Decreasing waste brine volume from anion exchange with nanofiltration: Implications for multiple treatment cycles

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Abstract

Ion exchange (IX) is a technology for removing hexavalent chromium from water, but waste brine disposal makes implementation cost prohibitive in many communities. Nanofiltration (NF) can be integrated to decrease the waste brine volume by 70% and reuse the permeate (NF-reuse) as brine in the next IX regeneration. However, the accumulation of impurities and resulting impact on IX regeneration and loading efficiency have not been evaluated through comparative mass balances or post-regeneration batch tests. Combining pilot-scale experiments with response surface modeling, impurities in waste brine are predicted to reach a pseudo steady state over 10 loading-regeneration-NF-reuse cycles, simulating long-term operation at full-scale facilities. Side-by-side regenerations show that NF-reuse brine does not impact the IX regeneration efficiency of chromium, sulfate or inorganic carbon. Regeneration efficiency increases for vanadium and uranium by 30-60% using the NF-reuse brine, which may decrease long-term fouling and reduce the frequency for strong acid regenerations. With NF-reuse, additional nitrate loads onto the IX resin during regeneration, which may impact the timing and

magnitude of chromatographic peaking. During loading, arsenic exhibited chromatographic peaking at concentrations 220% higher than the influent concentration, exceeding regulatory thresholds under all regeneration scenarios. Arsenic leakage also occurred during the first 500 bed volumes with NF-reuse. Vanadium and chromium both exhibited faster breakthrough in the second loading cycle, demonstrating the importance of evaluating pilot-scale processes over multiple loading and regeneration cycles. Bench-scale studies need to be guided by full-scale IX operating constraints and evaluate factors beyond the contaminant of concern to fully identify potential impacts of implementing NF brine management. A supplemental spreadsheet is included for utilities to screen NF for system-specific testing.

Keywords: Ion exchange, regeneration, nanofiltration, chromium, arsenic, nitrate, vanadium, chromatographic peaking

1 Introduction

When hexavalent chromium (Cr(VI)) occurs in groundwater aquifers due to either natural or anthropogenic sources, groundwater may require additional treatment before water is suitable for potable consumption^{1–3}. Of the two common oxidation states, Cr(VI) is toxic compared to trivalent chromium⁴. Total chromium (i.e., hexavalent and trivalent combined) is regulated at 100 µg/L in the United States, and the World Health Organization recommends a provisional guideline value of 50 µg/L⁵. In 2014, California, USA set a more stringent maximum contaminant level (MCL) for Cr(VI) at 10 µg/L, which was repealed in 2017 due to economic considerations⁶. The most common treatment techniques include strong base anion exchange (SBIX)^{7–11}, weak base anion exchange^{10,12–15}, and chemical reduction processes^{10,12–19}. Although SBIX has been identified as a best available technology with many full-scale installations, the costs of regeneration chemicals and waste brine disposal often make implementation uneconomical,

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especially in small communities. Decreasing the waste brine volume and recovering regenerant salt would make Cr(VI) treatment affordable for more communities.

SBIX uses a polymeric resin with positively charged functional groups that exchange anions based on selectivity and concentration. In general, multivalent anions (e.g., sulfate, chromate, uranium-carbonate complexes) are more selective than monovalent anions (e.g., nitrate, bicarbonate, chloride)^{20,21}. Raw water passes through a contactor containing SBIX resin until exhaustion, which is operationally defined depending on the contactor configuration and target effluent water quality. For a single contactor configuration, the loading process may terminate when the effluent Cr(VI) concentration approaches a regulatory threshold. For a lead-lag configuration, exhaustion is defined when the effluent Cr(VI) concentration from the lead contactor equals the raw water concentration. Upon exhaustion, SBIX resin is regenerated using a concentrated solution, commonly 2-4 N sodium chloride (NaCI)^{7–11}. Regeneration produces a hazardous waste brine, and brine handling and disposal determine the economic feasibility of the entire treatment process⁸. Several approaches have been explored to minimize the amount of hazardous waste, including multi-stage regeneration, direct brine reuse, chemical treatment (with or without brine reuse), and membrane treatment (with or without brine reuse).

Multi-stage regeneration uses solutions of increasing salt concentration sequentially. A 1-Stage regeneration commonly uses 2 N NaCl, which elutes most anions with 2-4 bed volumes (BV) of solution. An example 2-Stage regeneration uses 0.2 N NaCl followed by 2 N NaCl^{8,11,22}. Bicarbonate, arsenic, and some sulfate predominantly elute during the 0.2 N stage, and the 2 N stage elutes the remaining anions, such as sulfate, nitrate, and oxyanions of chromium, uranium, vanadium, etc.^{8,11}. The benefit of multi-stage regeneration is waste separation based on selectivity by eluting bicarbonate and sulfate prior to chromium.

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One approach for reducing SBIX waste volume is brine recycling, where the waste brine is reused in a subsequent regeneration cycle rather than using a fresh solution for each regeneration^{7,8,10,23,24}. Without treatment, studies have observed consistent chromium loading for up to 3 cycles prior to capacity loss due to the suspected accumulation of other anions in the reused brine^{7,8}.

Waste brine can also be treated prior to reuse. For example, on-site treatment of waste brine by nanofiltration (NF) and reuse of NF permeate (abbreviated NF-reuse) has a strong potential to 1) reduce disposal costs by decreasing the hazardous waste volume requiring off-site disposal and 2) recover regenerant salt (i.e., sodium chloride) for the next regeneration cycle. NF treatment has demonstrated waste volume reductions of 70-90%, depending on waste brine composition, with high chromium rejection for field test sites in California^{8,11}.

NF treatment has been proposed in other ion exchange applications with notable differences. Sugar refining applications have only evaluated model solutions, do not include sulfate, and have not characterized regeneration efficiency after subsequent loading cycles ^{25,26}. Cation exchange softening applications have divalent cations and focus on salt usage as the primary economic driver²⁷. SBIX processes use softened water for regeneration to deliberately exclude calcium and magnesium from the regeneration process, and hazardous waste volume is the primary economic driver for Cr(VI) treatment. Compared to chemical treatment approaches explored in other studies^{8,28–31}, adding NF does not introduce any new chemicals (e.g., barium, calcium, or iron containing salts) for chemical precipitation and is effective towards a wide range of co-occurring constituents, such as arsenic, uranium, vanadium, and sulfate.

A shortcoming of SBIX brine reuse studies thus far is a disconnect between bench and pilot experiments and the process control approaches at full scale. Regeneration efficiency and resin loading performance depend not only on the composition of the reused brine, but also Paper is published as: Korak, J. A., Flint, L. C. & Arias-Paić, M. Decreasing waste brine volume from anion 4 exchange with nanofiltration: implications for multiple treatment cycles. *Environmental Science: Water Research*

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regeneration solution volumes and salt concentrations. Bench and pilot studies often lack important details that would define regeneration conditions at full scale with brine reuse strategies. For example, the volume of rinse water collected with brine for reuse is often unspecified. Collecting brine with interstitial and rinse solutions increases the regeneration solution volume each reuse cycle. Salt dose (i.e., mass of salt per volume of resin) also would increase if make-up salt is added to achieve the same conductivity setpoint⁸. In such cases, the regeneration performance of the next cycle is actually assessed at a higher salt dose than the first cycle with fresh brine, leading to an unequal comparison. Full-scale systems have controls that automate regeneration sequences, systematically controlling salt dose, rinse water, and waste brine generation through instrumentation. Representative mass balances need to be incorporated in the design of bench and pilot studies to determine the benefits of brine reuse.

In addition, there is no inexpensive, practical, or accessible approach for water utilities to determine the advantages of integrating NF for waste volume reduction or salt recovery over many loading-regeneration cycles. Previous studies did not assess the effect of reusing NF permeate on regeneration efficiency for the broad spectrum of constituents found in SBIX waste brine^{8,32}. This study combines pilot-scale experiments with response surface modeling to 1) develop an empirical model for NF flux and rejection for SBIX waste brines, 2) estimate the cyclical accumulation of impurities in NF-reuse brine *under ideal conditions*, and 3) evaluate the impact of impurities on regeneration efficiency and chromatographic peaking. Unlike a mechanistic study of a specific unit operation, this approach assesses the practical application and potential benefits of implementing NF-reuse for Cr(VI) SBIX, using real water matrices from a water utility in Oklahoma.

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2 Methods

Safety and hazards associated with the following experimental methods are documented in SI Text 1.

2.1 Synthetic SBIX waste brine nanofiltration experiments

Batch nanofiltration experiments were conducted with synthetic SBIX brines to develop a response surface model describing the relationship between major anion composition, membrane flux, and rejection. Response surface methodology (RSM) is an industrial engineering approach to model the effect of factors (e.g., composition and pressure) on a process response (e.g., membrane flux and rejection). RSM assumes that constrained design spaces can be modeled using low order polynomials to inform engineering decisions, process development, and optimization, rather than to elucidate mechanistic behaviors³³.

RSM experiments were conducted using a factorial experimental design covering a design space relevant to SBIX waste brines. Chloride ranged from 1.15 to 1.7 N (4 levels), and sulfate ranged from 0 to 1.3 N (4 or 5 levels), resulting in 19 synthetic brines shown in Figure 1. Overlaid on the design space are the ranges of chloride and sulfate concentrations for SBIX brines from field sites for both Cr(VI)^{7,8,28,32} and arsenic processes^{34–36}. Chloride was not commonly reported in arsenic studies; the range shown assumes a 6-8% NaCI regeneration solution and similar dilution by interstitial and rinse water as Cr(VI) processes. As waste brine concentrates by NF, the composition trajectory from previous work shows that sulfate increases and chloride ultimately decreases due to negative membrane rejection³². Figure 1 demonstrates that the design space used to develop response surface models is broadly applicable to SBIX processes for oxyanion (i.e., chromium and arsenic) removal.

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Figure 1. Design space for response surface models compared to SBIX waste brines. Synthetic brine markers indicate the experimental combinations tested for the response surface model. Dash outlined regions show the range of compositions reported for chromium^{7,8,28,32} and arsenic^{34–36} field applications. Two line series show the composition trajectory for concentrating Cr(VI) waste brine (filled markers) by NF with increasing recovery (unfilled markers) from previous work³².

Experiments were conducted in 4 batches, starting with an initial solution containing sodium chloride, sodium nitrate, and sodium bicarbonate for buffering capacity. Sulfate was added sequentially for each test condition. Nitrate and bicarbonate concentrations and pH were held constant (Table S5 and SI Text 5.1).

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Membrane flux and observed anion rejections were determined for each synthetic solution using a flat sheet cell (SEPA, Sterlitech Corp., Kent, Wash.) with an NF membrane (NF5, Applied Membranes, Vista, Calif.) shown in Figure S5. At moderate salt concentrations (e.g., 2000 mg/L), the NF5 specification reports high rejection (>97%) of divalent ions and moderate rejection of monovalent ions (50%), which is ideal for recovering regenerant salt (i.e., NaCl) and rejecting waste brine impurities (i.e., SO₄²⁻). The unit was operated under full recycle to maintain the composition of the feed solution until periodic sampling. The feed flow rate was held constant at 1.9-2.0 L/min using a positive displacement pump (HydraCell, Wanner Eng. Minneapolis, MN) corresponding to a cross flow velocity of about 0.3 m/s. Manufacturer-supplied spacers were used on both feed and permeate sides of the membrane. Feed solution temperature was 23-25 °C, and a back-pressure valve maintained a constant transmembrane pressure (TMP). All model solutions were tested at a TMP of 250 psi (17.2 bar). A subset was tested at 150 and 200 psi to determine the effect of TMP and flux on anion rejection, independent of feed solution composition. The NF skid was instrumented with flow, pressure, temperature, and conductivity sensors integrated into Labview. After a 15-minute stabilization period, permeate was diverted to a digital scale (Entris 8201-1S, Sartorius, Göttingen, Germany) integrated into Labview to calculate flux. Feed and permeate grab samples were also collected for composition analysis.

Prior to testing, the membrane was compacted for 2 hours using deionized water until flux stabilized. Temperature-corrected pure water permeability, measured before and after each batch, decreased from $16.7 \pm 0.1 \text{ L/m}^2/\text{hr/bar}$ to $14.4 \pm 0.2 \text{ L/m}^2/\text{hr/bar}$ over the course of testing, which could be the result of additional membrane compaction or scaling.

2.2 Field SBIX experiments

2.2.1 Resin loading

Pilot-scale columns (1.5" nominal diameter) filled with SBIX resin (36" depth, A600e/9149,

Purolite) were loaded in a downflow configuration at 0.61 m/min (15 gpm/ft²) at a well site in Paper is published as: Korak, J. A., Flint, L. C. & Arias-Paić, M. Decreasing waste brine volume from anion 8 exchange with nanofiltration: implications for multiple treatment cycles. *Environmental Science: Water Research and Technology* **7**, 886–903 (2021). doi: 10.1039/d1ew00001b

Oklahoma, USA, where the raw water Cr(VI) concentration was $86.2 \pm 0.7 \mu g/L$ (0.0033 meq/L). Chromium speciation was dominated by Cr(VI) (Table S1). A600e resin is a Type I quaternary amine with a gel polystyrene polymer structure and a manufacturer-reported capacity of 1.6 eq/L. Five columns were loaded in parallel over 37,000 BV until complete exhaustion (Figure S2), of which three columns were used in this study. The raw groundwater quality is summarized in Table S1.

Over the 7-week loading period, samples were regularly collected and analyzed for Cr(VI). Column pressures, flows, and bed depths were monitored several times each week, and flows were adjusted as needed to maintain a constant loading rate in each column. After complete exhaustion for Cr(VI), columns were disconnected from the frame and shipped back to a lab in Denver, CO for controlled regeneration experiments. After regeneration, columns were reloaded at the well site for 8,000 BV. Columns were stored in a fridge when not in use.

2.2.2 Column regeneration

Exhausted columns were regenerated with either fresh solutions or a solution representative of NF-reuse regeneration brine. Regeneration was performed using co-current flow, a volumetric loading rate of 0.30-0.34 gpm/ft³, and a surface loading rate of 0.83-0.95 gpm/ft². Effluent from each column was fractionated into high density polyethylene bottles of varying volumes to adjust sampling resolution. In contrast to collecting grab samples, fractionation allowed for a mass balance to be calculated for each constituent without interpolation. The concentration is plotted at the average bed volume for each bottle. Water quality analysis is described in Section 2.3.

2.2.3 Batch regeneration

Before and after column regeneration, 10 mL aliquots of resin were collected from the top, middle, and bottom of the columns through access fittings. Aliquots were batch regenerated in 20 BV of 2 N NaCl on a shaker table for about 70 hours. After batch regeneration, resin was Paper is published as: Korak, J. A., Flint, L. C. & Arias-Paić, M. Decreasing waste brine volume from anion 9 exchange with nanofiltration: implications for multiple treatment cycles. *Environmental Science: Water Research and Technology* **7**, 886–903 (2021). doi: 10.1039/d1ew00001b

separated using a strainer, and the supernatant was analyzed for trace metals, sulfate, nitrate, pH, conductivity, and alkalinity. Following batch regeneration with 2 N NaCl, the same resin aliquots were subsequently batch regenerated with 20 BV of 6% (w/w) hydrochloric acid (HCl) and analyzed for trace metals. The fraction of active sites occupied by each constituent was calculated assuming a resin capacity of 1.6 eq/L.

2.3 Water quality analysis

Raw water quality (Table S1) was analyzed by Ana-Lab or the City of Norman, Oklahoma following standard methods. In the batch NF and regeneration experiments, pH and conductivity were measured on site (HQ40d, Hach, Loveland, CO). For the NF experiments, chloride, sulfate, and nitrate were quantified by ion chromatography at the University of Colorado Laboratory of Environmental and Geological Studies. Analytical duplicates (n=2) had relative percent differences (RPD) of <1%, <10%, and <1% for chloride, nitrate, and sulfate, respectively. Nitrate concentrations (6-10 mg/L as NO_3^{-1}) were two orders of magnitude lower than chloride and sulfate.

For the column and batch regeneration experiments, the University of California Davis analyzed samples for trace metals, alkalinity (bicarbonate (HCO_3^{-1}) and carbonate ($CO_3^{2^-}$)), nitrate (NO_3^{-}), and sulfate ($SO_4^{2^-}$). Trace metals (chromium (Cr), vanadium (V), molybdenum (Mo), arsenic (As), selenium (Se), and uranium (U)) were analyzed by inductively coupled plasma mass spectrometry (ICP-MS). Samples were acidified with nitric acid prior to analysis and diluted as needed with 1% nitric acid based on the instrument calibration range. The average RPD for replicate quality control standards was 4.3%, and standard recovery ranged from 92-107% (n=31). Total chromium was analyzed as a surrogate for Cr(VI), as trivalent chromium is not anionic. Sulfate was quantified by inductively coupled plasma atomic emission spectroscopy (ICP-AES) as total sulfur with an average RPD of 3.5% (n=8). Bicarbonate and carbonate alkalinities were quantified following Standard Method 2320. Since bichromate/chromate has a pKa of 6.5³⁷,

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its protonation was accounted for during titration using trace metal data and was subtracted from the measured bicarbonate alkalinity. It was assumed that all remaining alkalinity was attributable to the carbonate system. Results are presented as total inorganic carbon (IC) for clarity using IC (eq/L) = HCO_3^{-} (eq/L) + 0.5 CO_3^{2-} (eq/L). Nitrate was analyzed using flow injection analysis. The average RPD between nitrate duplicates was <2% (n=10).

For the chromatographic peaking analysis, trace elements were analyzed at the University of Colorado Boulder by ICP-MS (Agilent 7900, helium gas mode, high matrix introduction) following quality control procedures in EPA Method 6020B. An additional spectral interference standard was included. The RPD for duplicate analyses ranged from 0.2-8% for Cr, As, and V (n=10). Matrix spike recoveries were within 80-110% (average recovery=96%, n=9).

Concentrations are presented on a charge equivalents basis. For the trace metals, mass concentrations were converted to charge equivalents by assuming oxidizing conditions and alkaline pH (Table S2).

3 Nanofiltration Brine Reuse Model

Developing a process-level model is important to define the brine reuse water balance. Figure 2 presents a process flow diagram to account for mass flows throughout the NF-reuse process. The process-level model 1) aligns controlled experiments with full-scale operating constraints, 2) evaluates if the reused brine composition will reach a pseudo steady state *under ideal conditions*, and 3) estimates the composition of NF-reuse brine to guide further experimentation.

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Figure 2. Waste brine management using NF-reuse. [An] refers to the concentration of any non-chloride anion. Nomenclature for the stream labels is provided in the ESI Text 4. Briefly, the first subscript refers to the stream (waste (w), incremental permeate (p), composite permeate (P_{comp}), and disposal (D)). The regeneration cycle is denoted by *i*. *Rec* is the NF batch recovery percentage, and *RecMax* is the maximum recovery percentage.

3.1 Model Overview

The process-level model estimates the regeneration solution composition and disposal volumes over multiple cycles under the scenario depicted in Figure 2. Briefly, an objectively defined waste brine fraction is collected. Then, waste brine is concentrated using batch NF, and permeate is returned to the Regeneration Vessel. Finally, make-up salt and water are added (if needed) prior to the next regeneration cycle based on operational constraints. Proper nouns (capitalized) are used when referring to a specific unit in Figure 2.

More specifically, operating constraints are defined that would be integrated into a control system to objectively evaluate the feasibility of NF-reuse for Cr(VI) SBIX processes. At the start of the regeneration process, a regeneration solution is formed with an initial volume (V_R) and NaCl regenerant salt concentration ([CI]_R), both representing process control setpoints. The Paper is published as: Korak, J. A., Flint, L. C. & Arias-Paić, M. Decreasing waste brine volume from anion 12 exchange with nanofiltration: implications for multiple treatment cycles. *Environmental Science: Water Research and Technology* **7**, 886–903 (2021). doi: 10.1039/d1ew00001b

regeneration solution passes through the Contactor and displaces the interstitial water remaining after the loading cycle, gradually increasing the effluent conductivity. Initially and while the effluent conductivity is low, Contactor effluent is collected in Flex Vessel 1, as commonly practiced at full-scale installations. When an effluent conductivity setpoint is reached (e.g., $Cond_{sp}=20 \text{ mS/cm}$), the Contactor effluent is sent to the Collection Vessel signaling the start of waste brine collection (BV_{start}). After a designated regeneration throughput (BV_{end}), softened service water rinses the regeneration solution out of the Contactor before the next water treatment cycle. Rinse water is initially captured in the Collection Vessel before diversion back to Flex Vessel 1. The green shaded areas in Figure 2 (inset graph) illustrate the fraction of waste captured in the Collection Vessel for 1- and 2-Stage regenerations.

Waste brine in the Collection Vessel is concentrated by batch NF using a response surface model (*vide infra*, Section 4.1) and mass balances calculated at each discretized recovery step. The brine volume ($V_{w,i,Rec}$) and anion composition ($[An]_{w,i,Rec}$) in the Collection Vessel depend on reuse cycle (*i*) and batch NF recovery percentage (*Rec*). [An] represents the concentration of any anion except for chloride, the regenerant salt. The batch NF process continues until reaching a terminal recovery (*RecMax*), defined by a limited flux (e.g., < 5 L/m²/hr)³². After reaching *RecMax*, concentrated brine remaining in the Collection Vessel is sent as blowdown to the Disposal Vessel.

When the NF process reaches terminal recovery, the volume ($V_{P,i,RecMax}$) and chloride concentration ([Cl]_{Pcomp,i,RecMax}) in the NF Permeate Vessel are compared to the requirements for the next regeneration cycle (i.e., V_R and [Cl]_R). Two scenarios can occur resulting in a decision tree. In both scenarios, make-up salt is added using saturated salt solution ($V_{sat,i}$) from the Salt Saturator, which dilutes recycled impurities and reduces the permeate volume that can be recycled ($V_{P,i,RecMax} + V_{sat,i} = V_R$). In the first scenario, the NF process becomes flux-limited before enough permeate is produced for the next regeneration cycle if initial sulfate concentrations are

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high. In this case, both saturated salt solution (V_{sat,i}) and softened service water (V_{H2O,i}) are added to match the initial V_R and [CI]_R conditions. Alternatively, NF could produce more permeate than is needed for the next regeneration if initial sulfate concentrations are low (i.e., V_{P,I,RecMax} > V_R). Excess permeate volume is possible, because the volume captured in the Collection Vessel is greater than the initial regeneration solution volume (i.e., V_{w,i,0} > V_R) due to interstitial and rinse water. Waste with lower initial sulfate concentrations ([SO₄]_{w,i,0}) can achieve higher batch recoveries and produce more permeate than needed for the next regeneration. In this case, excess permeate (V_{EP,I}) would be sent to Flex Vessel 2, which could be used to prepare low ionic strength regeneration solutions (e.g., 0.2 N NaCI) or potentially be disposed of as non-hazardous waste. To reiterate, previous studies investigating brine reuse have seldom defined a water balance or used realistic operational setpoints to assess how impurities will accumulate in waste brine and align research with full-scale operational strategies.

3.2 Model Assumptions and Constraints

In this study, several specific assumptions were made. Full mass balance calculations are provided in SI Text 4.

- The volume of resin (V_{resin}) is constant for each cycle, and there is no resin loss across cycles.
- 2. For each cycle, the regeneration solution volume (V_R) and chloride concentration ([CI]_R) are constant and maintained through addition of saturated NaCl solution ([CI]_{sat}) and softened service water (V_{H20,i}). The volume and concentration of the regeneration solution matches the pilot-scale regeneration conditions. This assumption is important, because some approaches allow the regenerant concentration to decline with each reuse cycle¹⁰ while others add make-up salt each cycle^{7,8,23,24}. In this study, the salt dose is constant.

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- Following common full-scale process controls, solution that elutes at the beginning of the regeneration is captured in Flex Vessel 1 until the conductivity reaches a setpoint (20 mS/cm), after which waste brine is diverted to the Collection Vessel.
- 4. Regeneration is terminated when nitrate elution is substantially complete. Based on pilot-scale regeneration data, a comparable ending bed volume (BV_{end}) is set for both the 1-Stage (4.5 BV) and 2-Stage (8 BV) regeneration approaches. At BV_{end}, each regeneration has the same effluent nitrate concentration (2.5 x10⁻⁴ eq/L, 15.5 mg/L as NO₃⁻) and achieves 99% nitrate recovery.
- 5. The first 0.5 BV of rinse water is captured in the Collection Vessel. Remaining rinse water is diverted back to Flex Vessel 1.
- 6. Loading and regeneration efficiencies are the same in each cycle (*i*). The model assumes ideal conditions as a starting basis. The same mass and composition of anions accumulate on the resin during each loading cycle. The release of anions from the resin during regeneration follows the same profile as measured experimentally during the first loading-regeneration cycle. This is a conservative assumption, because it assumes that the loading and regeneration efficiency is unaffected by impurities or incomplete regeneration from the previous cycle. Testing the validity of this assumption is a study objective and is evaluated in Section 4.4.
- 7. Concentrating waste by nanofiltration terminates when flux across the membrane decreases to 5 L/m²/hr due to increasing sulfate concentrations in the waste brine. Previous work³² showed NF reaches a point of diminishing returns due to decreased anion rejection at low flux (Figure S12).

Using experimental regeneration data and an empirical batch NF model (*vide infra*), the quantity of constituents collected and recycled is calculated over multiple loading and regeneration cycles. SI Text 4 provides the mass balances incorporated into MATLAB code. For Paper is published as: Korak, J. A., Flint, L. C. & Arias-Paić, M. Decreasing waste brine volume from anion 15 exchange with nanofiltration: implications for multiple treatment cycles. *Environmental Science: Water Research and Technology* **7**, 886–903 (2021). doi: 10.1039/d1ew00001b

the 2-Stage regeneration approach, the model only captures and implements NF on the high ionic strength (2 N NaCl) brine as illustrated in Figure 2.

4 Results and Discussion

4.1 Nanofiltration response surface model

4.1.1 Response surface models with synthetic brines

The impact of implementing NF-reuse for waste brine management (Figure 2) ultimately depends on the rejection and flux across the NF membrane. Response surface models were developed using synthetic solutions representative of a wide range of SBIX brines (Section 2.1). A supplemental spreadsheet accompanies this study and incorporates the response surface models developed in this section. Utilities and other decision makers can enter a waste brine composition and assess if integrating NF is a competitive approach for reducing the waste brine volume. The intent is to help utilities identify a shortlist of brine management approaches for system-specific testing.

To improve the batch NF model developed using field brines in Korak et al. (2018), NF experiments were conducted using synthetic solutions containing sodium chloride, sodium sulfate, sodium nitrate, and sodium bicarbonate (the dominant ions in SBIX brine). This approach removes confounding effects by independently varying concentrations of chloride and sulfate. A stepwise regression approach was followed to identify significant model terms, perform a residuals analyses, and compare models. The full details are presented in SI Text 5.2.

Figure 3a and Equation 1 show that at a TMP of 250 psi, flux depends on both the chloride and sulfate concentration. The model was fit using the natural logarithm of flux (ln(Flux)) as a variance stabilizing transformation (Figures S6 to S8). The best-fit relationship in Figure 3a yielded 4 statistically significant model terms (coefficient p-values <0.001), random and normally

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distributed residuals, and an adjusted coefficient of determination (R^2_{adj}) statistic of 0.997. Flux depended most strongly on sulfate concentration and to a lesser extent on chloride concentration. With no sulfate in the feed solution, flux decreased as chloride concentration increased. As sulfate concentrations increased, the relative effect of chloride decreased, aligning with previous fundamental studies^{36,37}.

$$\ln(Flux \tfrac{L}{m^2 hr}) = 5 - 1.5[SO_4] - 0.34[Cl] - 0.63[SO_4]^2$$
 Equation 1



Where all concentrations are in eq/L

Figure 3. Response surface models for flux and rejection of major anions in synthetic SBIX brines at a TMP of 250 psi. Subplots A-C only show results within the model scope where flux >5 L/m²/hr. The dashed line in Figure 3d is the 95% prediction interval for the non-linear regression.

Figure 3Figure 3b and 3c present response surface models for chloride and nitrate rejection in the synthetic SBIX brines. Observed chloride rejection (R_{obs,Cl}) depended on five statistically significant model terms (coefficient p <0.01), including an interaction term (Equation 2). Chloride rejection became increasingly negative as the sulfate concentration increased and Paper is published as: Korak, J. A., Flint, L. C. & Arias-Paić, M. Decreasing waste brine volume from anion 17 exchange with nanofiltration: implications for multiple treatment cycles. *Environmental Science: Water Research*

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chloride decreased (albeit with a smaller effect). Observed nitrate rejection ($R_{obs,NO3}$) depended on both chloride and sulfate concentrations following a first order model (Figure 3c and Equation 3, coefficient p <0.02). Higher order models were not statistically significant (coefficient p >0.05). The nitrate rejection model had the most uncertainty ($R_{adj}^2=0.898$). Nitrate concentrations in the feed solution (2.5-3 meq/L) were 2 to 3 orders of magnitude lower than chloride and sulfate concentrations, presenting analytical challenges. It is likely that a model of similar form to Figure 3b for chloride, with non-linear and interaction terms, would have been significant at higher nitrate concentrations. Full details of the model development and residuals analyses are presented in SI Text 5.2.

Figure 3d presents an empirical relationship (Equation 4) for observed sulfate rejection ($R_{obs,SO4}$) and shows that sulfate rejection decreased as flux decreased, in agreement with previous experimental results³². Models of a similar form to the chloride and nitrate rejection (Figure 3b and c) were explored but could not adequately capture the rejection behavior at sulfate concentrations less than 0.5 eq/L.

$$R_{obs,Cl} = 0.2 - 0.5[SO4] - 0.07[Cl] + 0.1[SO4][Cl] + 0.07[SO4]^2$$
 Equation 2
$$R_{obs,NO3} = -0.2 - 0.2[SO4] + 0.14[Cl]$$
 Equation 3

$$R_{obs,SO4} = \frac{1.06 \ln Flux}{0.35 + \ln Flux}$$
 Equation 4

Conceptually, the empirical relationships are consistent with behaviors observed in fundamental/mechanistic studies. Sulfate is the most abundant divalent anion in SBIX waste brines by several orders of magnitude. Increasing the sulfate concentration increased the difference in osmotic pressure across the membrane thus reducing flux³⁸. Chloride, the most abundant monovalent anion in SBIX brine, only had an effect on flux when sulfate concentrations

were low (e.g., <0.2 eq/L). The mole fraction of chloride in a sodium-chloride-sulfate ternary Paper is published as: Korak, J. A., Flint, L. C. & Arias-Paić, M. Decreasing waste brine volume from anion 18 exchange with nanofiltration: implications for multiple treatment cycles. *Environmental Science: Water Research and Technology* **7**, 886–903 (2021). doi: 10.1039/d1ew00001b

mixture impacts the Donnan equilibrium at the membrane interface, and this behavior was captured by the higher order terms in Equation 2. Increasing sulfate relative to chloride favored the passage of monovalent anions leading to increasingly negative rejections for chloride and nitrate³⁸⁻⁴⁰. Previous studies have also derived expressions that yield sharp decreases in sulfate rejection at low fluxes^{38,39,41,42}, aligning with observations in synthetic SBIX brines. Developed for high ionic strength mixtures (>1M) relevant to SBIX brines, these response surface relationships offer a tool for utilities to screen, through the supplemental spreadsheet, if NF has the potential to improve waste brine management.

Chloride, nitrate, and sulfate rejection models were not sensitive to TMP between 150 and 250 psi. The impact of TMP on rejection was evaluated at two sulfate concentrations (i.e., 0.4 and 0.8 eq/L) across all nominal chloride concentrations (i.e., 1.2, 1.3, 1.5, and 1.7 eq/L) (Table S6). Flux scaled linearly with TMP. The empirical relationships developed at 250 psi TMP for the full dataset were applied to predict the rejection measurements at 150 and 200 psi TMP. Chloride and nitrate rejection equations (Equation 2 and 3) showed no systematic biases at lower TMPs (or a strong dependence on flux) (Figure 4a and b). Equation 4 yielded good predictions of sulfate rejection using measured flux at lower TMPs (Figure 4c). These results demonstrate that even though the batch NF model was developed using experiments conducted at one TMP (i.e., 250 psi), the rejection relationships (Equation 2 to Equation 4) would be broadly applicable for a range of moderate operating pressures.

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Figure 4. Comparison of observed and predicted rejections at multiple TMPs (150, 200 and 250 psi) for chloride (A), nitrate (B), and sulfate (C). Predicted values are calculated using the empirical relationships (Equation 2 - Equation 4) determined at 250 psi TMP. Solid line is 1:1 relationship.

4.1.2 Validation of response surface models with field brine

The four empirical relationships in Equation 1 to Equation 4 were validated using a batch NF model and comparing the predicted flux and concentrations to previously published pilot-scale results³². SI Text 5.3 defines the mass balance equations for each constituent in the Collection and NF Permeate Vessels as the SBIX brine concentrates during the batch NF process. Since the synthetic SBIX solutions did not include all trace anions found in SBIX brine, average trace metal rejections from three field brines in Korak et al. (2018) were used and assumed to be constant (Table 1). Figure S13 shows that constant rejection is a reasonable assumption at fluxes greater than 5 L/m²/hr for oxyanions of trace elements. Vanadium and bicarbonate rejections ($R_{obs,V}$ and $R_{obs,HCO3}$, respectively) depended on brine composition, and the reliance on the average rejection does introduce uncertainty.

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Table 1. Average observed NF membrane rejections for field SBIX brines evaluated in Korak et al. (2018).Uncertainty represents the 95% confidence interval on the mean.

Analyte	Average Observed Rejection (R _{obs})
Bicarbonate	0.42 ± 0.088
Cr	0.95 ± 0.013
V	0.91 ± 0.036
U	0.99 ± 0.004
Se	0.91 ± 0.069
As	0.99 ± 0.003
Мо	0.98 ± 0.004

Figure 5 applies the batch NF model using the relationships in Equation 1 to Equation 4 to experimental data from a pilot-scale brine (Korak et al (2018)) and showed good agreement for flux, chloride, sulfate, nitrate, and most trace elements. The impact of applying an average rejection for bicarbonate (R_{obs,HCO3}) led to systematic differences, but the fit can approximate concentrations within 20%. These results demonstrate that response surface models developed for synthetic solutions can be applied to independent field brines to predict flux and major anion rejection. The presence of other anions at comparatively lower concentrations do not interfere. The supplemental spreadsheet allows users to enter a waste brine composition and generate plots similar to Figure 5.

Although the overall objective of this study was waste management for Cr(VI) SBIX processes, the general relationships relating dominant anion composition, flux, and rejection are applicable to a wide range of SBIX applications. Waste brine produced from arsenic SBIX processes would be dominated by the same major anions (i.e., chloride, sulfate, nitrate, and bicarbonate)^{34,36,43}, and Figure 5 shows that the empirical equations fit using model solutions performed well for a real SBIX waste brine. Assuming similar operating conditions and the same membrane, these response surfaces could be used to assess the feasibility of NF for waste minimization in other SBIX applications.

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Figure 5. Validation of batch NF model developed from model solutions applied to experimental data for Brine B published in Korak et al. (2018)

4.2 Pilot-scale resin loading and regeneration

Building up to the NF brine reuse model (Section 3) that incorporates the NF response surface relationships (Section 4.1), pilot-scale IX columns were loaded to 1) generate real regeneration elution profiles as model inputs and 2) provide a holistic opportunity to test the impact of impurities in NF-reuse solutions. Three columns with new resin were loaded in parallel and exhausted for Cr(VI) after about 37,000 BV (Figure S2). Effluent from the columns had non-detectable Cr(VI) concentrations (<3 μ g/L) up to 20,000 BV. Breakthrough for each column and the combined effluent showed good agreement with each other. Based on the reproducibility of

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chromium breakthrough, it was assumed that the initial resin-phase composition was consistent between columns for side-by-side comparisons.

Using softened well water with added NaCl, two columns were regenerated using a conventional 1-Stage and a segmented 2-Stage regeneration process, respectively. These regenerations represent the scenario for which fresh regeneration solution is mixed each cycle. The 1-Stage regeneration used 4 BV of 2 N NaCl. The 2-Stage regeneration used 4 BV of 0.2 N NaCl followed by 4 BV of 2 N NaCl. Figure 6 shows the elution profiles for the 1-Stage (a-c) and 2-Stage (d-f) regenerations. The general elution trends for anions agreed with previous studies^{8,11}. For the 1-Stage regeneration, sulfate, chromium, uranium, and vanadium co-eluted with little separation. Arsenic eluted before sulfate, and nitrate exhibited a broad elution peak after sulfate and chromium due to selectivity reversal⁴⁴. In the 2-Stage regeneration, less selective anions, namely arsenic and bicarbonate, eluted during the 0.2 N NaCl stage. About 55% of the total recovered sulfate eluted with 4 BV of 0.2 N NaCl. Transitioning to the 2 N NaCl stage, the remaining sulfate eluted along with chromium, vanadium, and uranium. Nitrate eluted last with a broad elution peak like the 1-Stage regeneration. Under both regeneration approaches, vanadium exhibited a pronounced tailing behavior and did not return to near-zero concentrations. Significant tailing with incomplete vanadium recovery after 3-10 BVs has been observed in previous studies using both NaCl^{8,11} and NaOH⁴⁵ as regenerant salts, but the underlying mechanisms have not been investigated.

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Figure 6. Elution profiles for 1-Stage (A-C) and 2-Stage (D-F) regeneration approaches. Note the different chromium scales on B and E. Arsenic concentrations are multiplied by 10 for plot visibility. The shaded regions denote the fractions captured in the Collection Vessel (BV_{start} to BV_{end}) for concentration by NF prior to reuse.

A notable difference, the 2-Stage regeneration recovered 52% more chromium than the 1-Stage regeneration (Figure S3). A previous study that used the same resin found no difference in chromium recovery for the same two regeneration methods at a different test location¹¹. The samples with peak chromium in this study were reanalyzed to confirm the difference. The only other study known to compare 1- and 2-Stage regenerations did not comment on cumulative chromium recovery⁸. The resin-phase composition prior to regeneration in this study had some other notable differences compared to Korak et al. (2017). In this study, the calculated active sites occupied by bicarbonate (25% vs. 15%), chromium (4.6% vs. 3.1%) and vanadium (1.5% vs 0.12%) were higher and nitrate was lower (1.0% vs. 7.3%). Elucidating the mechanism behind differences in chromium recovery would require a controlled bench study, which is outside the

scope of this study. Since the 2-Stage regeneration recovered more chromium, further pilot-scale Paper is published as: Korak, J. A., Flint, L. C. & Arias-Paić, M. Decreasing waste brine volume from anion 24 exchange with nanofiltration: implications for multiple treatment cycles. *Environmental Science: Water Research and Technology* **7**, 886–903 (2021). doi: 10.1039/d1ew00001b

experiments evaluating NF-reuse only tested the 2-Stage approach (Section 4.4). The NF-reuse process model, however, was applied to both regeneration approaches to determine the relative impact of regeneration method on impurity accumulation in a cyclical NF-reuse scenario.

4.3 Cyclical Model Predictions

The cyclical NF-reuse process model was executed using pilot-scale regeneration profiles (Figure 6) as inputs to compare the effect of regeneration approach on potential impurity accumulation and provide a design basis for additional pilot-scale experiments. For both 1-Stage and 2-Stage regenerations scenarios, the termination point (BV_{end}) was the bed volumes needed to achieve the same regeneration efficiency (i.e., 99%) for nitrate. The fraction of waste collected for NF-reuse is shaded in Figure 6 for each regeneration. The NF-reuse scenario was simulated over 10 cycles, which represents about 400 days of operation for this well (40 days per loading cycle).

From a water balance perspective, the NF model predicted overall batch recoveries of 87% and 93% for the 1- and 2-Stage regenerations, respectively, prior to flux limitations. Higher recovery is possible for the 2-Stage approach due to a lower initial sulfate concentration in the Collection Vessel. For both regeneration scenarios, however, NF would produce more permeate than needed for the next regeneration cycle, leading to blowdown of about 25% of the treated permeate to Flex Vessel 2.

Initially (cycle = 0), the regeneration solution is composed of only sodium and chloride at 2 eq/L (Figure 7). With each loading-regeneration-NF-reuse cycle, anions other than chloride (i.e., impurities) pass through the NF membrane and accumulate in the regeneration solution. Chloride concentration is set at 2 eq/L as a model constraint, which determines the permeate volume recycled (V_{RU}) and make-up salt (V_{sat}) requirements. The concentration of sodium increases with each cycle to maintain electroneutrality as impurities accumulate (Figure 7a). For the 1-Stage Paper is published as: Korak, J. A., Flint, L. C. & Arias-Paić, M. Decreasing waste brine volume from anion 25 exchange with nanofiltration: implications for multiple treatment cycles. *Environmental Science: Water Research and Technology* **7**, 886–903 (2021). doi: 10.1039/d1ew00001b

scenario, the sodium concentration would increase from 2 to 2.13 eq/L over 10 NF-reuse cycles, indicating 6.5% anion equivalents of impurities. In contrast, only 2% of the anion equivalents would be non-chloride impurities in the 2-Stage scenario. Therefore, the 2-Stage regeneration is preferred to reduce the total amount of impurities that could get recycled in an NF-reuse process.

When NF-reuse is implemented using a strategy that maintains the water balance and chloride concentration in the Regeneration Vessel, a pseudo steady-state concentration is predicted under ideal conditions (Figure 7). Impurity concentrations plateau after the 2nd NF-reuse cycle for impurities with high membrane rejections, and concentrations plateau after 8-10 cycles for nitrate and inorganic carbon (low to negative membrane rejection). This practical steady state occurs because the cyclical process is not a closed loop. In each NF-reuse cycle, impurities would be wasted through 1) concentrate blowdown from the Collection Vessel to the Disposal Vessel and 2) blowdown to Flex Vessel 2 if excess permeate is produced. For this field site, the sulfate concentrations were low enough to produce about 25% more NF permeate than is required for the next regeneration cycle for both 1- and 2-Stage scenarios. Finally, when saturated salt solution is added to increase the chloride concentration back to 2 eq/L, impurities are further diluted. Building off previous studies that attributed diminished performance to impurity accumulation^{8,10}, these modeling results demonstrate that, with an appropriate water balance, a brine reuse strategy does not continuously accumulate impurities.

Regeneration approach also impacts the predicted composition of impurities. For sulfate, inorganic carbon, and arsenic, the predicted NF-reuse concentrations were higher for the 1-Stage regeneration, because nearly all the eluted mass was captured in the Collection Vessel. For the 2-Stage regeneration, in contrast, a significant portion of these anions elute during the 0.2 N NaCl regeneration segment (Figure 6) and are not captured for NF treatment. Chromium concentration was higher in the 2-Stage NF-reuse scenario. More chromium was not only recovered during

regeneration (Figure S3), but the brine volume was smaller due to more efficient nitrate elution. NF also achieved higher batch recoveries for the 2-Stage scenario, which led to higher predicted concentrations of vanadium and uranium. Differences in bicarbonate and sulfate concentration in a regeneration solution can be important for vanadium and uranium recovery^{11,46,47}, the impacts of which are investigated in Section 4.4 for the 2-Stage scenario.



Figure 7. Model predictions for the concentration of constituents (A-K) in NF-reuse brine over 10 loadingregeneration cycles. Disposal volume (L) with NF-reuse is the worst-case scenario including the excess permeate captured in Flex Vessel 2.

Integrating NF-reuse reduces regenerant chemical costs by 62-67%, softened service water volume requirements by 85%, and most importantly, hazardous waste disposal volumes by 68-71% (Table 2). For this test site with an initial chromium concentration of 85 μ g/L, the steady-state chromium concentration in the permeate (34-65 mg/L) would exceed the soluble threshold

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limit concentration (STLC) of 5 mg/L under State of California Title 22 regulations. For reference, the initial waste brine concentrations before batch NF treatment were 280 and 426 mg/L for the 1- and 2-Stage regenerations, respectively. As a worst-case scenario, it was assumed that none of this excess permeate volume can be repurposed and was included in the hazardous waste disposal volumes in Figure 7*l* and Table 2. For systems with lower raw water chromium concentrations, or those operating in areas with higher thresholds for hazardous waste disposal non-hazardous disposal may be an option for the excess permeate, further reducing disposal costs.

Table 2. Resource requirements for regeneration with and without NF-reuse. Softened surface water volume includes the actual requirements to achieve 99% nitrate elution. Hazardous waste disposal includes brine, excess permeate, interstitial water and rinse water captured for disposal.

Regeneration Method	Brine Management	Solid NaCl q/L _{resin}	Softened Service Water BV	Hazardous Waste Disposal BV
1-stage (4 BV of 2 N NaCl)	None	455	3.9	4.7
	NF-Reuse	174	0.60	1.4
	% Reduction	62%	85%	71%
2-stage (4 BV of 0.2 N NaCl, 4 BV of 2 N NaCl)	None	470	3.6	4.5
	NF-Reuse	154	0.53	1.4
	% Reduction	67%	85%	68%

These simulation results demonstrate that the operational context in which brine is collected and reused is important to estimate impurities that may accumulate. Without these process constraints, a pseudo steady state would not be realized and inter-study comparisons made difficult. In general, most brine reuse studies do not specify the volume of brine collected, the volume of rinse or interstitial water, and/or the mechanism for make-up salt addition^{7,8,10,23}. One report recognized the shortcoming mid-study²³. Some studies add make-up NaCl, but none have specified whether a saturated solution or solid was used^{7,8,24}. Operationally, adding a Paper is published as: Korak, J. A., Flint, L. C. & Arias-Paić, M. Decreasing waste brine volume from anion 28 exchange with nanofiltration: implications for multiple treatment cycles. *Environmental Science: Water Research and Technology* **7**, 886–903 (2021). doi: 10.1039/d1ew00001b

saturated solution is preferred to dry solids in full-scale operations. In this simulation, using a saturated solution reduces the volume that can be recycled by about 15% and dilutes impurities in the NF-reuse brine. Lastly, a comprehensive analysis of impurities with specified blowdown mechanisms is needed to facilitate inter-study comparisons. A high-level process model and realistic constraints need to guide research studies for transferability to full-scale applications.

4.4 Regeneration with synthetic NF-reuse brine

The cyclical model (Section 4.3) made an important assumption that the loading and regeneration efficiency was the same in each NF-reuse cycle. The validity of this assumption was tested using a synthetic NF-reuse brine. Since the 2-Stage approach eluted more chromium with fresh regeneration solution (Figure S3), this method was selected for further pilot testing. A synthetic NF-reuse brine (Table 3) was formed based on the predicted composition in Figure 7 for the 10th NF-reuse cycle. A third pilot-scale column, loaded in parallel with the original columns (Figure S1), was regenerated with the synthetic NF-reuse solution. An advantage of this approach is that the impact can be evaluated on a new column unaffected by the regeneration efficiency of a previous treatment cycle, allowing for an objective comparison.

Figure 8 compares the 2-Stage regeneration profiles for fresh and synthetic NF-reuse brines. Since fresh 0.2 N NaCl solution was used for the first regeneration stage in both scenarios, both elution profiles showed good reproducibility up to 4 BV. During the 2 N stage, the impurities in the NF-reuse brine generally did not impact the bed volume at which constituents eluted or bulk conductivity (Figure 8a). Mass balances on each constituent, in conjunction with batch tests, were used to understand how impurities in the reuse brine impact regeneration efficiency. In most studies, qualitative regeneration profiles, chromium breakthrough, and nitrate chromatographic

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peaking upon reloading are the only metrics presented^{7,8,24}, but these are indirect measures of regeneration efficiency.

Table 3. Composition of synthetic regeneration solution modeling the 2-Stage, 2 N NaCl brine after 10 NFreuse cycles. All anions were added using the sodium form of the salt.

Constituent	Units	Synthetic NF-reuse Brine
рН	SU	8.24
Conductivity	mS/cm	145.3
Chloride	eq/L (g/L)	2 (71)
Sulfate	meq/L (mg/L)	8.7 (417)
Nitrate	meq/L (mg/L as NO ₃ -)	9.1 (562)
Bicarbonate	meq/L (mg/L as HCO ₃ -)	22.5 (1,373)
Chromate	meq/L (mg/L as Cr)	2.0 (51)



Figure 8. Regeneration elution profiles using fresh regeneration solution and synthetic brines based on the batch NF model for conductivity (A), pH (B), and individual constituents (C-H). Horizontal lines for sulfate, nitrate, inorganic carbon, and chromium indicate the concentration in the NF-reuse synthetic brine. Insets plots show elution profiles on a logarithmic scale for clarity.

The NF-reuse synthetic brine had less than a 10% impact on regeneration efficiency for chromium, sulfate, and inorganic carbon. Chromium recovery was 9% lower with NF-reuse brine,

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but it is difficult to interpret if this difference is statistically significant due to error propagation without additional pilot-scale replication. There was no practical impact on the elution timing (Figure 8c, e, and f) with NF-reuse brine, so utilities implementing NF-reuse would not have to adjust control systems each cycle. At the end of the regeneration cycle (6 to 8 BV), effluent concentrations stabilized at the background concentration in the NF-reuse brine. Plummer et al. (2018) interpreted the elevated concentrations, termed 'floors', as incomplete regeneration but did not compare the floor concentrations to the background concentration show that practically the same mass of sulfate, inorganic carbon, and chromium was recovered during regeneration with fresh and NF-reuse brines shown in Figure 9a, b, and e. Therefore, elevated concentrations at the end of regeneration should not be interpreted as inefficient recovery when brine recycling is implemented without accounting for background concentrations.

Elevated effluent concentrations at the end of regeneration (6-8 BV) increase the potential for leakage in the next loading cycle due to potentially higher resin-phase concentrations. Increased leakage, however, would not be expected based on batch tests. At the bottom of the columns after the 2-Stage regeneration, resin-phase chromium concentrations were similar for both fresh and NF-reuse solutions (0.3-0.5% of active sites) (Figure 10a). Similar to Korak et al. (2017), the 1-Stage regeneration with fresh solution left significantly higher chromium concentrations (4%) on the bottom of the column, revealing an advantage in mitigating leakage using a 2-Stage over a 1-Stage approach. Leakage is directly assessed in Section 4.5 during reloading.

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Figure 9. Cumulative elution of individual constituents (A-F) in each regeneration scenario. The mass of a constituent that entered the column in the NF-reuse solution is reported as background and termed 'Bkgd.' 'Net' subtracts the background mass in the synthetic NF-reuse solution from the total mass eluted.

In contrast, nitrate exhibited a noticeably different behavior around 6 BV shown in Figure 8d. For NF-reuse brine, the effluent nitrate concentration decreased below, then increased to the background concentration. An effluent concentration below the background concentration indicates that the resin was accumulating nitrate in the middle of the regeneration sequence. Accounting for background concentrations, the net nitrate recovered from the resin not only decreased but was slightly negative with NF-reuse brine (Figure 9d). Comparing batch tests, about 1% of the resin active sites were occupied by nitrate before regeneration (Figure 10b). After regeneration with fresh 2 N NaCl solution, nitrate occupied <0.07% of the active sites. With the NF-reuse brine, nitrate occupied 1.15% of the active sites post-regeneration, which was greater than the resin-phase concentration prior to regeneration. A net accumulation may explain why Plummer et al. (2018) observed nitrate peaking earlier with each reuse round. However, the batch data only weakly supports the hypothesis of higher concentrations deeper in the bed as shown in Figure 10b, where nitrate increases from 1.1% to 1.2% from the top to the bottom of the bed. This

study directly demonstrates that even a small nitrate impurity (0.5%) compared to chloride in the NF-reuse brine impacts nitrate regeneration efficiency and can lead to nitrate accumulation during regeneration. Assessing nitrate accumulation will be an important consideration for utilities where contactors could be staggered to dampen peaking.



Figure 10. Percent of resin active sites occupied for resin aliquots collected before and after regeneration for the fresh regeneration solution (1- and 2-Stage) and NF-reuse scenarios for each constituent (A-F). Resin aliquots were regenerated with 20 BV of 2 N NaCl followed by 20 BV of 6% HCl. Error bars represent the standard deviation of samples collected from three columns before regeneration.

Uranium and vanadium recovery increased using the NF-reuse brine shown in Figure 9c and f. Since there was no vanadium or uranium added to the synthetic NF-reuse brine, net recovery could be calculated directly, without subtracting a background concentration. Uranium recovery increased by 57% with sustained elution 7 times higher than fresh regeneration solution through 8 BV (Figure 8h). Increased recovery is likely due to elevated background sulfate and bicarbonate^{11,46}. After regeneration, residual uranium was detected throughout the length of the column following the 1-Stage regeneration but not the 2-Stage regenerations (Figure 10e). Under

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both 2-Stage scenarios, uranium displaced from the top of the column is less likely to exchange back onto the lower sections of the column and reduce total recovery.

For both 2-Stage regenerations, vanadium did not show a defined peak but a comparatively sustained release from the resin (Figure 8g). With the synthetic NF-reuse brine, vanadium recovery increased by 28%. Previous work has shown that increased sulfate can suppress vanadium recovery^{11,46}. Figure 8g shows that vanadium did not start eluting until after peak sulfate elution for both 2-Stage scenarios, however for the 1-Stage regeneration with fresh solution, the highest vanadium concentrations were observed concomitantly with the highest sulfate concentrations (Figure 6b and c) . Plummer et al. (2018) also did not observe the same vanadium suppression and suggested it may be due to a higher background alkalinity. Batch tests post-regeneration showed that vanadium recovery was less than 50% at the bottom of the column compared to pre-regeneration tests (Figure 10f). Resin-phase concentrations systematically increased along the length of the column. Although NF-reuse increases vanadium recovery, as a whole, vanadium recovery is inefficient and incomplete.

Poor regeneration efficiency of uranium and vanadium could have long-term impacts on utility operation. Accumulation over many loading cycles may lead to decreased capacity if unrecovered material fouls the resin. Uranium can form insoluble uranium oxides⁴⁸, and potential adverse effects are unknown. In this source water, the chromium concentration (3.3 µeq/L) is similar to vanadium (2 µeq/L) on an equivalent basis. Poor recovery of vanadium may start to impact chromium capacity if there are competitive effects. Accumulation may necessitate periodic regeneration with a strong acid. This study shows that higher recovery with NF-reuse in each cycle will reduce the accumulation rate of uranium and vanadium and delay or eliminate the need for an alternative acid regeneration.

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4.5 Chromatographic peaking

The three regenerated columns (i.e., fresh 1-Stage, fresh 2-Stage, and NF-reuse 2-Stage) were reloaded at the well site to evaluate how each regeneration impacted chromatographic peaking and breakthrough. Figure 11 shows the reloading trends for arsenic, chromium, and vanadium. Previous work at the pilot scale has largely focused on nitrate chromatographic peaking or did not have the sampling resolution to evaluate arsenic peaking¹⁴. Nitrate can peak at 2-3 times the raw water concentration between 500-4,000 BV depending on raw water sulfate^{8,10,14,23,49}. In this study, raw water concentrations were too low (1.6 mg/L as NO₃⁻) compared to the commercial lab method reporting limits to assess nitrate chromatographic peaking.

For arsenic, neither timing (~2,500 BV) nor magnitude (14 μ g/L) of the peak was impacted by the regeneration method. In all cases, at least one sample was above the USEPA arsenic MCL of 10 μ g/L. Compared to the raw water concentration of 6.4 ± 0.8 μ g/L, the maximum observed arsenic concentration was about 220% greater. A notable difference, however, was that following regeneration with NF-reuse brine, there was arsenic leakage during the first 500 BV that also exceeded the regulatory limit for the first sample collected at 107 BV.

An important conclusion from this work is that arsenic peaking and leakage will be an important design and operational consideration for full-scale SBIX chromium processes, even for low sulfate waters. Parks et al. (2017) demonstrated at lab scale that arsenic can peak at 140 - 460% of the raw water concentration, and peak magnitude increases (width decreases) with increasing sulfate concentration. Based on the 2017 study, the sulfate concentration in this study (14 mg/L) would have anticipated an arsenic peak of less than 140%; however, a significantly larger peak (220%) was observed. For this raw water, dampening the arsenic peak to less than 8 μ g/L (i.e., 80% of the MCL) through blending would require at least 5 staggered contactors

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(assuming equal flow in each contactor and a raw water arsenic concentration of 6.4 µg/L). If nitrate is also present in the raw water, selectivity alone would suggest that nitrate would peak before arsenic. In previous bench-scale work, however, nitrate and arsenic peaked at similar bed volumes, and the arsenic peak was similar to or greater in relative magnitude than the nitrate peak⁴⁹. Quantifying peak magnitude and timing for both arsenic and nitrate will be an important design consideration to adequately stagger contactors. This pilot study demonstrates that leakage will also be important if brine reuse techniques are used. Therefore, pilot studies need to specifically evaluate arsenic peaking and leakage whenever arsenic is detected in the raw water as it is likely to be a design-controlling factor.



Figure 11. Arsenic and vanadium breakthrough and chromium leakage during reloading after each regeneration method. The minimum reporting limit for each analyte was 1 µg/L. Dashed lines show the raw water and applicable maximum contaminant levels (MCLs). Due to a sampler malfunction, peak arsenic for the 1-Stage regeneration was not captured.

All reloaded columns had chromium leakage, as shown in Figure 11b, with higher concentrations for the 1-Stage regeneration (5 μ g/L) compared to both 2-Stage regenerations (2 μ g/L). From batch test data (Figure 10a), the bottom of the 1-Stage column had higher resinphase concentrations after regeneration (3.8% of active sites) compared to both 2-Stage

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regenerations (~0.5%). Compared to an initial resin-phase concentration of 4.6%, chromium regeneration efficiency was low at the bottom of the 1-Stage column leading to leakage. At about 2,500 BV, chromium concentration started to increase for all three columns reaching about 20 µg/L (25% of the influent concentration) for the 1-Stage column. The loading cycles for the other columns were terminated early. In the first loading cycle with new resin (Figure S2 and Figure 11), the effluent chromium concentration did not increase before 20,000 BV. The magnitude of leakage for this well site would be problematic for any Cr(VI) regulatory limits less than 20 µg/L. Early breakthrough would adversely impact installations that are sized based on one loading cycle. Regeneration frequency would increase, thus increasing the operating expenses of waste disposal. The columns with fresh regeneration solutions were stored about a year between regeneration and reloading due to project logistics. If time is an important factor for the apparent reduced chromium capacity, systems that experience prolonged shut downs will need to consider resin condition prior to a loading cycle.

Vanadium exhibited a distinctly different breakthrough behavior for the reloaded columns compared to the initial loading with new resin. With new resin, vanadium breakthrough started about 2,500 BV with full breakthrough occurring around 30,000 BV (Figure 11c). On the reloaded columns, complete vanadium breakthrough occurred at about 3,000 BV and showed a stepwise behavior. Breakthrough occurred in two steps rather than a self-sharpening S-curve like other oxyanions. The effluent concentration for the fresh 1-Stage and 2-Stage regenerations increased to about 40 µg/L, plateaued for about 1,000 BV, and then increased to match the raw water concentration around 2,500-3,000 BV. For the NF-reuse regeneration, effluent vanadium decreased from 1,000-2,000 BV before continuing breakthrough. All three reloaded columns exhibited leakage during the first 300 BV. Chromatographic peaking was not observed, agreeing with previous observations for arsenic SBIX processes, despite differences in resins³⁶.

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These results suggest that incomplete regeneration impacts the selectivity of vanadium upon reloading. If the stepwise behavior could be attributed to a difference in raw water vanadium speciation, it would have also been observed when loading new resin. In oxidizing and alkaline conditions, the most common forms for vanadium are H₂VO₄⁻ and HVO₄²⁻, and the pKa between forms is about 8 ⁵⁰. Polyprotic anions have also been shown to deprotonate in the resin phase due to proton exclusion⁵¹, and vanadium can form polynuclear forms as concentration increases⁵². The multi-step breakthrough could be indicative of a transition to polynuclear forms in the resin phase as solid-phase concentrations increase, thus impacting selectivity. Overall, these results demonstrate that the reloading behavior is distinctly different. Multiple cycles should be evaluated at the pilot scale to understand long-term behavior. The potential for vanadium accumulation impacting removal of target contaminants needs further study.

5 Conclusions

Brine management is the primary economic barrier for installing SBIX for Cr(VI) removal. This study advances the methodology for assessing NF-reuse and quantifying the impact on regeneration and loading efficiency. Key conclusions and outcomes from this study include the following:

• A practical model was developed for water utilities to estimate how NF can decrease waste brine volume. The model design space is broadly applicable to SBIX waste brines (>1M) dominated by chloride and sulfate and predicts rejection at a wide range of operating pressures (150-250 psi). Building this model into a supplemental spreadsheet allows stakeholders to shortlist technologies for site-specific testing.

• Research studies need to define realistic operating constraints to evaluate brine reuse. Previous studies have assumed that reused brine would accumulate impurities until becoming unsuitable for reuse. Similar to full-scale installations, modeling that constrained the regeneration Paper is published as: Korak, J. A., Flint, L. C. & Arias-Paić, M. Decreasing waste brine volume from anion 39 exchange with nanofiltration: implications for multiple treatment cycles. *Environmental Science: Water Research and Technology* **7**, 886–903 (2021). doi: 10.1039/d1ew00001b solution volume and concentration found cyclical NF-reuse reaches a practical steady state for impurity concentrations, which is simpler to assess and manage at a utility.

• Anion recovery efficiency varies when regenerating resin with synthetic NF-reuse brine. Resin-phase nitrate concentration increases, which may impact chromatographic peaking during loading. Chromium recovery may decrease by 9%. NF-reuse brine is beneficial to increase uranium and vanadium recovery and may reduce long-term accumulation.

Arsenic chromatographic peaking may control full-scale design by dictating the minimum number of contactors operating in a staggered parallel configuration needed to maintain concentrations below an MCL of 10 µg/L. Chromium exhibited early breakthrough and leakage upon reloading, which could prove catastrophic for facilities basing design on a single loading cycle test. Early vanadium breakthrough suggests differences in selectivity upon reloading. Combined with poor regeneration efficiency, vanadium accumulation and the potential for fouling needs to be further assessed.

6 Conflicts of interest

There are no conflicts of interest to declare.

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