaches and compare performance in terms of 1) total constituent elution, 2) waste production and 3) regenerant salt requirements.

2. Materials and methods

2.1. Column loading

Groundwater from a well in California with naturally-occurring Cr(VI) at concentrations above the California regulatory MCL was used as the source water for the pilot-scale SBA columns (Table S-1). Three columns (2 inch diameter polyvinylchloride) were operated in parallel to produce loaded resins of similar exchanger phase composition. Fig. S-1 includes a process flow diagram. Each column was loaded with 2 L of Purolite A600E/9149 resin, which is a Type I quaternary amine, gel polystyrene resin crosslinked with divinylbenzene and has a minimum capacity of 1.6 eq/L. Columns were operated at a loading rate of 8 gpm/ft² (325 L/min/m²). Samples were collected 2–3 times per week from each column effluent and analyzed for Cr(VI). Columns were operated until full exhaustion with respect to Cr(VI), when equal influent and effluent concentrations were measured. Column pressures, flows and bed height were recorded 3–4 times per week, and flows were adjusted as needed to maintain a constant loading rate.

2.2. Column regeneration

After the first water treatment loading cycle, the columns were regenerated following three approaches. As summarized in Table 1, the first regeneration method using Column 1 applied a single

sodium chloride (NaCl) concentration of 2 N NaCl (1-Stage). The second regeneration method applied to Column 3 used two concentrations of NaCl, 0.2 N NaCl followed by 2 N NaCl (2-Stage). Column 2 was regenerated with a modified 2-Stage approach but was not fully characterized. Deionized water (DI) with a resistivity of at least 16 MΩ-cm was used as the background water for regenerations R1-R3. After regeneration, the columns were put back in service and loaded to Cr(VI) exhaustion. In the second regeneration cycle, Columns 1 and 3 were regenerated with a 1-Stage and 2-Stage approach, respectively. Column 2 was regenerated with a 2 N NaCl brine followed by a mixed 2 N NaCl with 0.2 N sodium bicarbonate (NaHCO₃) brine. The second regeneration cycle used softened well water from the pilot site. Analytical grade NaCl and NaHCO₃ were used in all regeneration tests.

Each regeneration process was conducted co-current to flow during water treatment. Regeneration loading rate was 49 ± 4 L/min/m³ (0.37 ± 0.03 gpm/ft³). The nominal bed volumes of brine used in each regeneration are summarized in Table 1. Actual regenerant solution contact is calculated using elution data and presented in the results section.

During regeneration, effluent from the column was fractionated into high density polyethylene bottles between 250 and 1000 mL depending on required elution resolution. Small sample bottles were used for dynamic segments of the regeneration to better define elution peaks (e.g. initial increase of conductivity after interstitial water is displaced). By collecting entire fractions rather than grab samples, a mass balance could be performed with minimal data interpolation. The mass and volume of each fraction was measured, and the average bed volume (BV_{avg}) was calculated for each fraction collected. BV_{avg} is defined as the average cumulative volume of the fraction divided by the resin bed volume. For example, if a fractionated sample was collected between 1 L and 1.5 L of cumulative elution from a 2 L resin bed, the BV_{avg} of that fraction would be 0.625 (i.e., average quantity of 1.5 L and 1 L divided by 2 L of resin). The term bed volume (BV) will be used to describe a normalized solution volume relative to resin volume, irrespective of the regeneration elution sequence. BV_{avg} will only be used in the context of the regeneration elution profile regarding the timing of the elution profile.

After the second regeneration cycle, the columns were regenerated with analytical grade hydrochloric acid (HCl) to evaluate the elution efficiency of trace metals. Following manufacturer recommendations, three BVs of 6% (w/w) HCl was prepared. Upon elution of the first HCl BV, the pump was turned off. After a 2 h HCl soaking period, the final 2 bed volumes were eluted from the column before rinsing.

2.3. Batch regeneration

For the first regeneration cycle, aliquots of resin were collected from the top, middle and bottom of the loaded columns and regenerated as a batch experiment to determine the spatial profile of constituents throughout the resin bed. 10 mL resin samples were added to 250 mL Erlenmeyer flasks with 200 mL of 2 N NaCl and agitated for about 70 h. All regenerant solutions were made using DI. A strainer was used to separate the resin from the supernatant, and the supernatant was analyzed for trace metals, sulfate, nitrate and alkalinity.

2.4. Analytical methods

During column loading, raw water quality was monitored using standard methods listed in Table S-1. Column effluent samples were collected about every 2500 BV to monitor Cr(VI) breakthrough and analyzed using EPA Method 218.6. During regeneration, samples

Table 1

Summary of regeneration approaches conducted on three pilot scale columns on consecutive loading cycles.

Regeneration Number	Cycle	Column	Stage 1		Stage 2		Description
			Regenerant	BV	Regenerant	BV	
R1	1	1	2 N NaCl	4	—	—	1-Stage DI
R2 ^a	1	2	0.4 N NaCl	1	2 N NaCl	2	2-Stage Modified
			0.1 N NaCl	6			
			0.2 N NaCl	7			
R3	1	3	0.2 N NaCl	4	2 N NaCl	2	2-Stage DI
R4	2	1	2 N NaCl	4	—	—	1-Stage GW
R5	2	2	2 N NaCl	1.25	2 N NaCl	2.75	NaCl/NaHCO ₃
					+ 0.2 N NaHCO ₃		
R6	2	3	0.2 N NaCl	4	2 N NaCl	4	2-Stage GW

DI: Deionized water.

GW: Softened raw groundwater from pilot study site.

^a Regeneration R2 was only analyzed for uranium elution and is only presented for context when interpreting the second regeneration cycle of Column 2 (R5).

were analyzed for conductivity and pH (HQ40d, Hach, Loveland, CO). Meters were calibrated daily. Total, carbonate and bicarbonate alkalinity was determined using sulfuric acid titration following Standard Method 2320. It was assumed that bicarbonate alkalinity was representative of bicarbonate concentrations, and other alkalinity contributors were negligible.

A suite of elements in the regeneration brine were measured using inductively coupled plasma mass spectrometry (ICP-MS) (7500, Agilent, Santa Clara, CA). Samples were acidified with nitric acid prior to analysis and diluted as needed with 1% nitric acid based on the instrument calibration range. The instrument was calibrated with a multi-element solution (SPEX CertiPrep 2A) between 0.1 µg/L and 1 mg/L and also calibrated with a chloride standard (Hach, 1000 mg/L as Cl) from 1 mg/L to 200 mg/L. Duplicates and matrix spikes were analyzed every 10 samples, and a NIST 1643f standard was used to verify the calibration curve. In the regeneration brine, total chromium was analyzed as a surrogate for Cr(VI). Negligible concentrations of trivalent chromium were measured in the raw water, and reduction reactions during ion exchange were assumed to be negligible. Total elemental chlorine was used as a surrogate for chloride as no other common sources of elemental chlorine (e.g., perchlorate) were measured in the source water. The average relative percent difference (RPD) between duplicate samples was 2.0% for elemental sodium, chlorine, chromium and uranium. Matrix spike recoveries for chromium and uranium were within an acceptable range (85–109% and 89–97%, respectively).

Nitrate was analyzed using flow injection analysis (QuikChem Method 10-107-04-1-A). The average RPD between nitrate duplicates was 11% (< 0.2 mg-N/L, *n* = 14), and matrix spike recoveries ranged from 83 to 111%. Sulfate was also analyzed by flow injection analysis (QuikChem Method 10-116-10-1-A). The average RPD for sulfate duplicates was 5%, and matrix spike recovery ranged from 74 to 101% (*n* = 11).

2.5. Mass balance assumptions

To facilitate mass balance calculations during regeneration, several assumptions were made regarding the anionic form of constituents in the exchanger phase. For elements measured by ICP-MS that have a propensity to form oxyanions in aqueous systems, anionic forms were assumed based on oxidation state and pH. It was assumed that the oxidized form would be most abundant since more than 97% of chromium was found in the oxidized, hexavalent form. At a pH of 8, chromium is present as predominantly chromate (CrO₄²⁻) (Sengupta and Clifford, 1986b). Comparing the reduction potential of chromate with other oxyanions, it would be expected that vanadium, arsenic, selenium, molybdenum and uranium would also be found in an oxidized state. Despite non-detection in the raw

water (Table S-1), selenium, molybdenum and uranium accumulated on the resin and resulted in significant concentrations in the regeneration waste due to the high affinity and high water throughput until chromium exhaustion. The most abundant form of vanadium in oxic groundwater was assumed to be the monovalent oxyanion vanadate (H₂VO₄⁻) (Wright et al., 2014). Arsenic and selenate (SeO₄²⁻), respectively (Bissen et al., 2003; Horng and Clifford, 1997; White and Dubrovsky, 1994). Molybdenum was assumed to be present as molybdate (MoO₄²⁻). Uranium was assumed to be present in its most selective and stable form as a uranyl carbonate complex (UO₂(CO₃)₃⁴⁻) (Langmuir, 1978; Zhang and Clifford, 1994).

The form of polyprotic anions and polynuclear metals within the exchanger phase were also assumed. Although found predominantly as bicarbonate at pH 8 in groundwater, bicarbonate (HCO₃⁻) has been shown to deprotonate to form a more selective carbonate (CO₃²⁻) divalent anion within the resin, increasing the relative selectivity to chromate (Horng and Clifford, 1997). Vanadium may also be present as a divalent anion (HVO₄²⁻) or polynuclear complex (HV₂O₇³⁻) in the exchanger phase (Horng and Clifford, 1997; Rice, 1983). For the purpose of calculations, only the monovalent forms (i.e., HCO₃⁻ and H₂VO₄⁻) were assumed. Chromium and molybdenum can form polynuclear complexes (i.e., Cr₂O₇²⁻ and Mo₇O₂₄⁶⁻) within the exchanger phase, but these polynuclear forms were assumed to be absent for mass balance calculations due to the alkaline operating pH (Sengupta, 1986).

Natural organic matter (NOM) can compete in SBA processes due to the negative surface charge of humic substances (Thurman, 1985) but was assumed to be absent for mass balance purposes. Total organic carbon was not detected in the raw water entering the SBA columns (Method Reporting Limit (MRL) = 0.3 mg/L). The majority of NOM present in the groundwater was likely removed by the granular activated carbon pre-filter, which also removed any free chlorine residual from normal well operations. The insignificant effect of NOM is confirmed in SI Text 1.

3. Results

3.1. Raw water quality and column loading

The source water for the pilot-scale SBA columns was an operational groundwater well at a municipal water district in California that has Cr(VI) concentrations of 40 µg/L as summarized in Table S-1, which is above the California MCL. More than 97% of the total chromium in the raw water was measured as the Cr(VI) form based on paired samples where hexavalent and total chromium were both quantified.

Columns were fully exhausted around 50,000 BV with respect to

Cr(VI). Loading until exhaustion is representative of an ion exchange process operating in a lead-lag configuration. Fig. 1 shows consistent breakthrough of Cr(VI) from all three columns. The California MCL for Cr(VI) of 10 $\mu\text{g/L}$ was exceeded at $36,000 \pm 850$ BV.

The observed run-time is significantly longer than reported data from other studies using the same resin and is due to different concentrations of competing anions (i.e., sulfate). One pilot study with half as much raw water Cr(VI) 0.61–0.65 $\mu\text{eq/L}$ (16–17 $\mu\text{g/L}$) exceeded the California MCL at a similar throughput (30,000–35,000 BV), a difference that can be attributed to higher raw water sulfate concentrations around 0.42 eq/L (20 mg/L) (Seidel et al., 2014). Another pilot study using a raw water with half as much Cr(VI) (0.65 $\mu\text{eq/L}$, 17 $\mu\text{g/L}$) but six times as much sulfate (1.0 eq/L, 48 mg/L) reached the California MCL at about 13,000 BV (Gorman et al., 2016). These results demonstrate that SBA is well-suited to treat this raw water due to reduced competition from sulfate compared to other reported studies.

3.2. Three regeneration approaches

3.2.1. 1-Stage regenerations

The 1-Stage regeneration process was designed to model a conventional SBA regeneration process with NaCl at a constant concentration (2 N NaCl). This regeneration was performed on Column 1 after each loading cycle (Table 1, Regenerations R1 and R4). In the first regeneration (R1), deionized water used as the background regenerant solution (1-Stage DI), whereas the second cycle (R4) used softened raw water (1-Stage GW).

The elution profiles for regenerations R1 and R4 are shown in Fig. 2a–d and Figs. S-2 and S-3. A mass balance between chloride exchange (Fig. 2b) and anions eluted (Fig. 2c) was in good agreement (3% difference) and found that 79% of the active sites exchanged during regeneration. Details are provided in SI Text 1. Fig. 2c illustrates the chromatographic elution of major anions for regeneration R1. Sulfate and bicarbonate began eluting from the column as soon as it was contacted with regenerant solution (0.66 BV_{avg}). Sulfate concentrations peaked around 1.1 BV_{avg} and tailed off by 1.9 BV_{avg} . Bicarbonate and chromium concentrations peaked around 1.4 BV_{avg} and tailed off by 2 BV_{avg} . Nitrate exhibited a broader elution peak centered near 1.9 BV_{avg} . Without additional data between 2.5 and 4 BV_{avg} , it is difficult to assess the true breadth of the nitrate elution peak for regeneration R1. Uranium co-eluted with chromium and bicarbonate with a peak between 1.25 and 1.4 BV_{avg} and a peak fraction concentration of 1.5 meq/L

(92 mg/L). Elution of other trace metals (i.e., arsenic, molybdenum and selenium) is provided in Fig. S-2.

The effects of selectivity reversal on elution order are apparent comparing Fig. 2c to typical monovalent and divalent selectivity (chromate > sulfate > nitrate > chloride > bicarbonate) in low ionic strength groundwater (Clifford and Weber, 1983). Fig. 2c, however, shows that nitrate elutes after sulfate. At high ionic strengths, selectivity reversal shifts resin selectivity to favor monovalent anions (e.g., nitrate) over divalent anions (Boari et al., 1974). In resin regeneration for nitrate removal, sulfate elutes first and more efficiently than nitrate (Guter, 1995). The retardation of nitrate can also be due its hydrophobic character coupled with the hydrophobicity of the exchanger phase (Clifford and Weber, 1983), which has divinylbenzene crosslinking. The co-elution of bicarbonate and sulfate may also be due to acid-base reactions, where more selective carbonate molecules present in the exchanger phase have a selectivity similar to sulfate and protonate when released into the bulk solution (Horng and Clifford, 1997). pH increased (Fig. 2a) as bicarbonate and carbonate eluted from the resin indicating protonation of weak acids in the regeneration solution.

In both regenerations (R1 and R4), the bed volumes of solution required for complete regeneration is governed by nitrate rather than chromium elution. Using sodium as a conservative tracer, a mass balance was used to calculate the total volume of regenerant solution eluted from the column at complete nitrate elution. For the 1-Stage DI regeneration (R1), 3.2 BVs of regenerant solution were passed through the column corresponding to samples collected up to 4 BV_{avg} of total liquid elution (initial interstitial volume plus regenerant solution). In the 1-Stage GW regeneration (R4), additional bed volumes of regenerant solution were used to ensure complete elution, but only data up until complete nitrate elution are shown. To manage leakage and potential chromatographic peaking during the water treatment cycle, complete nitrate elution was defined as effluent concentrations less than 2% of the peak concentration. For regeneration R4, nitrate elution was complete at 4.7 BV_{avg} , which equated to 3.4 BV of regenerant solution (Fig. S-3). A mass balance between chloride and other anions was calculated to confirm that the column tests agree with batch tests, and no significant constituents were missing from the analytical suite (SI Text 1).

3.2.2. 2-Stage regenerations

The 2-Stage regeneration process exposed the resin to a low strength stage with 0.2 N NaCl (0.2 N Stage) followed by a high strength stage with 2 N NaCl (2 N Stage) to control the elution of constituents based on selectivity. This regeneration was performed on Column 3 after each loading cycle (Table 1, Regenerations R3 and R6). In regeneration R6, the volume of the 0.2 N Stage was decreased from a nominal 7 BV to 4 BV, and the volume of the high strength stage was increased from 2 BV to 4 BV for complete nitrate elution. The elution profiles for the 2-Stage DI (R3) and 2-Stage GW (R6) regenerations are presented in Fig. 2e–h and Fig. S-5, respectively.

Focusing on the 2-Stage DI regeneration (Fig. 2e–h), the 0.2 N Stage primarily eluted sulfate, bicarbonate, arsenic, and some vanadium from the resin, and these constituents exhibited elution peaks in the low strength stage. Sulfate concentrations peaked between 4.25 and 5.75 BV_{avg} (Fig. 2g), but non-consecutive fractions were analyzed (indicated by the dashed line). Chromium and nitrate exhibited increases in concentration throughout this stage. Chromium concentrations increased monotonically from 0.78 meq/L (20 mg/L) at 0.9 BV_{avg} to 2.9 meq/L (75 mg/L) at the end of the stage (7.2 BV_{avg}). A similar trend was observed for nitrate with concentrations increasing monotonically from 2.9 meq/L (40.7 mg-N/L) to 9.1 meq/L (127 mg-N/L) for the same BV_{avg} range. Uranium concentrations were below

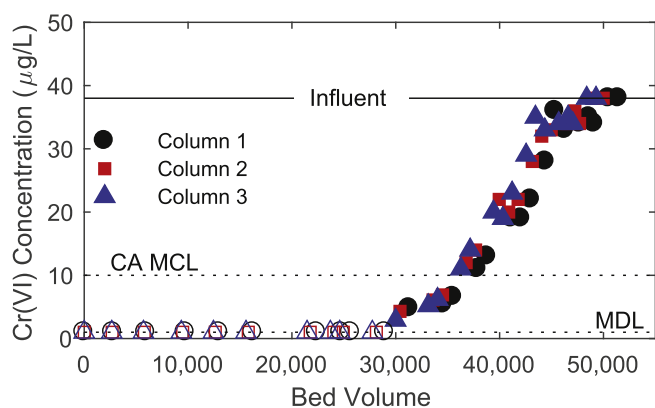


Fig. 1. Hexavalent chromium breakthrough from pilot scale columns for the first loading cycle. Dashed lines indicate California (CA) MCL for Cr(VI) and method detection level (MDL). Unfilled markers indicate samples measured at the MDL.

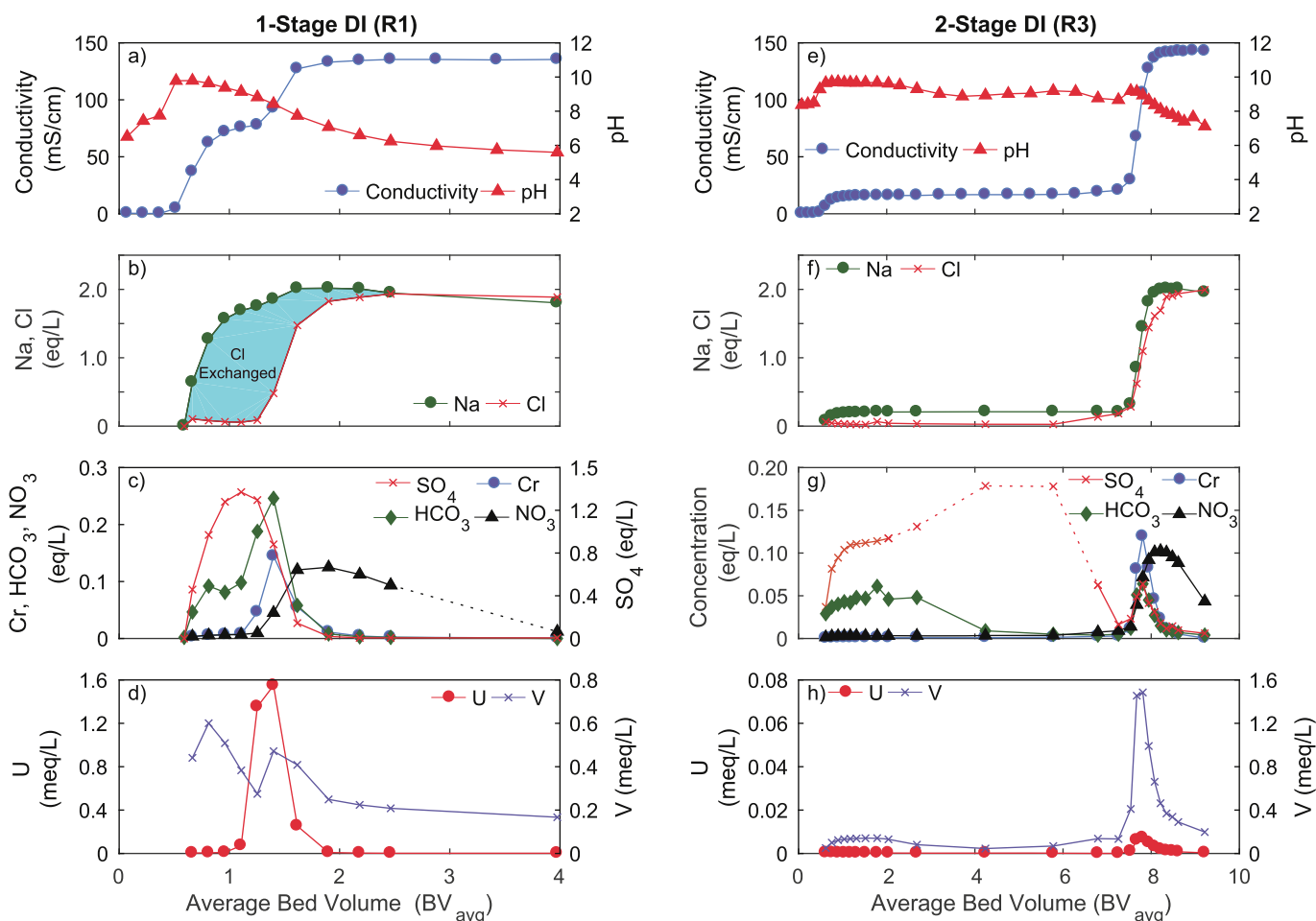


Fig. 2. Elution profile from the 1-Stage DI (R1) regeneration (a–d) and 2-Stage DI (R3) regeneration (e–h) represented as conductivity and pH (a, e), sodium and chloride (b, f), sulfate, bicarbonate, chromium and nitrate (c, g) and uranium and vanadium (d, h). Dashed lines for nitrate and sulfate indicate analysis of non-consecutive sample fractions.

the method reporting limit (0.1 mg/L). Some vanadium eluted during the 0.2 N Stage shown in Fig. 2h.

By the end of 0.2 N Stage in regeneration R3, the concentration of both sulfate and bicarbonate decreased, indicating that elution was not limited by the number of 0.2 N bed volumes. Simultaneously, chloride concentrations in the effluent increased eventually equaling sodium concentrations at 7.25 BV_{avg}, prior to the 2 N Stage transition. The increase in eluted chloride at the end of the 0.2 N Stage indicated that active sites in the exchanger phase reached an equilibrium with respect to major anions (i.e., sulfate, bicarbonate), and chloride in the regenerant solution was not limiting. The 2-Stage GW regeneration (R6), differed by decreasing the bed volumes used in the 0.2 N Stage. As a result, sulfate exchange was not complete before transitioning to the 2 N Stage (Fig. S-5).

The 2 N Stage eluted chromium, nitrate, vanadium, molybdenum and some uranium from the column. The delayed elution of nitrate compared to chromium, vanadium and uranium demonstrated selectivity reversal and/or retardation similar to the 1-Stage regenerations. Uranium elution differed between the two 2-Stage regenerations (R3 and R6). In the 2-Stage DI regeneration (R3), the maximum uranium fraction concentration was only 7.2 µeq/L (0.4 mg/L) at 7.8 BV_{avg} (Fig. 2h). In the 2-Stage GW regeneration (R6), the maximum uranium fraction concentration was 2 meq/L (122 mg/L) at 4.9 BV_{avg} (Fig. S-5). To confirm the absence of a significant uranium peak in regeneration R3, samples were reanalyzed in the 2 N Stage brine at a lower dilution factor (lower detection

limit) and were in good agreement (RPD < 10%). Uranium was also analyzed from regeneration R2 (Table 1, Fig. S-6), which followed a similar approach, affirming the low uranium concentrations in regeneration R3.

By sodium mass balance, regeneration R3 exposed the resin to a total of 6.7 BV of 0.2 N NaCl followed by 1.6 BV of 2 N NaCl. Complete nitrate elution was not observed in regeneration R3. Regeneration R6 exposed the resin to 3.9 BV of 0.2 N NaCl followed by 3.6 BV of 2 N NaCl for complete nitrate elution.

3.2.3. 1-Stage NaCl with NaHCO₃ addition

Based on the elution results from the first regeneration cycle, a hybrid regeneration approach was conducted on Column 2 (Table 1, Regeneration R5), which included 2 N NaCl followed by 2 N NaCl buffered with 0.2 N NaHCO₃. The elution profiles for this regeneration are presented in Fig. 3 and Fig. S-7. Up until the addition of NaHCO₃, the elution profiles are similar to those observed during 1-Stage regeneration. Addition of NaHCO₃ increased pH and eluted additional chromium, uranium and vanadium (Fig. 3). The peak vanadium concentration observed with NaHCO₃ was greater than any regeneration that only used NaCl (Fig. 3c). At complete nitrate elution, the resin was exposed to 1.1 BV of 2 N NaCl and 2.5 BV of 2 N NaCl/0.2 N NaHCO₃.

4. Discussion

The differences between regeneration approaches were

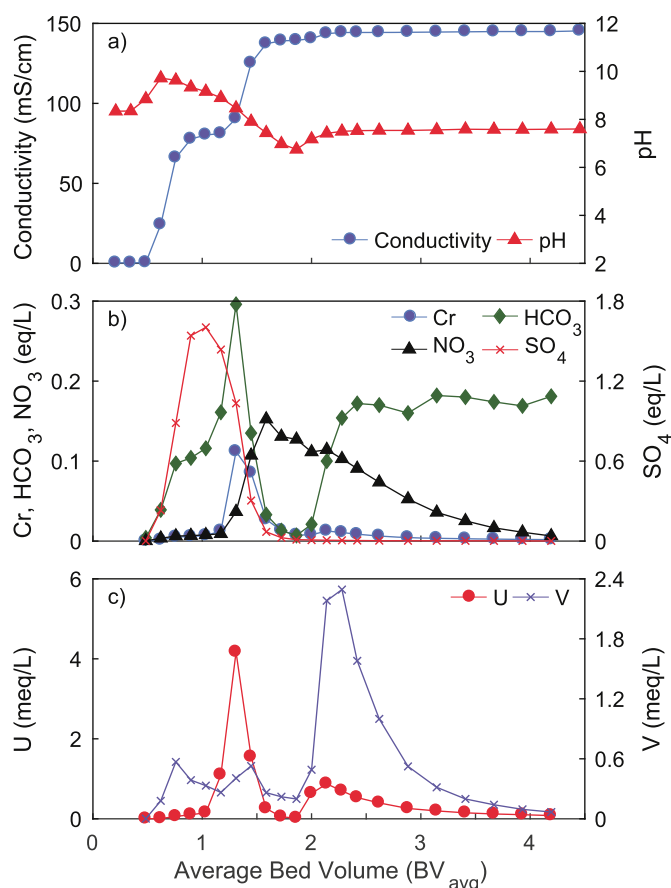


Fig. 3. Elution profile from the NaCl/NaHCO₃ regeneration (R5) represented as a) conductivity and pH, b) sulfate, bicarbonate, chromium and nitrate and c) uranium and vanadium.

evaluated by comparing constituent elution efficiency, salt chemical requirements, and waste production. Elution efficiency was evaluated based on cumulative mass recovery, peak sharpness, and the presence of tailing, all of which impact overall process performance. Salt use directly compares regeneration chemical consumption. Waste volume is directly related to operating costs (Jensen and Darby, 2016).

To minimize waste in full-scale regeneration processes, the leading and tail edge of the regeneration are often recycled to the

SBA process headworks or secondary holding tanks for use in a subsequent regeneration cycle. To allow for comparison between regeneration approaches, standard operating criteria were assumed. Under these criteria, brine at the beginning of regeneration with a conductivity less than 20 mS/cm would be recycled to the SBA process headworks and would not require disposal. This fraction would include the 0.2 N Stage in the 2-Stage approaches and leading edge in the 1-Stage and NaCl/NaHCO₃ approaches. An additional criterion on the tail end of the regeneration sequence assumed that once the effluent chromium concentration equaled 5 meq/L (~130 mg/L), the process would switch to rinse water. This concentration is less than 5% of the maximum measured chromium concentration. At this point, it was assumed that 0.5 BV of the relevant brine was still present in the interstitial pore space (~50% porosity). This volume was included in the salt dose and waste calculations. It was also assumed that an additional 1 BV of rinse water would require disposal and was included in the waste calculations.

4.1. Elution efficiency

4.1.1. Chromium elution efficiency

For total chromium elution, the 2-Stage approaches eluted more chromium, but the mass in the waste fraction was similar between all approaches. Within each regeneration cycle, the 2-Stage regeneration approaches eluted 20–30% more chromium than the 1-Stage approaches (i.e., R1 vs R3 and R4 vs R6) (Table 2, Fig. S-8). Cumulative chromium elution from the NaCl/NaHCO₃ regeneration (R5) was similar to the 1-Stage regenerations. The increased total recovery of chromium during the 2-Stage regenerations was attributed to the elution that occurred during the 0.2 N Stage, not increased removal efficiency during the 2 N Stage. From a system mass balance perspective, the impact of the increased chromium elution using the 2-Stage approach depends on the fate of the brine produced during the 0.2 N Stage. Some full-scale implementations of 2-Stage regeneration recycle the 0.2 N brine to the SBA process headworks over the water treatment cycle. Under this approach, capacity for chromium could decrease as the influent sulfate and chromate concentrations increase. The impact of recycling brine to the SBA headworks on influent concentrations depends on the recycle rate. If the 0.2 N brine produced were recycled back to the headworks and bled in over 20,000 BV, the influent sulfate concentration would increase 26% or 16% for the R3 and R6 regenerations, respectively. Influent chromate concentration would increase 29% or 12% for the R3 or R6 regenerations,

Table 2

Comparison of regeneration approaches in terms of chromium, uranium and nitrate elution, salt dose and waste produced.

Regeneration number	Approach	Stage	Duration (BV _{avg})		Contaminant elution				Salt dose		Waste produced	
			Start	Stop	Cr	NO ₃	U	V	eqCl-/L _{resin}	gNaCl/(1000 L _{H2O}) ^a	BV	L _{waste} /(1000 L _{H2O}) ^a
R1	1-Stage	— ^d	0.59	2.2	1.3	6.70	30	^b	4.0	4.6	3.1	0.06
R3	2-Stage	0.2 N ^c	0	7.1	0.23	1.7	0.06	32	1.4	1.6	8.6	0.17
		2.0 N ^d	7.1	8.6	1.4	6.1	0.23	47	3.0	3.5	3.1	0.06
		Total	0	8.6	1.6	7.8	0.3	78	4.4	5.2	—	—
R4	1-Stage	— ^d	0.50	2.0	1.0	7.3	50	26	3.7	4.4	3.0	0.06
R5	NaCl/NaHCO ₃	— ^d	0.60	2.8	1.2	10.3	92	87	5.1	5.9	3.7	0.07
R6	2-Stage	0.2 N ^c	0	4.4	0.08	0.9	0.22	13	0.8	0.9	5.9	0.12
		2.0 N ^d	4.4	5.7	1.3	4.5	47	29	2.7	3.2	2.7	0.05
		Total	0	5.7	1.3	5.4	48	42	3.5	4.1	—	—

^a Treated water volume (L_{H2O}) assumes throughput of 50,000 BV (resin exhausted for chromium).

^b Not calculated.

^c Stage transitions to 2 N Stage with no rinse water.

^d Salt dose includes extra 0.5 BV of interstitial brine. Waste calculation includes 0.5 BV of interstitial brine plus 1 BV of rinse water.

respectively. Therefore, the benefit of increased chromium removal during the 2-Stage regeneration approach could be limited by recycling the chromium and sulfate during the subsequent treatment cycle due to the inverse relationship between influent sulfate concentration and throughput to chromium breakthrough (Gorman et al., 2016).

Using the conductivity and effluent chromium concentration criteria as process setpoints to define the waste fraction, all regeneration approaches exhibited little difference in chromium elution when exposed to 2 N NaCl (Table 2). Fig. 4 illustrates that the peak height and breadth of the chromium elution peak were similar between approaches. If chromium elution under 2 N NaCl ultimately governs the net mass of chromium removed from the system, this metric did not favor selecting one regeneration approach over another.

A significant difference between regeneration approaches, however, was the presence of effluent chromium concentration tailing. Since the effluent chromium concentration is a direct indication of residual chromium in the exchanger phase, tailing is indicative of inefficient regeneration at the end of the cycle. Fig. 4a

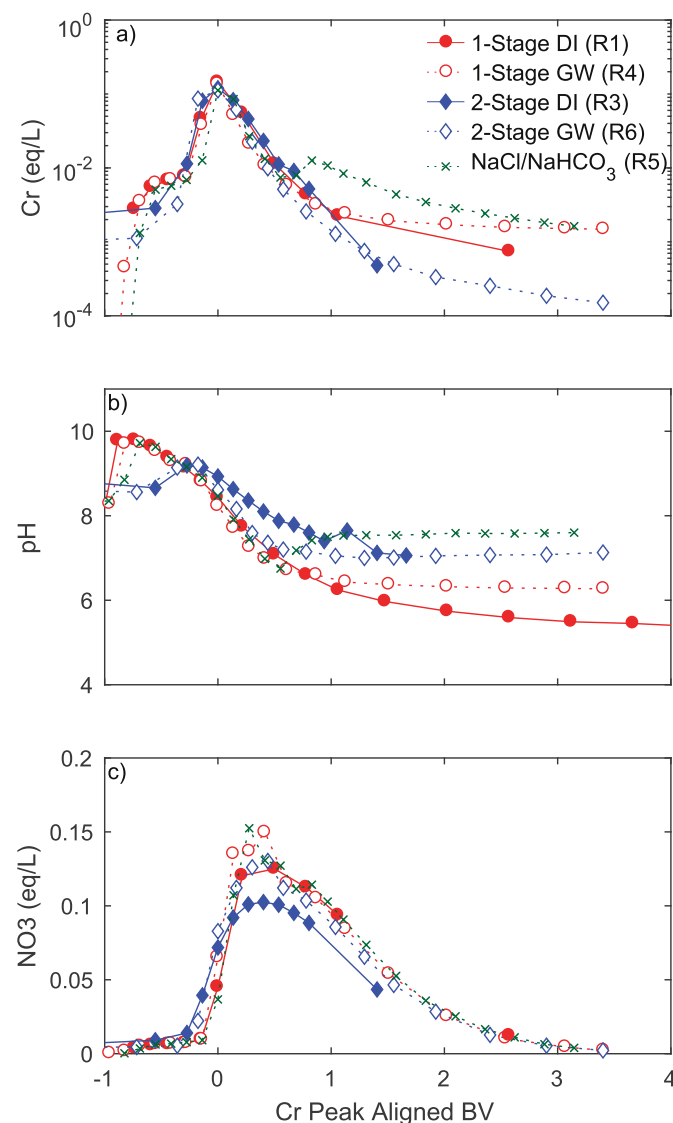


Fig. 4. Comparison of elution curves for a) chromium, b) pH and c) nitrate for all regeneration approaches. Bed volumes are plotted with chromium elution peaks aligned.

highlights the differences in tailing and shows that the 1-Stage (R1 and R4) and NaHCO₃ (R5) regenerations exhibited tailing where effluent concentrations decreased asymptotically. Differences in chromium elution efficiency were confirmed by batch regeneration tests conducted on resin aliquots removed from the column after the first regeneration cycle. Fig. S-9a shows that more chromium remained at the bottom of the resin bed post-regeneration for 1-Stage DI (R1) compared to 2-Stage DI (R3).

Comparing the 1-Stage (R1 and R4) and 2-Stage (R3 and R6) regenerations, differences in pH may explain some of the differences in elution efficiency at the end of the regeneration cycle. After the elution of bicarbonate, pH decreased through the remainder of the regeneration process. One BV_{avg} after peak chromium elution, the pH values in the 2-Stage regenerations were 0.5–1 unit higher than the 1-Stage regenerations (Fig. 4b). While using softened groundwater (R4) led to systematically higher pH values at the end of regeneration, the background alkalinity was not sufficient to prevent pH decreases relative to the raw water (pH = 8) due to alkalinity uptake by the resin.

In both 1-Stage regenerations, the effluent pH dropped below 6.5. This transition from alkaline to acidic pH has multiple impacts on ion exchange mechanisms. Under acidic conditions, the Cr(VI) speciation in the bulk liquid phase shifts from chromate to bichromate (HCrO₄⁻). In the exchanger phase, however, the formation of dichromate (Cr₂O₇²⁻) through the dimerization of bichromate is favored, because the selectivity of dichromate is greater than that of bichromate (Sengupta, 1988; Sengupta et al., 1986). Dichromate will occupy half the number of exchange sites at acidic pH and decrease the fraction of active sites occupied in the exchanger phase without changing the total mass of Cr(VI). Not only does the selectivity for Cr(VI) increase at acidic pH, but the nature of the Cr(VI)-chloride isotherm also changes from favorable at alkaline pH to unfavorable at acidic pH (Sengupta et al., 1986). Regeneration is more difficult at low pH using NaCl alone, because regeneration now requires two steps: deprotonation by a hydroxide ion followed by chloride ion exchange (Sengupta et al., 1988). For this reason, regeneration of SBA resin operated under acidic conditions often uses caustic soda and NaCl during regeneration (Sengupta, 1995).

The NaCl/NaHCO₃ regeneration (R5) demonstrates that pH is not the only factor impacting chromium elution. Upon NaHCO₃ addition, pH increased to 7.5, which was greater than the effluent pH in the 2-Stage regenerations. After an initial increase, effluent chromium concentrations also exhibited tailing. At 3 BV_{avg} after peak chromium elution (Fig. 4a), the effluent chromium concentration in the NaCl/NaHCO₃ regeneration was 20 times higher than the 2-Stage GW (R6) regeneration at the same point. Therefore, additional factors other than pH impact chromium tailing and warrant further investigation for regeneration optimization.

A key difference in elution efficiency between approaches was the location of residual chromium in the exchanger phase. Residual chromium at the bottom of the column can cause leakage during the next loading cycle, which was observed for Column 1 (Fig. S-10). For the 2-Stage approach, the 20–30% of additional chromium that eluted in the 0.2 N Stage would be recycled to the headworks, exchange with the resin due to its high selectivity, but likely not have a significant impact on the throughput to chromium saturation compared to the 1-Stage approach (neglecting the effects of increased sulfate concentration). The 0.2 N Stage recycled chromium, however, would be reloaded on the top of the column and be less prone to leakage.

4.1.2. Uranium elution efficiency

Regeneration approach impacted the elution efficiency of uranium. To compare regeneration efficiency, only select regeneration

profiles could be compared directly, because the elution efficiency of the first regeneration cycle (R1–R3) directly impacted the initial exchanger phase uranium concentration for the second loading cycle (R4–R6).

Comparing the first cycle, the 1-Stage DI (R1) removed 100 times more uranium than the 2-Stage DI (R3) approach. Previous work has shown that uranium regeneration depends on both the regenerant solution concentration and total salt dose, but these factors cannot explain differences in uranium elution efficiency. At the same total salt dose ($\text{eq}_{\text{Cl}}/\text{eq}_{\text{resin}}$), previous work has shown that more uranium is eluted at higher salt concentrations (Clifford and Zhang, 1995; Zhang and Clifford, 1994). Over the entire 1-Stage DI regeneration (Fig. 2a–d), the resin was exposed to a total of 3.3 $\text{eq}_{\text{Cl}}/\text{eq}_{\text{resin}}$. The uranium elution peak tailed off by 1.9 BV_{avg} , at which point the column had been exposed to only an excess of 0.65 $\text{eq}_{\text{Cl}}/\text{eq}_{\text{resin}}$ with a maximum concentration of 1.8 eq/L chloride. Peak uranium removal preceded complete chloride breakthrough in the column. During the 2 N Stage of the 2-Stage DI (R3) regeneration, the column was exposed to an excess of 1.2 $\text{eq}_{\text{Cl}}/\text{eq}_{\text{resin}}$ at concentrations greater than 1.9 eq/L, yet negligible uranium elution was observed. Therefore, a difference in uranium regeneration efficiency could not be accounted for by chloride dose or concentration.

Differences in uranium regeneration efficiency are partially attributed to bicarbonate concentrations. In the 1-Stage regeneration, uranium concentrations peaked at 1.4 BV_{avg} with a concomitant bicarbonate concentration of 0.25 eq/L. In the 2-Stage regeneration approach, the mobile phase was depleted in

bicarbonate during the 2 N Stage. Peak uranium elution occurred at 7.8 BV_{avg} at which point chromate was the most abundant counterion (0.12 eq/L) other than chloride (1.1 eq/L). The bicarbonate concentrations never exceeded (0.06 eq/L) in the 2 N Stage. Previous work investigating the hydrometallurgical processes to concentrate and purify uranium has recognized the importance of carbonate in the regenerant to prevent the hydrolysis and precipitation of uranium (Hollis, 1958; Streat and Naden, 1987). As a general guideline, Streat and Naden (1987) suggests that sodium carbonate concentrations around 0.1 M are needed to prevent hydrolysis and precipitation of uranium complexes. The mechanisms are summarized in Eqns (1)–(3) from Clifford and Zhang (1995). The uranyl carbonate complex can be displaced (Eqn (1)) by chloride during regeneration. At high pH or low carbonate concentrations, the equilibrium shifts to form solid sodium pyrouranate or uranium oxide while liberating carbonate (Eqn (2) and Eqn (3)). Compared to the 1-Stage approach, the 2-Stage DI (R3) had a higher pH (Fig. 2e) accompanied by lower peak bicarbonate concentrations (Fig. 5c–d), which may have promoted precipitate formation.

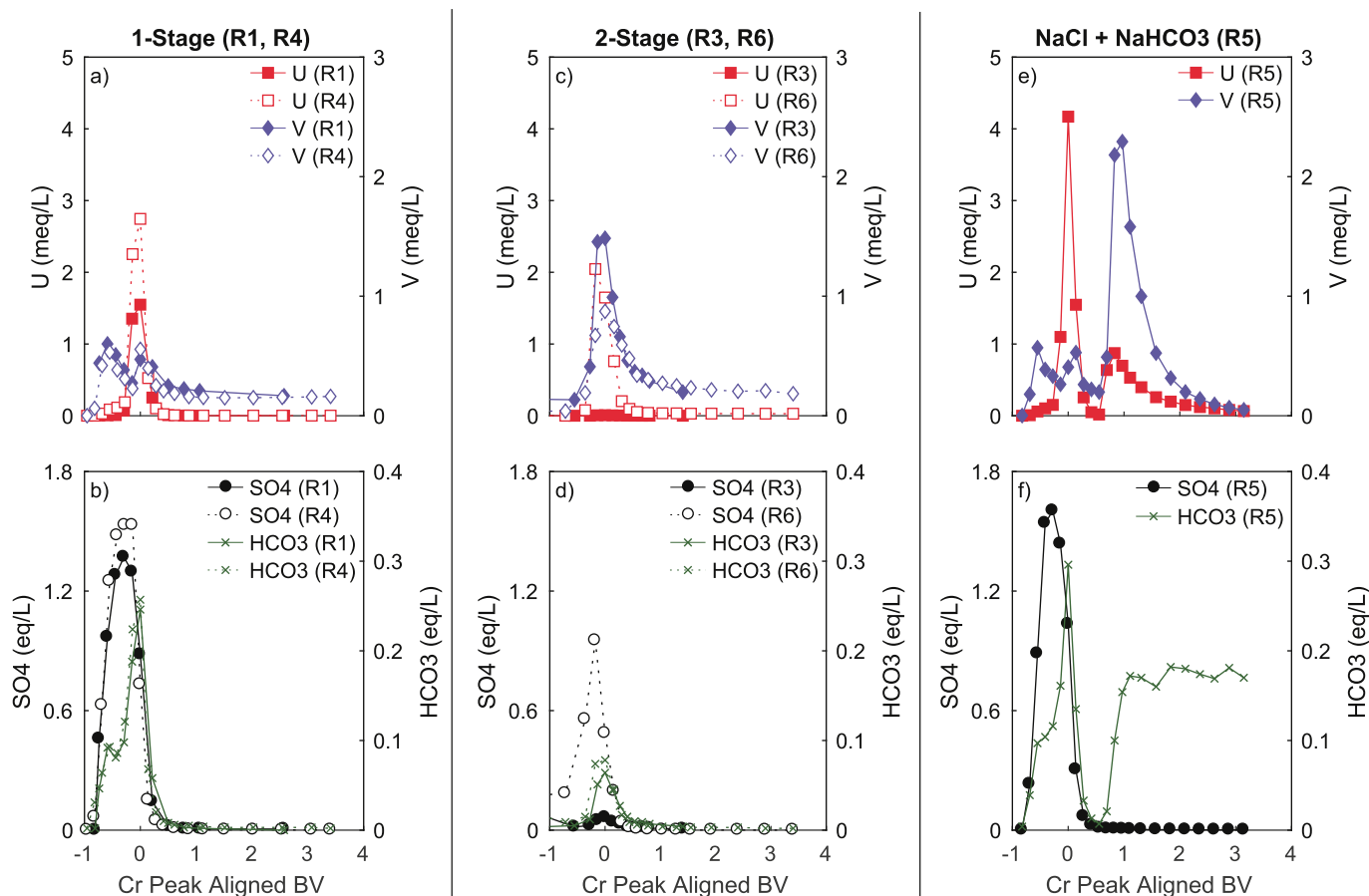
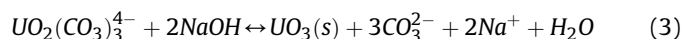
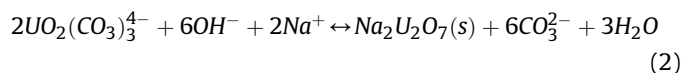
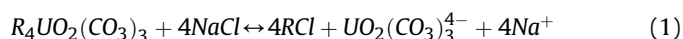


Fig. 5. Chromium peak aligned chromatograms for uranium and vanadium (top row) and sulfate and bicarbonate (bottom row) for each regeneration approach. The regeneration cycle is differentiated as 1st regeneration (solid) and 2nd regeneration (dashed) in a–d.

Differences in sulfate may also play a role in the stability of uranyl complexes. At peak uranium elution during the 1-Stage DI regeneration (R1) shown in Fig. 5a–b, sulfate was the most abundant counterion in the mobile phase (0.88 eq/L) compared to chloride (0.48 eq/L). In comparison, the 2-Stage DI regenerant solution (R3) was relatively depleted in sulfate (0.06 eq/L) at peak uranium elution shown in Fig. 5c–d. Uranyl ions can also form sulfate complexes (e.g., $\text{UO}_2(\text{SO}_4)_3^{4-}$), although the stability constants for uranyl sulfate complexes in bulk solutions are many orders of magnitude lower than those of uranyl carbonate complexes (Zhang and Clifford, 1994). Given the high exchanger phase sulfate concentration prior to regeneration (Table S-2), it is possible that some uranyl sulfate complexes may also be present in the exchanger phase. Gu et al. (2005) has shown that sulfate concentrations can play an important role in uranium recovery during regeneration using synthetic groundwater. Similar to uranyl carbonate, uranyl sulfate complex instability may also promote the formation of insoluble uranium oxides, preventing uranium recovery during regeneration.

For the second round of column regenerations, care must be taken in directly comparing the total mass of uranium eluted as R5 and R6 had a higher starting mass of uranium due to inefficient elution in the first cycle, and the availability of the uranium to be eluted by NaCl is unknown. Coupled with the acid regeneration performed after the second regeneration cycle, uranium elution trends emerge. The 2-Stage GW regeneration (R6) exhibited significant cumulative elution of uranium (1.8 meq), which is nearly 200 times more than the first regeneration cycle (2-Stage DI (R3)). Since the 0.2 N Stage removed most of the bicarbonate (Fig. 2e–h), stabilization of uranyl complexes depends on either background alkalinity in the groundwater or sulfate. At peak uranium elution for regeneration R6, the bicarbonate concentration was 0.07 eq/L, which is similar in magnitude to the concentrations observed in the 2-Stage DI regeneration (R3) and cannot explain the increased uranium elution in regeneration R6. Therefore, the difference can be attributed to the higher sulfate concentrations co-eluting with uranium during the 2-Stage GW regeneration (R6). Since the length of the 0.2 N Stage was shortened by nominally 3 BV in the 2-Stage GW regeneration (R6), complete elution of sulfate did not occur leading to a greater sulfate peak (0.95 eq/L) in the 2 N Stage. These results affirm that sulfate concentrations play an important role in uranium elution from ion exchange columns with high initial sulfate concentrations in the exchanger phase.

The NaCl/ NaHCO_3 regeneration (R5) reveals that uranium elution is incomplete under the two other regeneration approaches that only use NaCl. In regeneration R5, the first uranium peak concentration occurred concurrently with the chromium peak and was greater than other regenerations, which may be attributed to higher initial uranium concentrations on the resin. With the introduction of NaHCO_3 , additional uranium eluted from the resin (Fig. 5e), demonstrating residual uranium remained after regeneration with NaCl alone. Regeneration with HCl elutes uranium as a uranyl cation and is a common regeneration method in hydrometallurgy (Streat and Naden, 1987). Of the total mass of uranium eluted during both NaCl and HCl regenerations, 35–40% of the total recoverable uranium eluted by HCl (Table S-3) indicating significant residual uranium was left after NaCl regeneration for chromium removal.

Incomplete uranium elution may impact the resin capacity, disposal, subsequent regenerations and plant licensing requirements. Uranium could accumulate in the resin with each regeneration. Over time, entrained uranium precipitate could foul resin, reducing capacity during water treatment operations and requiring more frequent regeneration. Uranium accumulation could result in a plant requiring U.S. Nuclear Regulatory

Commission licensing and resin that must be handled and disposed of as technologically enhanced naturally occurring radioactive materials (TENORM).

4.1.3. Vanadium elution efficiency

Regeneration approach also impacted the elution of vanadium from SBA resin. While not regulated by the Safe Drinking Water Act, accumulation of vanadium through multiple loading cycles may also impact long-term operation of SBA for Cr(VI) removal.

During regeneration with only NaCl, multiple vanadium elution peaks indicate that either 1) vanadium moieties with different relative selectivities eluted from the resin and/or 2) the co-elution of other anions impacted vanadium elution. In the 2-Stage NaCl regenerations, vanadium eluted during both the 0.2 N and 2 N Stages (Fig. 2h) suggesting different relative selectivities of moieties. Two elution peaks were observed during the 1-Stage and NaCl/ NaHCO_3 regenerations spanning either side of the sulfate elution peak. The impact of sulfate is discussed below. In the NaCl/ NaHCO_3 regeneration, an additional and more concentrated vanadium peak was observed when a higher NaHCO_3 concentration was present (Fig. 5e–f). Significant tailing in vanadium elution was also observed indicating inefficient recovery during regeneration (Fig. 2d,h, Fig. S-3 to S-5).

Regeneration approaches with NaCl alone did not completely elute vanadium from the resin. Batch tests conducted after the first regeneration cycle recovered additional vanadium, specifically from the middle and lower column sections (Fig. S-9). Acid regeneration following the second cycle eluted 25–30% of the total recovered vanadium (Table S-3).

Insight into this behavior can be garnered from studies investigating the separation of uranium and vanadium from low-grade uranium ores, such as carnotite ($\text{K}_2(\text{UO}_2)_2(\text{VO}_4)_2 \cdot 3\text{H}_2\text{O}$) (Bailes, 1957; Ghorbani and Montenegro, 2016). In carbonate leachates from carnotite, vanadium exhibits a higher selectivity for SBA resins than uranium (Kaufman and Lower, 1954). At high concentrations, vanadium can undergo polymerization reactions similar to chromium to form anions with a greater charge, such as $\text{HV}_2\text{O}_7^{3-}$, $\text{V}_3\text{O}_9^{3-}$, and $\text{V}_6\text{O}_{17}^{4-}$ (Rice, 1983). While predominantly present as H_2VO_4^- in the raw groundwater, more selective forms through deprotonation (HVO_4^{2-}) or polymerization ($\text{HV}_2\text{O}_7^{3-}$) in the exchanger phase can explain the multiple elution peaks in the 2-Stage regenerations.

Incomplete elution of vanadium can be attributed to sulfate suppression. The 2-Stage DI (R3) regeneration exhibited a vanadium elution peak with the highest concentration compared to the other NaCl-only regeneration approaches (Fig. 5a,c,e). During this regeneration, co-eluting sulfate concentrations were also the lowest. One method for selectively eluting uranium over vanadium from SBA resins is by ammonium sulfate (Bailes et al., 1958). While poorly characterized, Bailes et al. (1958) suggests that vanadium elutes but converts to a sulfate complex and is re-adsorbed. In the same method, sodium carbonate is used to elute vanadium and any residual uranium for complete regeneration. The appearance of two vanadium peaks during the 1-Stage regeneration (Fig. 5a) may actually be the suppression of a single peak by sulfate. Only a single vanadium peak was observed during the 2 N Stage of the 2-Stage (R3) approach (Fig. 5c), where sulfate concentrations were significantly lower. The efficiency of carbonate to elute vanadium is evident in the NaCl/ NaHCO_3 regeneration approach (Fig. 5e–f). Table S-3 shows that the NaCl/ NaHCO_3 left less residual vanadium on the resin as indicated by the lower fraction recovered by acid regeneration. The absence of vanadium elution after sulfate elution suggests that sodium chloride alone is not sufficient for complete vanadium regeneration.

While not radioactive, accumulation of vanadium on resin could impact long-term operation of SBA processes for chromium

removal. Regeneration approaches tailored to vanadium and uranium elution may be periodically required to maintain long-term performance.

4.2. Salt use and waste production

4.2.1. Salt use

Differences in total salt use were largely governed by the chromium elution tailing, because the assumed operational setpoint to start the rinse cycle was an effluent chromium concentration of 5 meq/L. The salt requirements for the 1-Stage GW (R4) and 2-Stage GW (R6) regenerations were similar at 3.7 and 3.5 eq_{Cl}-/L_{resin}, respectively, as summarized in Table 2. These regenerations are the most comparable, because each improves upon disadvantages identified in the first regeneration cycle. Use of softened water maintained a higher pH in the effluent for the 1-Stage approach, and a shortened 0.2 N Stage in the 2-Stage approach improved uranium elution. The salt requirement for the NaCl/NaHCO₃ regeneration was greatest due to the second chromium peak and prominent tailing. While the chromium elution peak height and width were similar between all regeneration methods, the regenerant volume needed to reach this 5 meq/L setpoint varied up to 0.2 BV, which accounts for much of the variation in salt requirements. In the NaCl only regenerations, the chromium setpoint was triggered 0.6–0.8 BV after peak chromium elution. The 2-Stage GW regeneration (R6) exhibited the least chromium tailing and required the least salt to conduct regeneration (Table 2).

Defining an operational regeneration setpoint with respect to chromium would leave significant nitrate on the resin. With an assumed 0.5 BV of brine remaining in the bed pore space, nitrate elution would continue until about 1.1 BV – 1.3 BV after peak chromium elution. At this point, 20–30% of the total nitrate would be left on the resin. Little difference in nitrate elution was observed between methods (Fig. 4c). If complete nitrate elution is a regeneration objective, salt requirements would increase compared to Table 2, but there would be little difference between regeneration approaches.

4.2.2. Waste production

With the exception of the NaCl/NaHCO₃ regeneration (R5), there was little difference in waste production between approaches. The 1-Stage regenerations produced 3.1 BV and 3.0 BV of waste for regenerations R1 and R4, respectively (Table 2). If the 0.2 N Stage waste is recycled to the headworks, only the 2 N Stage and rinse water constitutes the waste volume for the 2-Stage approaches. Regenerations R3 and R6 generated 3.1 BV and 2.7 BV of waste, respectively. Due to prolonged chromium elution, the NaCl/NaHCO₃ regeneration generated 3.7 BV of waste. If the regeneration duration is governed by nitrate elution, the waste volume would increase compared to Table 2, but there would be little difference between regeneration approaches.

5. Conclusions

- 1-Stage and 2-Stage regeneration approaches with 2 N NaCl have trade-offs primarily associated with uranium, vanadium and chromium regeneration efficiency rather than waste production or salt use.
- Little difference was observed in the chromium elution efficiency using a 2 N NaCl regenerant solution, resulting in similar waste volumes and salt requirements.
- Tailing effects for chromium elution can be significant for 1-Stage co-current regeneration approaches and can promote leakage during the subsequent water treatment (loading) cycle.

- Uranium elution efficiency is improved by the co-elution of both bicarbonate and sulfate.
- Vanadium elution efficiency is suppressed by co-eluting sulfate and promoted by bicarbonate in the regenerant solution.
- Regeneration approaches specifically targeting removal of uranium and vanadium is important for long-term operation of SBA for Cr(VI) treatment to prevent constituent accumulation across water treatment loading/regeneration cycles.

Disclaimer

The views, analysis, recommendations, and conclusions in this report are those of the authors and do not represent official or unofficial policies or opinions of the United States Government and the United States takes no position with regard to any findings, conclusions, or recommendations made. As such, mention of trade names or commercial products does not constitute their endorsement by the United States Government.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.watres.2017.03.018>.

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Regeneration of Pilot-Scale Ion Exchange Columns for Hexavalent Chromium Removal

Supplemental Information

Julie A. Korak¹, Richard Huggins¹ and Miguel Arias-Paic¹

¹Bureau of Reclamation, U.S. Department of the Interior, PO Box 25007, Denver, CO 80225

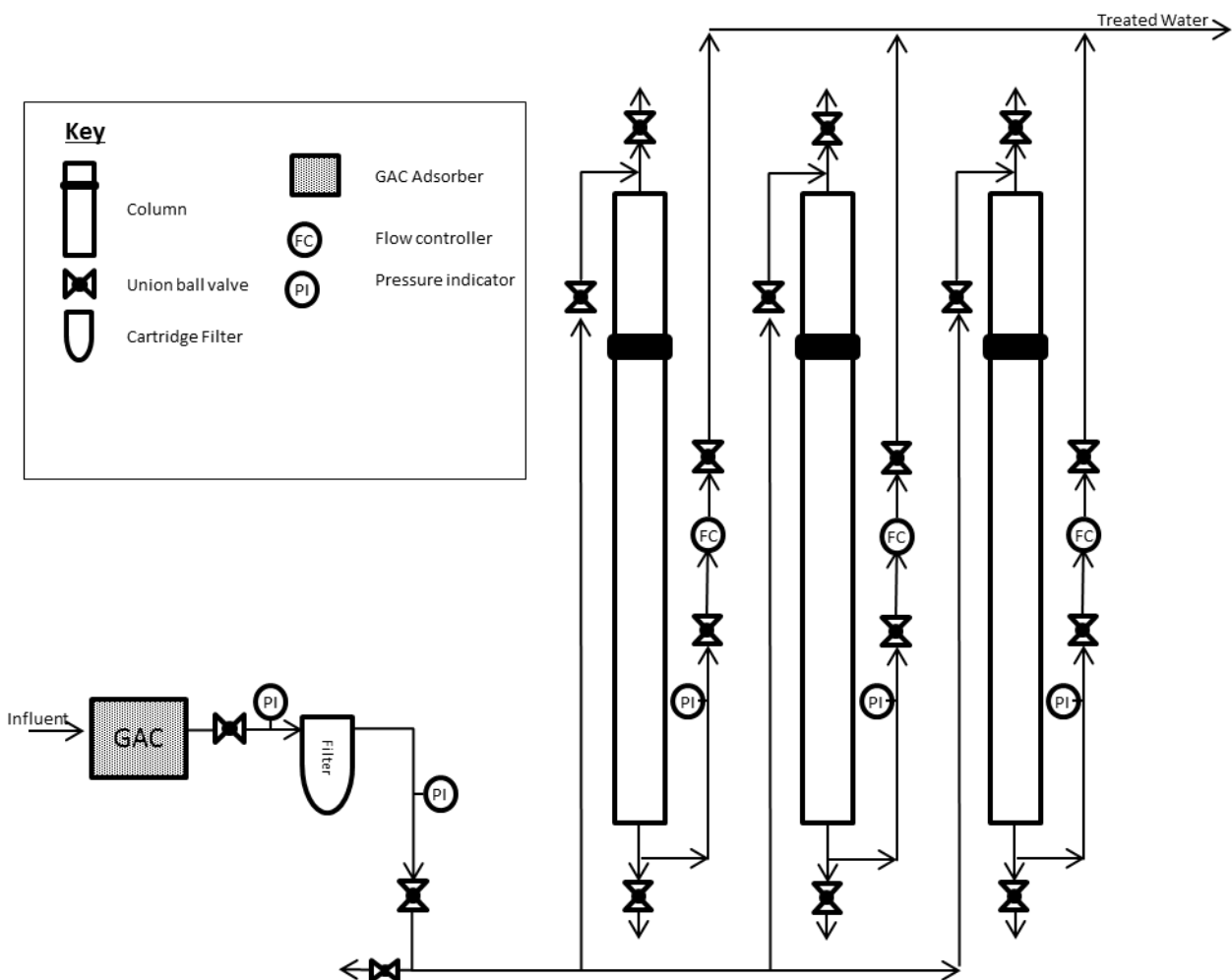


Figure S-1. Process flow diagram of pilot-scale ion exchange process.

Table S-1. Raw water quality analysis (Average \pm Standard Deviation) for influent samples collected during run (n=3). Values below the MRL are reported as ND.

Category	Parameter	Units	Value	MRL	Method
Wet Chemistry	Alkalinity, Total	mg/L as CaCO ₃	94.0 \pm 3.5	5	SM 2320B
	Bicarbonate	mg/L	116.7 \pm 5.8	5	SM 2320B
	Carbonate	mg/L	ND	5	SM 2320B
	Chloride	mg/L	8.0 \pm 0.9	1	EPA 300.0
	Cyanide	µg/L	ND	100	SM4500CNF
	Specific conductance	µmhos/cm	240.0 \pm 0	2	SM 2510B
	Fluoride	mg/L	0.6 \pm 0	0.1	EPA 300.0
	Hydroxide	mg/L	ND	5	SM 2320B
	MBAS (LAS Mole Wt. 340)	mg/L	ND	0.1	SM 5540C
	Nitrate as N	mg/L	2.9 \pm 0.1	0.4	EPA 300.0
	Nitrate + Nitrite (as N)	mg/L	2.9 \pm 0.1	0.4	EPA 300.0
	Nitrite as N	mg/L	ND	0.4	EPA 300.0
	Perchlorate	µg/L	ND	4	EPA 314.0
	pH	SU	8.0 \pm 0.2	0	SM 4500 HB
	Sulfate	mg/L	8.2 \pm 0.5	0.5	EPA 300.0
	TDS	mg/L	146.7 \pm 5.8	5	SM 2540C
	TOC	mg/L	ND	0.3	SM 5310B
Metals	Aluminum	µg/L	ND	50	EPA 200.7
	Antimony	µg/L	ND	6	SM 3113B
	Arsenic	µg/L	5.2 \pm 0.3	2	SM 3113B
	Barium	µg/L	ND	100	EPA 200.7
	Beryllium	µg/L	ND	1	EPA 200.7
	Boron	µg/L	ND	100	EPA 200.7
	Cadmium	µg/L	ND	1	EPA 200.7
	Calcium	mg/L	11.7 \pm 1.2	1	EPA 200.7
	Chromium (+6)	µg/L	40	1	EPA 218.6
	Chromium (Total)	µg/L	39.7 \pm 2.3	10	EPA 200.7
	Copper	µg/L	ND	50	EPA 200.7
	Iron	µg/L	ND	100	EPA 200.7
	Lead	µg/L	ND	5	SM 3113B
	Magnesium	mg/L	1.5 \pm 0.1	1	EPA 200.7
	Manganese	µg/L	ND	20	EPA 200.7
	Mercury	µg/L	ND	1	EPA 245.1
	Molybdenum	µg/L	ND	10	EPA 200.7
	Nickel	µg/L	ND	10	EPA 200.7
	Potassium	mg/L	1.5 \pm 0.2	1	EPA 200.7
	Selenium	µg/L	ND	5	SM 3113B
	Silver	µg/L	ND	10	EPA 200.7
	Sodium	mg/L	39.3 \pm 1.5	1	EPA 200.7
	Thallium	µg/L	ND	1	EPA 200.9
	Vanadium	µg/L	28.7 \pm 4.7	3	EPA 200.9
	Zinc	µg/L	ND	50	EPA 200.7
Calculated Values	Hardness (Total)	mg/L	35.3 \pm 2.3		—
	Total Anions	meq/L	2.5 \pm 0.11		—
	Total Cations	meq/L	2.5 \pm 0.05		—
Uranium	Uranium	pCi/L	ND	1	EPA 908.0

1. Regeneration Mass Balances

1.1. Column Depth Profiles for Key Constituents

Aliquots (~10 mL) of resin sampled from the top, middle and bottom third of the column were regenerated in separate batches to determine the spatial distribution of constituents throughout the column. Samples were analyzed to determine the relative distribution of key constituents (Table S-2) relative to the total number of active sites on the resin to facilitate a mass balance across the system for comparison in subsequent sections. All concentrations were compared on an equivalents basis taking into account the valence and oxidation state of each anion as described in Section 2.5 of the main text.

Compared to the total active sites on the resin, sulfate was the most abundant anion accounting for 48% of total equivalent sites on average followed by bicarbonate (16%) and nitrate (7.3%) as summarized in Table S-2. Chromium accounted for 3.1% of the total equivalents eluted from the resin. Vanadium only accounted for 0.12% of equivalents recovered. As discussed in Section 4.1.3, elution of vanadium may not have been complete. Selenium and arsenic were present at trace levels in the regeneration brine compared to other constituents. With the exception of uranium, all constituents were evenly distributed along the length of the column. Uranium was enriched at the top of the column (0.5%) but only present at trace amounts at lower depths. Uranium was not detected above the detection limit (1 pCi/L, ~1.4 µg/L) in the raw water, but trace levels were present and exchanging with the resin. The enrichment found only at the top of the column attests to the slow progression of the uranium mass transfer zone within the column limited by the low raw water uranium concentration coupled with the high affinity for resin active sites. Even though influent iron was below detection limits, iron fouling was visible in the upper 4-6 inches of the columns indicated by red discoloration and lower total exchange capacity (69%± 6.8%) compared to the bottom of the column (78% ± 1.8%). Some iron (60-120 mg) was recovered when columns were regenerated with HCl. The combination of these results demonstrate that when the strong base anion exchange column is exhausted with respect to chromium, the majority of the exchanged constituents are sulfate, bicarbonate and nitrate with other constituents present at an order of magnitude lower concentrations.

Table S-2. Distribution of Anionic Equivalents relative to total resin capacity for regenerations R1 and R3 (Average ± Standard Deviation, n=2)

Anion	Top	Middle	Bottom	Average
Sulfate (SO_4^{2-})	42.7% ± 6.7%	49.2% ± 2.4%	51.7% ± 0.3%	47.9% ± 5.2%
Nitrate (NO_3^-)	6.5% ± 0.7%	7.6% ± 0.130%	7.7% ± 0.4%	7.3% ± 0.68%
Bicarbonate (HCO_3^-)	16.3% ± 0%	15.6% ± 0.9%	15% ± 1.8%	15.6% ± 1.0%
Chromate (CrO_4^{2-})	2.7% ± 0.4%	3.4% ± 0.048%	3.3% ± 0.009%	3.1% ± 0.4%
Vanadate (H_2VO_4^-)	0.1% ± <0.001%	0.1% ± <0.001%	0.1% ± 0.001%	0.12% ± 0.010%
Uranium Complex ($\text{UO}_2(\text{CO}_3)_3^{4-}$)	0.5% ± 0.3%	0.003% ± <0.001%	0.008% ± 0.010%	0.09% ± 0.048%
Selenate (SeO_4^{2-})	0.006% ± <0.001%	0.006% ± 0.002%	0.006% ± <0.001%	0.006% ± 0.001%
Arsenate (HAsO_4^{2-})	0.006% ± 0.001%	0.007% ± <0.001%	0.007% ± <0.001%	0.007% ± 0.0004%
Molybdate (MoO_4^{2-})	0.183% ± 0.028%	0.228% ± 0.007%	0.227% ± 0.004%	0.005% ± 0.0030%
Total	69% ± 6.8%	76% ± 2.5%	78% ± 1.8%	

1.2. 1-Stage DI Regeneration (R1)

The number of active sites occupied with anions other than chloride before regeneration was determined by comparing the breakthrough of sodium (conservative tracer) and chloride, which exchanged with the resin. Chloride breakthrough is complete at $2.5 \text{ BV}_{\text{avg}}$, approximately 1 BV after sodium breakthrough. Integrating the area under the sodium curve up to $2.5 \text{ BV}_{\text{avg}}$, 7.0 equivalents of sodium eluted from the column. Comparing the same area for chloride, 4.5 equivalents of chloride eluted. The difference between equivalents of chloride and sodium eluted was 2.5 equivalents, which corresponds to the exchange of chloride onto the resin (Figure 2b). Using the resin bed volume (2 L) and resin capacity (1.6 eq/L) along with the integrated area between chloride and sodium, 79% of the resin sites were exchanged during the 1-Stage DI regeneration process. This mass balance was verified by calculating cumulative equivalents of all anionic constituents other than Cl in the elution profile (i.e., sulfate, bicarbonate, nitrate, chromate, etc.). The relative percent difference (difference divided by average) between both approaches was 3%. These results demonstrate that the constituents selected for measurement in Table S-2 are representative of the principal constituents present on fully loaded resin (with respect to Cr(VI)) prior to a regeneration. Other typical water anionic constituents, such as phosphate or NOM, are present at negligible concentrations compared to the overall system mass balance. This data demonstrates that at chromium exhaustion, about 21% of the active sites on the resin are still in the chloride form.

1.3. 2-Stage DI (R3)

Performing a mass balance on the cumulative elution of sodium and chloride at $7.26 \text{ BV}_{\text{avg}}$, 2.1 eq of chloride exchanged with the resin, representing 65% of the total resin capacity. During the subsequent 2 N Stage, an additional 0.5 eq of chloride exchanged with the resin, corresponding to an additional 16% of the total resin capacity. At the end of the 2-Stage regeneration process, 81% of the total resin capacity was exchanged with chloride, which correlates well with the exchanged capacity of the 1-Stage regeneration process. A mass balance on eluting anions other than chloride (e.g., sulfate, bicarbonate, nitrate, chromate, etc.) agreed with the loss of chloride (RPD = 1%). These results confirm that the suite of anions measured in the effluent account for the exchanged chloride, and any other anions (NOM, phosphate, etc.) were present in trace amounts.

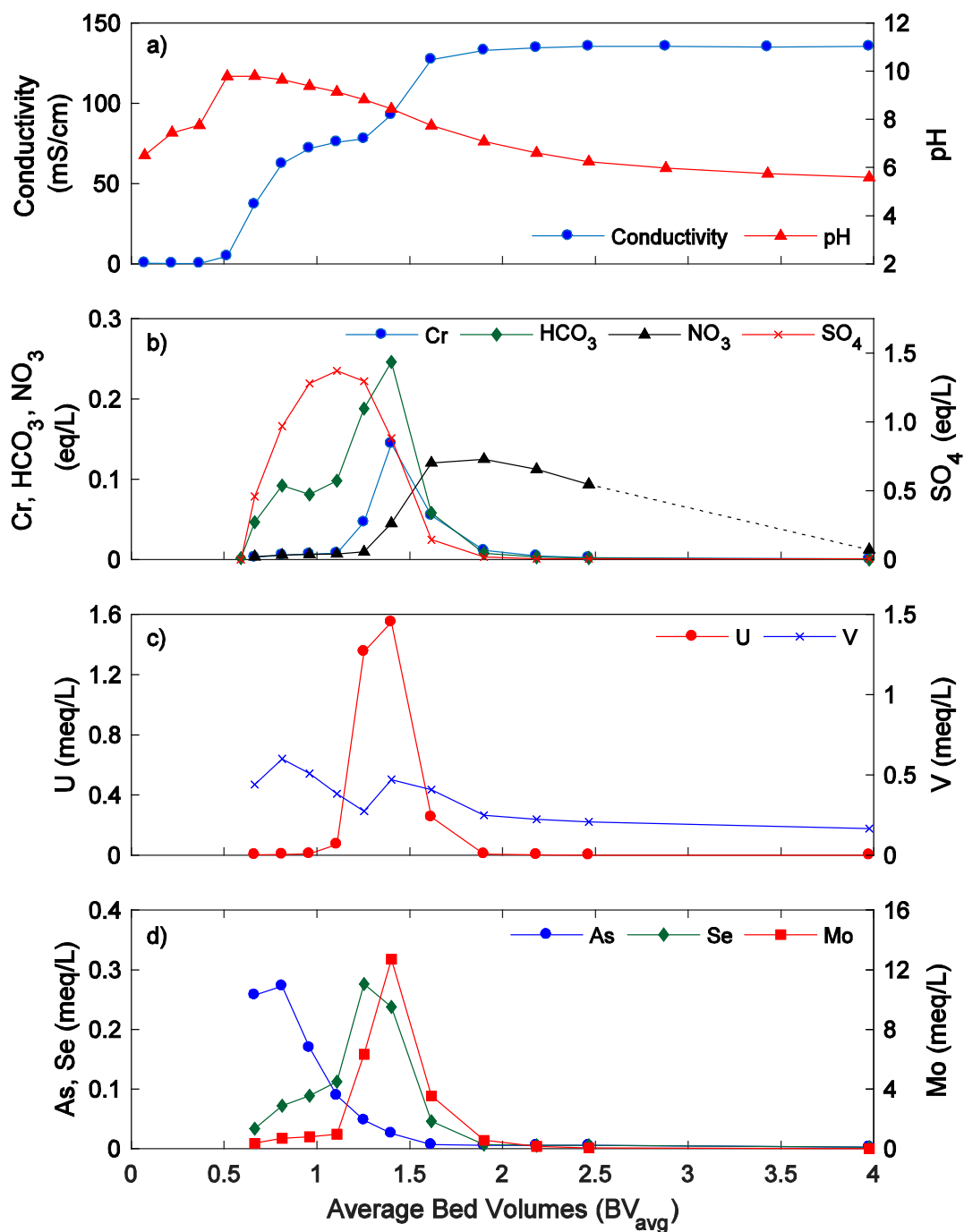


Figure S-2. Elution chromatograph for 1-Stage DI regeneration (R1) showing a) conductivity and pH, b) chromium, bicarbonate, nitrate and sulfate, c) uranium and vanadium, and d) arsenic, selenium and molybdenum concentration. Only concentrations above the method reporting limit are shown. Dashed line indicates non-consecutive brine fractions analyzed.

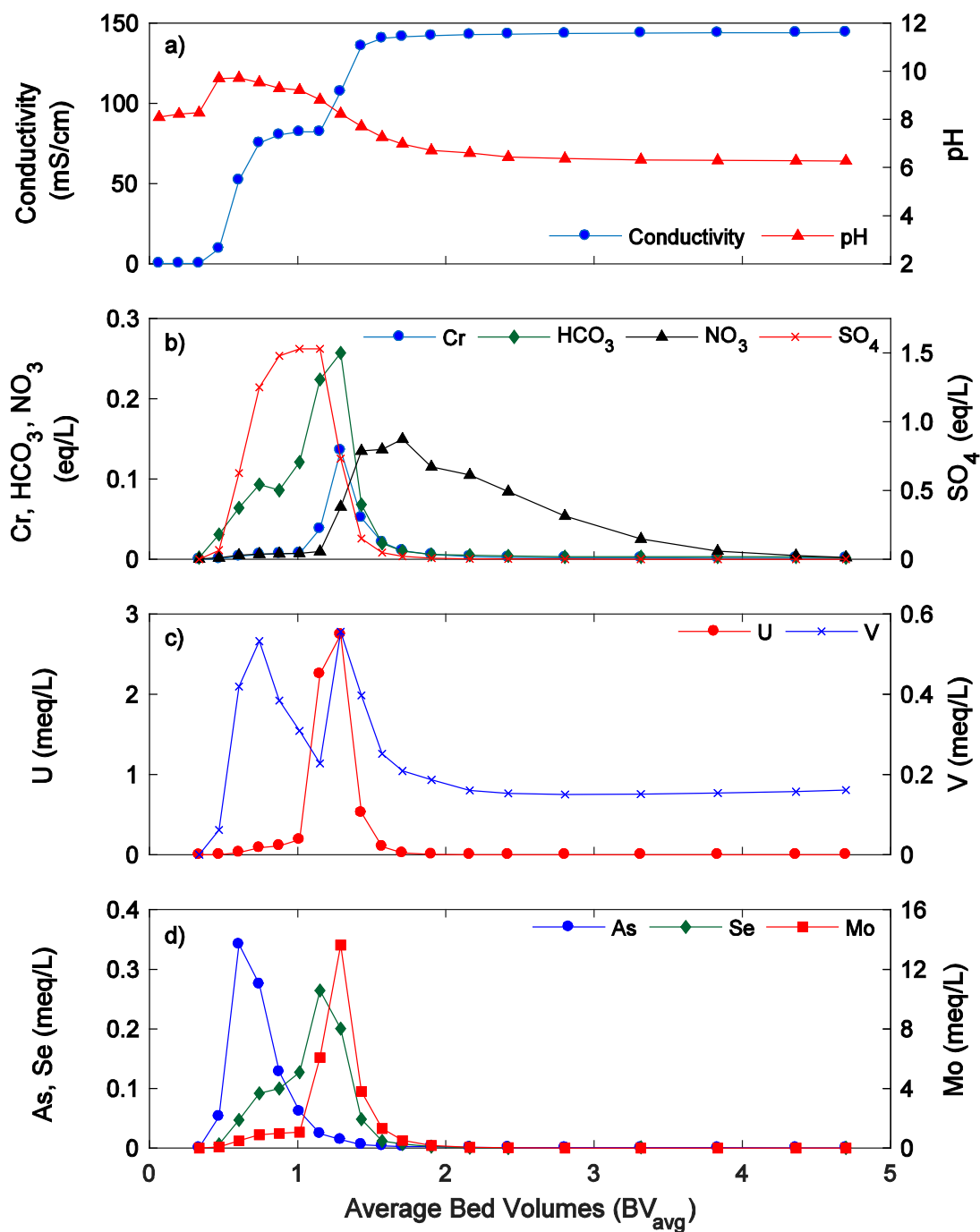


Figure S-3. Elution chromatograph for 1-Stage GW regeneration (R4) showing a) conductivity and pH, b) chromium, bicarbonate, nitrate and sulfate, c) uranium and vanadium, and d) arsenic, selenium and molybdenum concentration. Only concentrations above the method reporting limit are shown.

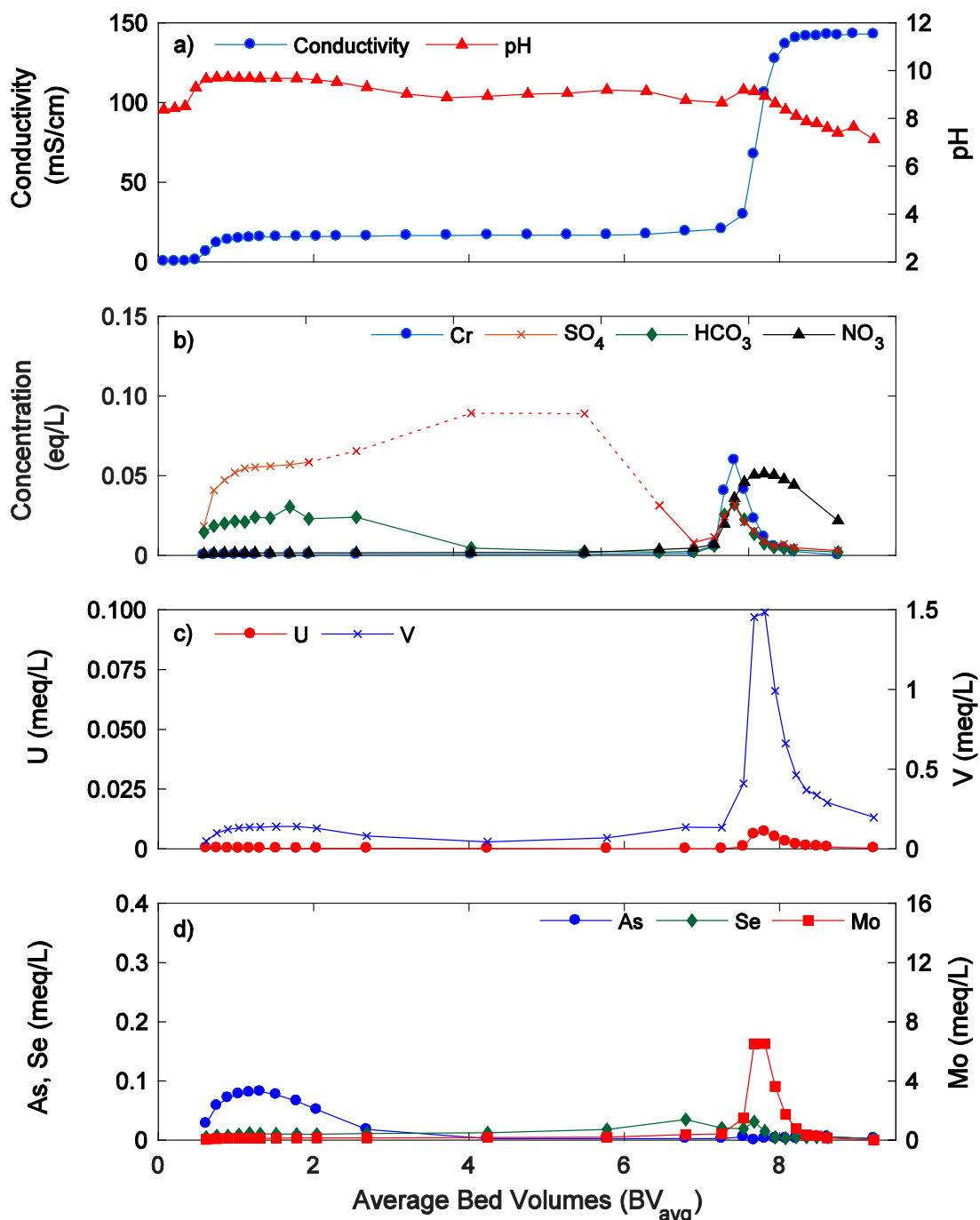


Figure S-4. Elution chromatograph for 2-Stage DI regeneration (R3) showing a) conductivity and pH, b) chromium, bicarbonate, nitrate and sulfate, c) uranium and vanadium, and d) arsenic, selenium and molybdenum concentration. Uranium concentrations below the MRL are plotted at MRL.

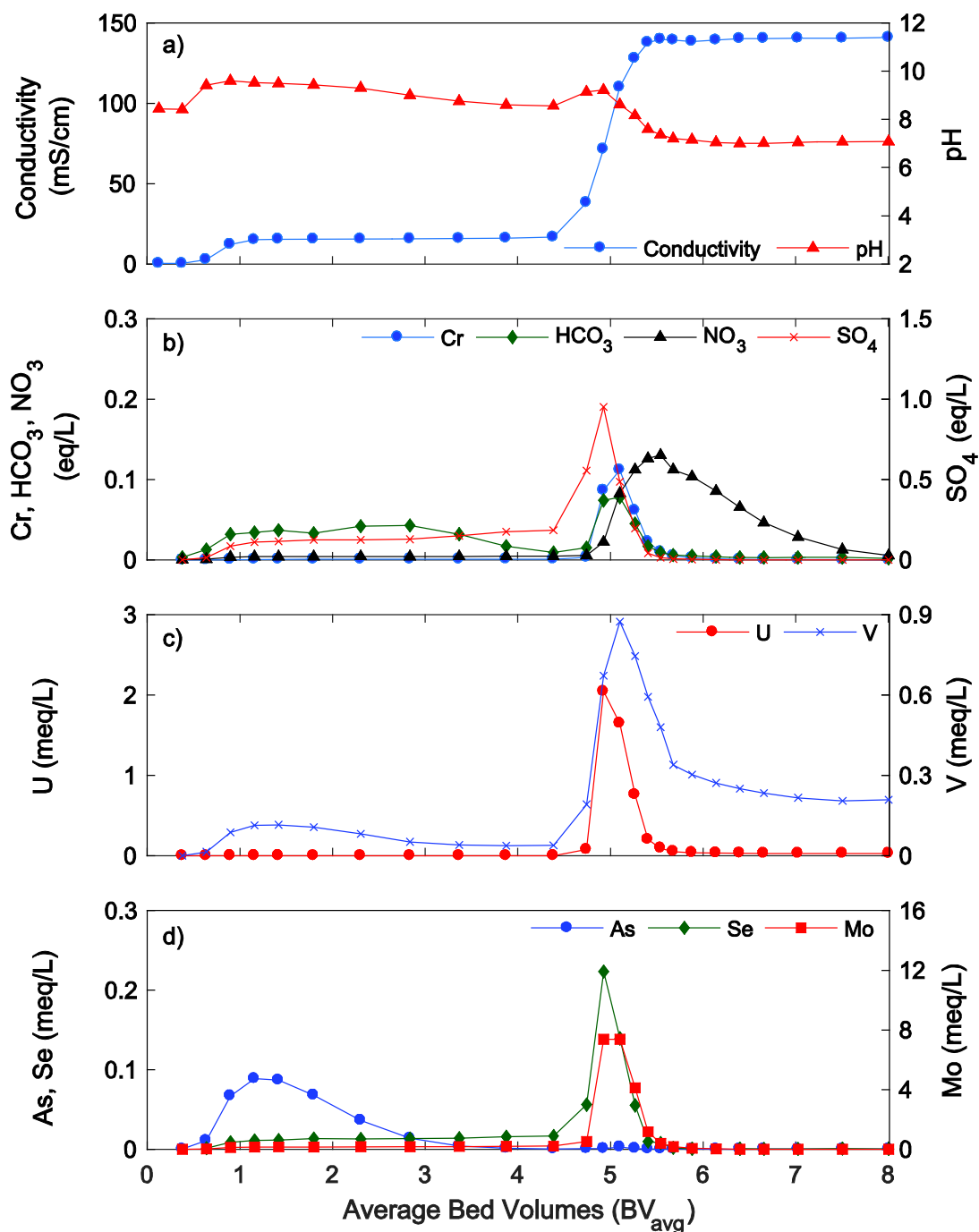


Figure S-5. Elution chromatograph for 2-Stage GW regeneration (R6) showing a) conductivity and pH, b) chromium, bicarbonate, nitrate and sulfate, c) uranium and vanadium, and d) arsenic, selenium and molybdenum concentration. Uranium concentrations below the MRL are plotted at MRL.

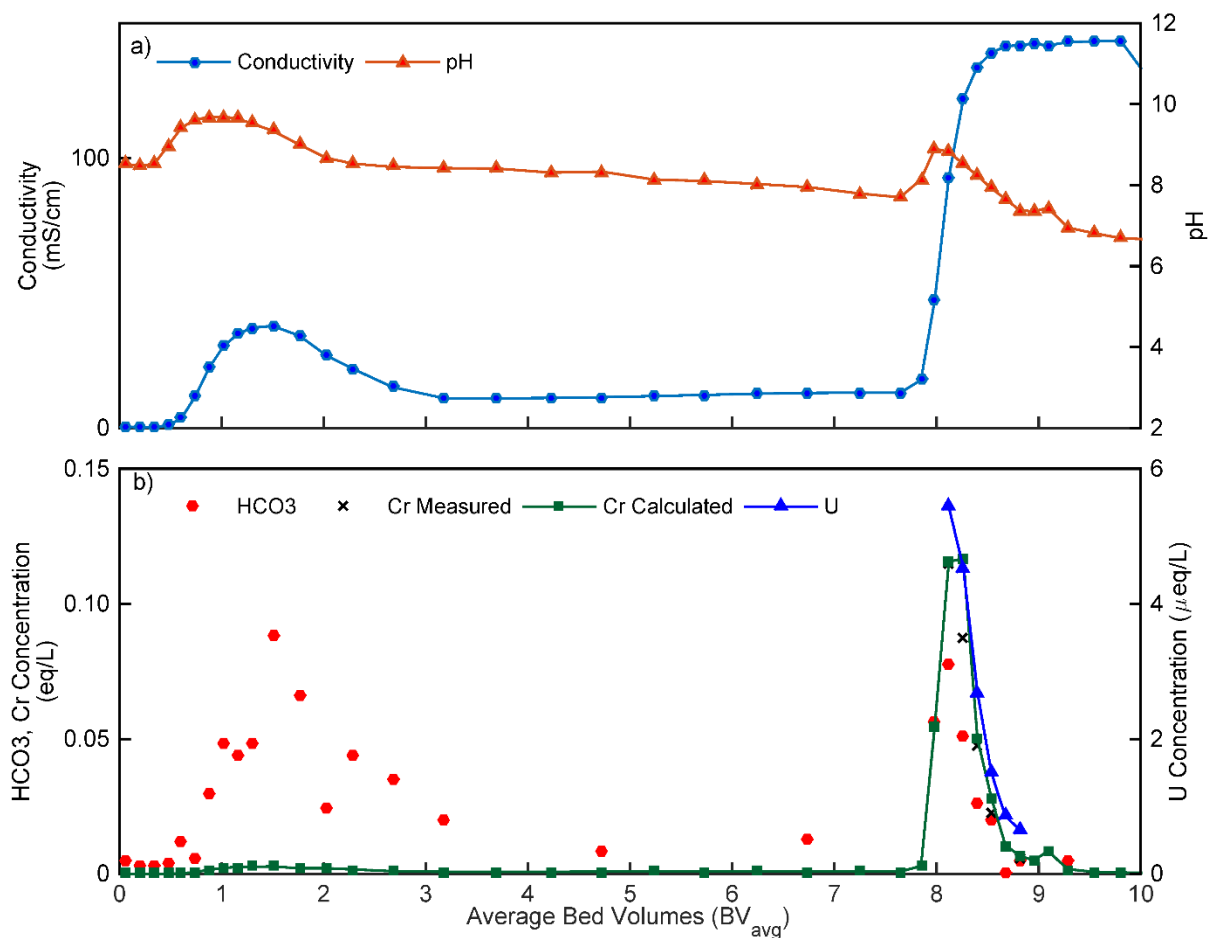


Figure S-6. Elution chromatograph for modified 2-Stage regeneration (R2) approach with a 0.8 N Stage followed by 0.1 N Stage and 2 N Stage presenting a) conductivity and pH, b) chromium, uranium and bicarbonate concentration. Calculated chromium concentrations are based on absorbance at 375 nm with measured verification samples.

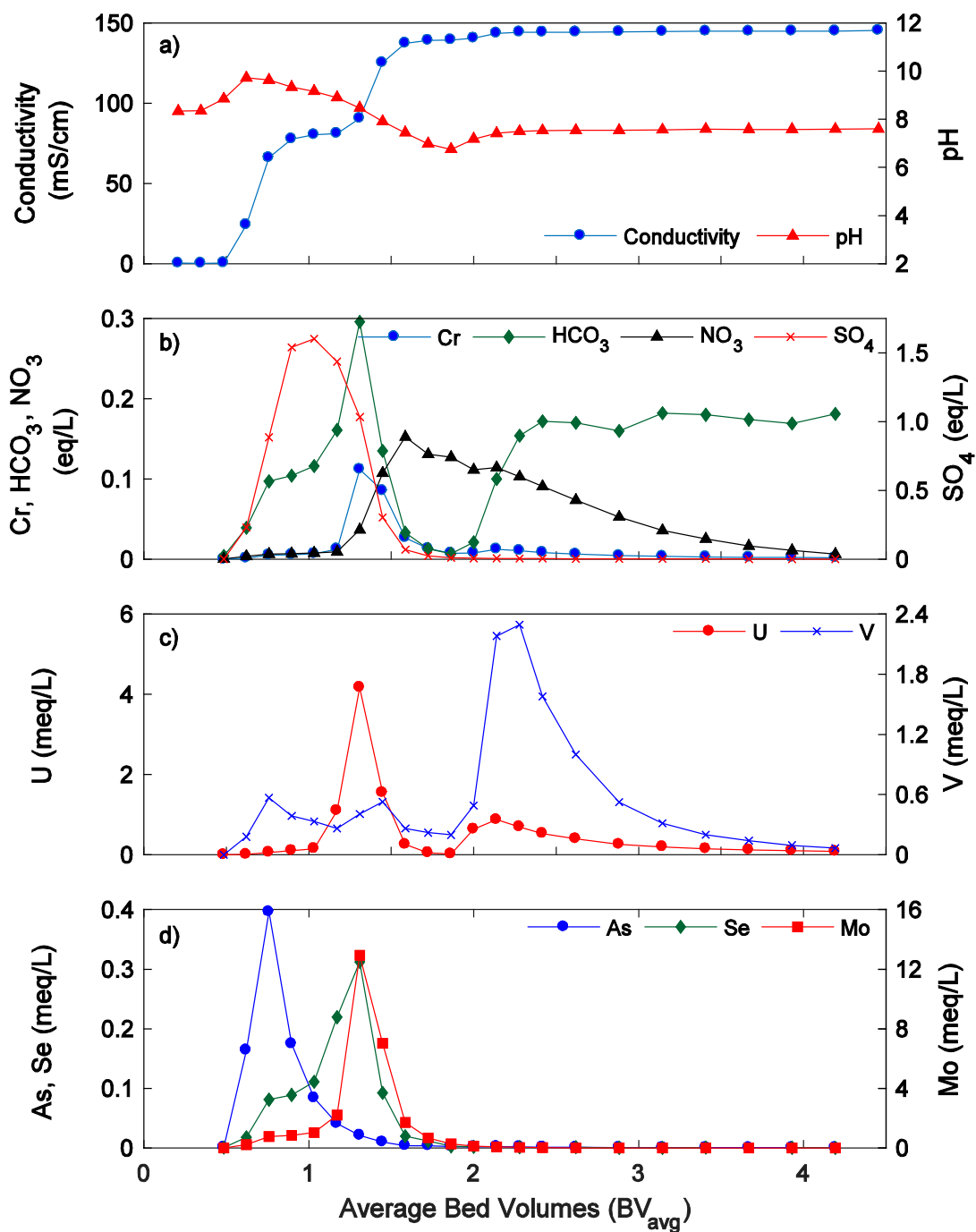


Figure S-7. Elution chromatograph for NaCl/NaHCO₃ regeneration (R5) showing a) conductivity and pH, b) chromium, bicarbonate, nitrate and sulfate, c) uranium and vanadium, and d) arsenic, selenium and molybdenum concentration.

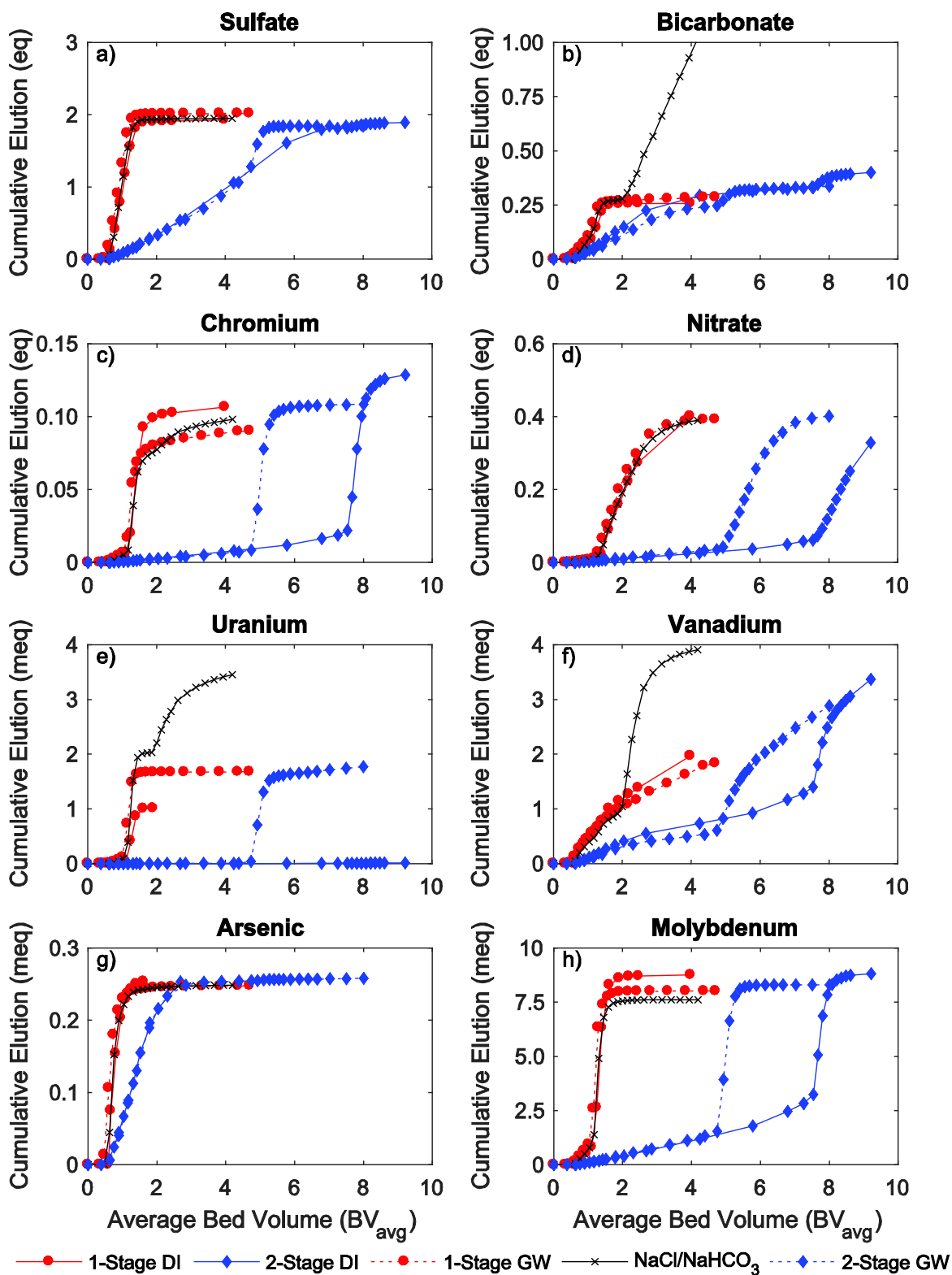


Figure S-8. Cumulative mass eluted from column as a function of regeneration bed volume for a) bicarbonate, b) nitrate, c) vanadium, d) molybdenum, e) arsenic and f) selenium.

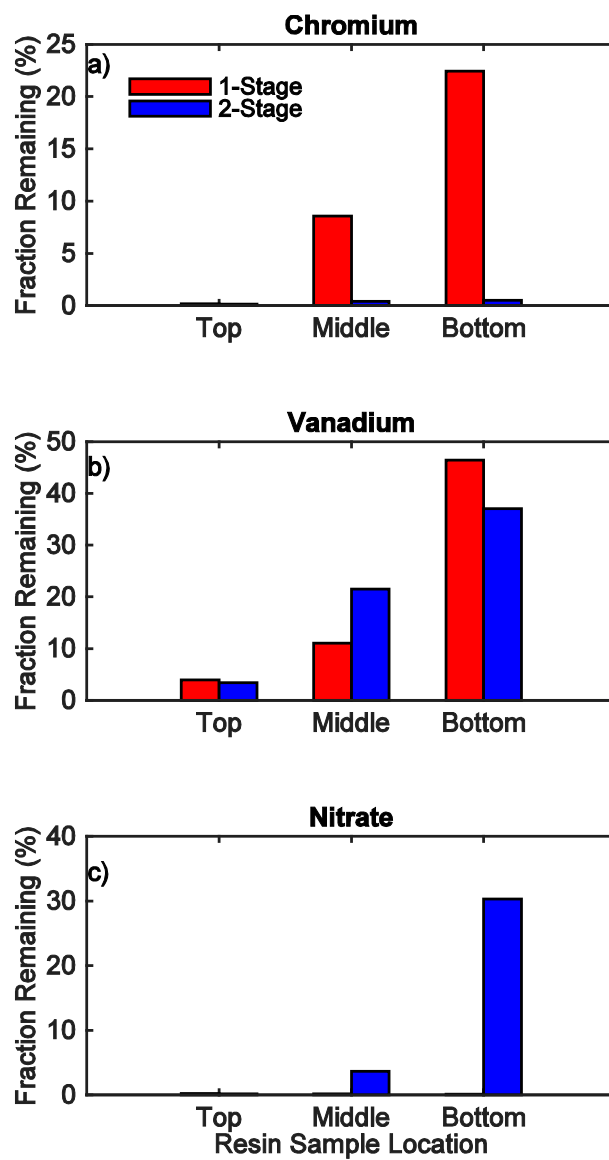


Figure S-9. Fraction of constituents remaining on resin aliquots after the 1st regeneration cycle (R1 and R3) compared to pre-regeneration batch elution for a) chromium, b) vanadium, and c) nitrate.

Table S-3. Cumulative elution of chromium, vanadium and uranium during regeneration for both loading cycles and during the acid wash after the second regeneration cycle. Cumulative elution values are separated by stage for the 2-Stage approaches (R3 and R6).

Background Water	Regen. Number	Approach	Stage	Cumulative Elution (meq)						Fraction Removed by Acid Wash ⁽¹⁾	
				Regeneration			Acid Wash				
				Cr	V	U	Cr	V	U	V	U
DI	R1	1-Stage DI	--	107	2.0	1.0	--	--	--	--	--
	R3	2-Stage DI	0.2 N	19	1.3	0.002	--	--	--	--	--
			2.0 N	110	2.1	0.008	--	--	--	--	--
			Total	129	3.4	0.010	--	--	--	--	--
Softened Well Water	R4	1-Stage GW	--	101	3.0	1.7	4.3	1.1	0.93	26%	35%
	R5	NaCl/NaHCO ₃	--	99	3.9	3.5	4.4	0.45	0.14	10%	4%
	R6	2-Stage GW	0.2 N	7.2	0.53	0.008	--	--	--	--	--
			2.0 N	101	2.5	1.8	--	--	--	--	--
			Total	109	3.1	1.8	1.7	1.3	1.3	29%	42%

Cumulative elution values are the total observed elution for the regenerations as shown in the Figures S-2 to S-7. Operational criteria to define waste fraction not applied.

⁽¹⁾Calculated as the mass of each element eluted during acid wash relative to the total mass eluted during both regeneration and acid wash

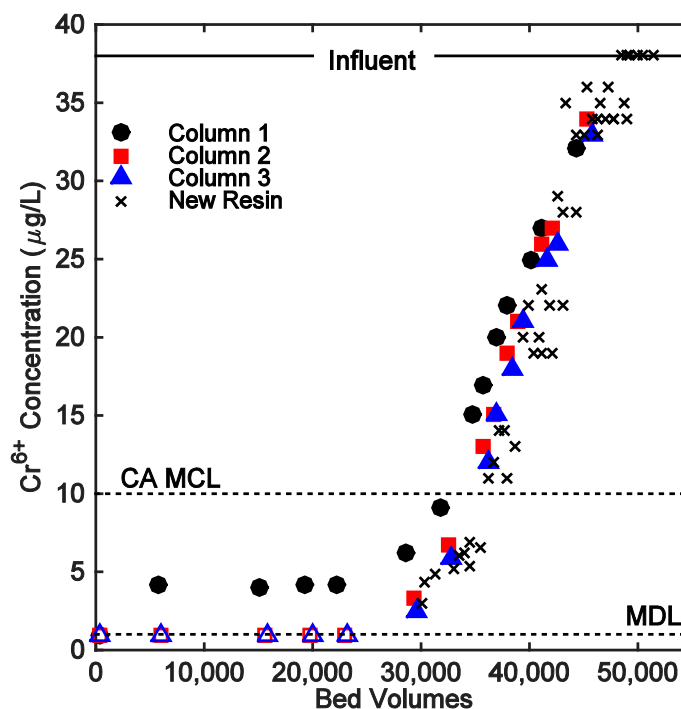


Figure S-10. Cr(VI) breakthrough during **second** loading cycle for columns subjected to different regeneration processes. Samples from first loading cycle indicated as New Resin.

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