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Interim Report - Sulfate Conversion of Reillex HPQ Anion Exchange Resin for Disposal

S. C. Mills

A. A. Denisenko

C. S. Morgan

M. S. Mills

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REVIEWS AND APPROVALS

AUTHORS:

SASHA MILLS (Affiliate) Digitally signed by SASHA MILLS (Affiliate) Date: 2025.10.16 11:03:37 -04'00'

S. C. Mills, Analytical & Materials Characterization Date

ALENA DENISENKO (Affiliate) Digitally signed by ALENA DENISENKO (Affiliate) Date: 2025.10.16 12:49:23 -04'00'

A. A. Denisenko, Production Technology Date

CLAIRE MORGAN (Affiliate) Digitally signed by CLAIRE MORGAN (Affiliate) Date: 2025.10.16 13:09:53 -04'00'

C. S. Morgan, Material Evaluation & NDE Date

MATTHEW MILLS (Affiliate) Digitally signed by MATTHEW MILLS (Affiliate) Date: 2025.10.16 13:37:04 -04'00'

M. S. Mills, Separations & Actinide Science Date

TECHNICAL REVIEW:

THOMAS SHEHEE (Affiliate) Digitally signed by THOMAS SHEHEE (Affiliate) Date: 2025.10.20 07:45:37 -04'00'

Thomas Shehee, Separation Sciences & Engineering, Reviewed per E7 2.60 Date

APPROVAL:

MARIA KRIZ (Affiliate) Digitally signed by MARIA KRIZ (Affiliate) Date: 2025.10.20 09:39:25 -04'00'

Maria Kriz, Manager Date
Analytical & Materials Characterization

PHILIP ALMOND (Affiliate) Digitally signed by PHILIP ALMOND (Affiliate) Date: 2025.10.20 10:02:30 -04'00'

Philip Almond, Analytical & Materials Characterization Date

MATTHEW BRANTLEY (Affiliate) Digitally signed by MATTHEW BRANTLEY (Affiliate) Date: 2025.10.30 13:09:48 -04'00'

Matthew Brantley, Manager Date
SRPPF Chemical Process Engineering

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EXECUTIVE SUMMARY

This report describes preliminary data to validate the Savannah River Plutonium Processing Facility's (SRPPF) flowsheet for conversion of used Reillex HPQ anion exchange resin from the nitrate form to the sulfate form. The nitrate form is an oxidizer and therefore does not meet acceptance criteria for disposal at the Waste Isolation Pilot Plant (WIPP). The purpose of this study is to develop data to support acceptance for this disposition pathway.

Due to the challenges characterizing the nitrate concentration on solid resin, the data developed to date are based upon indirect analysis of the ion exchange column effluent by ion chromatography. These challenges are discussed and two methods for quantification of nitrate directly on the resin are recommended for further development: TGA-MS and permanganate digestion followed by IC.

The resin used for this work was provided in the chloride form; this is the form in which resin is supplied by the manufacturer. However, it had to be converted to the nitrate form, which is the form that will be used in SRPPF's ion exchange process, prior to use in the sulfate conversion experiments. The chloride-form resin was characterized. A lab-scale procedure for the conversion of Reillex HPQ resin from the chloride to nitrate form was validated. The nitrate-form resin was assessed for particle size and chloride concentration to ensure it met SRPPF's facility specifications.

The baseline sulfate conversion flowsheet was tested. However, nitrate was still detectable in the effluent after approximately 10 bed volumes of 1 M sodium sulfate had been passed through the resin bed. Additional experiments were performed to assess the effect of increasing the feed volume, reducing the flowrate, the use of 2 M sulfuric acid instead of sodium sulfate, and the use of irradiated resin. The sulfuric acid test was the only one which provided a nondetectable nitrate concentration (<0.002 M) in the effluent. Detectable nitrate in the column effluent suggests that nitrate is still present on the resin itself.

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LIST OF ABBREVIATIONS

ARS	Aqueous Recovery System
BV	Bed Volume
DI	Deionized
DOE	Department of Energy
DSA	Documented Safety Analysis
DVB	Divinylbenzene
EDS	Electron Dispersive X-ray Spectrometer
FT-IR	Fourier Transform Infrared
IC	Ion Chromatography
ID	Inner Diameter
ISA	Ionic Strength Adjuster
ISE	Ion Selective Electrode
NAA	Neutron Activation Analysis
NIST	National Institute of Standards and Technology
NMR	Nuclear Magnetic Resonance
QC	Quality Control
SEM	Scanning Electron Microscopy
SRNL	Savannah River National Laboratory
SRPPF	Savannah River Plutonium Processing Facility
SVOA	Semi-volatile Organic Analysis
SwRI	Southwest Research Institute
TGA-MS	Thermogravimetric analysis - mass spectrometry
TIC	Total Inorganic Carbon
TOC	Total Organic Carbon
TRU	Transuranic
TTR	Technical Task Request
VOA	Volatile Organic Analysis
WIPP	Waste Isolation Pilot Plant

1.0 Introduction and Background

The Savannah River Plutonium Processing Facility (SRPPF) plans to utilize nitrate-form Reillex HPQ anion exchange resin to purify plutonium in the Aqueous Recovery System (ARS).[1] SRPPF currently plans to use a column of resin until it has been exposed to approximately 100 MRad, after which the column will be replaced with fresh resin. As with the majority of waste generated by the ARS, the planned disposition path for the used resin is the Department of Energy's (DOE's) Waste Isolation Pilot Plant (WIPP). Ion exchange resins containing oxidizing chemicals are not acceptable at WIPP without a verifiable basis that they are compliant with WIPP's program and facility requirements and present no additional facility hazard that has not been considered in the documented safety analysis (DSA).[2] Additionally, observable liquid in transuranic (TRU) waste is limited to less than 1% by volume of the outermost container.[3] Observable liquid is defined as liquid observable by radiography or visual examination. Therefore, the used resin must be converted to a non-oxidizing form and dried for acceptance at WIPP.[2,3]

A baseline flowsheet was proposed by the Savannah River National Laboratory (SRNL) to convert the used nitrate-form resin to the non-oxidizing sulfate form using 10 bed volumes (BV) of 1 M Na_2SO_4.[4] Note that a BV is defined as the total volume bound by the top and bottom of the resin bed.[5] It includes both the resin itself and the interstitial void space between the resin beads over this height. This conversion would be performed after the nitrate-form resin has undergone an extended elution with 0.35 M nitric acid to remove any remaining plutonium from the resin.[1]

SRPPF requested SRNL to validate the proposed flowsheet so that the data generated can be presented to WIPP to gain approval for the planned resin disposition path.[1] To assess the effectiveness of this flowsheet, SRNL was requested to:

1. Prepare a batch of nitrated Reillex HPQ anion exchange resin that had been exposed to 8 M nitric acid, stored in 0.35 M nitric acid, and irradiated up to 100 MRad.
2. Perform experiments and generate data to develop a plot representing nitrate remaining on the resin as a function of volume of 1 M Na_2SO_4 flowed through the resin bed at an equivalent linear velocity to the baseline ARS elution flowrate.
3. Optimize the vacuum drying process of the sulfate converted resin to remove the maximum amount of liquid in the shortest period of time.
4. Determine the specific volumes of the wet nitrate-form and sulfate-form resin as Reillex HPQ is known to swell and contract under various process conditions.

Prior to this work, the effectiveness of sulfate conversion of nitrate-form Reillex HPQ resin had never been characterized experimentally. In 1981, after multiple fires or explosions involving nitrate-form anion exchange resin had occurred at other nuclear sites, the JB-Line facility at the Savannah River Plant (now the Savannah River Site) ceased their practice of disposing of nitrate-form anion exchange resins as TRU waste.[6] Prior to disposal, it was recommended that resin be converted to a non-oxidizing form such as chloride, sulfate, or hydroxide, if digestion was not feasible logistically. Therefore, a procedure for the conversion of Dowex 21K anion resin – the resin used in JB-Line – from the nitrate to sulfate form was developed.[7] The primary reason for selecting sulfate over other anions was the monovalent anion selectivity sequence for Dowex 21K resin: $I^- > C_6H_5O^- > HSO_4^- > ClO_3^- > NO_3^- > Br^- > CN^- > HSO_3^- > NO_2^- > Cl^- > HCO_3^- > IO_3^- > HCOO^- > C_2H_3O_2^- > OH^- > F^-$.[7, 8] This sequence indicates that the resin has a strong affinity for the nitrate anion, making it difficult to displace by chloride or hydroxide.[7] However, a divalent anion, such as sulfate, should have an even greater affinity for the resin due to its greater charge. Based upon JB-Line's process conditions, Dow recommended conversion to the sulfate form with 1% w/w sodium sulfate at a linear velocity of 1-2 cm/min, with the total amount of sulfate equivalent to approximately 192% of the resin's theoretical exchange capacity. Although use of a dilute sulfate solution, such as 1% w/w (0.071 M)

Na_2SO_4, necessitated a larger liquid volume relative to a more concentrated solution, dilute sulfate was specified because precipitation of plutonium sulfate complexes is possible at sulfate concentrations above 0.17 M.[9] Prior to sulfate conversion, JB-Line eluted their resin in 0.35 M HNO_3 until the plutonium concentration on the resin was less than 1.25 g/L.[6]

To determine the effectiveness of the sulfate conversion, samples of sulfate-converted resin were equilibrated in 1% w/w sodium sulfate solution for 17 days.[10] This equilibration was performed to determine whether any additional nitrate could be removed from the sulfate-form resin. Aliquots of solution were removed after 3, 10, and 17 days and the nitrate concentrations were analyzed by ion chromatography (IC). The theoretical exchange capacity of the resin and the nitrate concentrations measured by IC were used to estimate that 0.5% of the active sites were still occupied by nitrate anions after the resin had been converted to the sulfate form.

Reillex HPQ is shipped from the manufacturer in the chloride form.[11] For plutonium nitrate processing lines, the resin must be converted to the nitrate form prior to deployment in the facility. The effectiveness of the conversion of chloride-form Reillex HPQ resin to the nitrate form was demonstrated at SRNL by Steimke et al.[11] This flowsheet utilized 1 M $NaNO_3$ for the conversion, which was fed to a process-scale ion exchange column at a linear velocity of 2.7 cm/min. The effluent conductivity and chloride concentration were monitored during the experiment using a conductivity probe and chloride test strips, respectively. The resin was subsequently dried, and the chlorine concentration measured using neutron activation analysis (NAA). NAA is an elemental analysis technique, so it measures chlorine, rather than chloride. However, all chlorine measured is assumed to be chloride anions. Chloride concentration in the effluent dropped drastically around 2.5 BV and approached zero near 3 BV. This procedure yielded post-conversion chloride concentrations on the resin below the HB-Line facility-specified maximum of 250 ppm.

Based upon the facile conversion of Reillex HPQ resin from the chloride to the nitrate form and that of the sulfate conversion for the Dowex 21K resin, Kyser recommended 10 BV of 1 M Na_2SO_4 for the sulfate conversion of used nitrate-form Reillex HPQ resin.[4] Kyser speculated that as little as 2 to 4 equivalents of sulfate, as a 1 M Na_2SO_4 solution, should be sufficient to remove 99% of the nitrate anions from Reillex HPQ resin. Therefore, Kyser concluded "10 BV of 1 M sodium sulfate solution will be more than sufficient to convert the nitrate-form resin to sulfate-form resin." However, it is reiterated that prior to this work, no known experimental characterization of the conversion of Reillex HPQ resin from the nitrate to the sulfate form had been done.

A good heuristic for designing an anion exchange flowsheet is that simple ion forms of strongly functional ion exchange resins may be prepared by feeding 5-10 bed volumes of a 10% w/v solution with the desired ion to a column at a rate of 1 BV / 3 minutes.[12] Weakly functional resins may only be converted from their acid or free-base forms using alkaline or acidic conditions, respectively. Additionally, for two anions of different electrovalencies, generally the anion with the higher charge has a greater affinity for the resin. However, the physical and chemical properties of a resin, in addition to process conditions, affect its selectivity[12,13] The Dowex 21K resin used in the studies performed for JB-Line, is a strong base polystyrene gel-type resin that is crosslinked at 4% with divinylbenzene (DVB) (Figure 1-2).[13,14] The anion exchange sites are a trimethyl benzyl ammonium group.[13] Reillex HPQ is a polyvinylpyridine-based macroporous resin that contains a mix of strong and weak base sites (approximately 63% and 37%, respectively) and is crosslinked at 30% with divinylbenzene (Figure 1-1).[15] The strong base sites are methylated pyridinium cations. The weak base sites are unquaternized pyridine rings that protonate in acidic solutions, forming an anion exchange site.

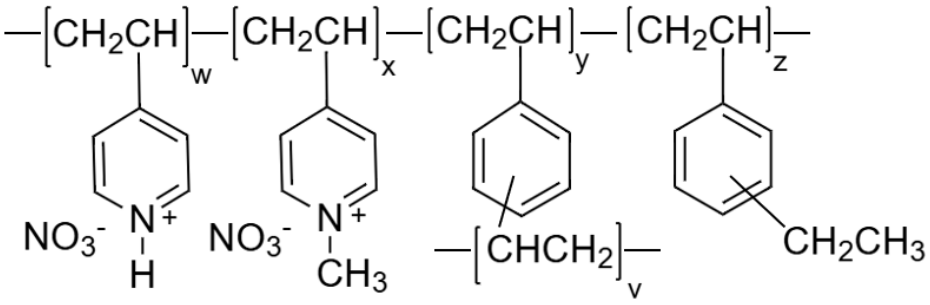

Figure 1-1. Chemical structure of Reillex HPQ resin[15]

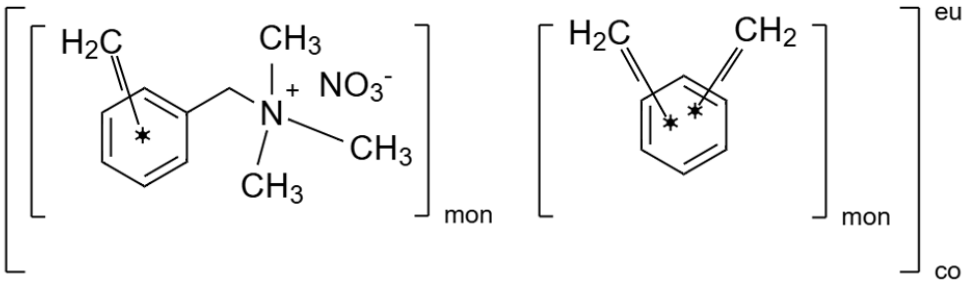

Figure 1-2. Chemical structure of Dowex 21K resin[16]

While divalent anions are generally favored over monovalent anions due to electroselectivity, it is critical that two exchange sites are available within close proximity to enable charge sharing.[12] Pyridinium anion exchange sites yield different selectivity and distribution characteristics than aliphatic ammonium-based resins.[17] Specifically, polyvinylpyridine resins are more monovalent selective than traditional polystyrene resins. Dowex 21K resin contains trimethyl benzyl ammonium anion exchange sites, which are selective to divalent anions, such as sulfate.[12,13] The degree to which a resin is crosslinked can also impact selectivity.[12] High crosslinking can slow the rate of mass transfer through the resin and create heterogeneous charge distribution. Selectivity towards nitrate generally increases with the degree of crosslinking, even if the ionogenic groups within the resin have a greater affinity for sulfate.[18] Crosslinking reduces the resin's ability to reorient to enable optimal charge sharing by two sites for a divalent anion, which could reduce the effectiveness of converting Reillex HPQ resin to the sulfate form, using 1 M Na_2SO_4, relative to Dowex 21K.

The degree to which Reillex HPQ resin can swell in different conditions impacts equipment and process design. With increasing crosslinking, the propensity of a resin to swell decreases.[12] Therefore, a highly crosslinked resin, like Reillex HPQ, should swell less than a low crosslinked gel-type resin. The degree of resin swelling also decreases with increasing counterion valency as there are fewer mobile ions in the resin phase, assuming there is no coion intrusion. Swelling generally increases with increasing dilution of the bulk solution and when counterions have a high affinity for solvation. Furthermore, the initial swollen ionic form of an ion exchange resin shrinks when contacted with an electrolyte solution. The degree to which this occurs is dependent upon the concentration of the external solution. Equilibration with water establishes its final volume.

At the time of this report, work is still in progress to meet all the requests described above. In FY2025, nitrate-form Reillex HPQ resin was prepared, exposed to nitric acid, and irradiated. Specific volumes for the chloride, nitrate, and sulfate forms were documented. Preliminary tests were done to characterize the efficacy of the sulfate conversion process. Continued work is needed to determine the nitrate concentration on the resin as a function of volume of 1 M Na_2SO_4 flowed through the resin bed and for resin bed drying optimization. Additionally, based upon the results from these preliminary tests, there is a potential to improve the conversion process with alternative flowsheets (e.g., different conversion reagents). A summary of the conversion experiments performed in FY2025 is shown below in Table 1-1.

Table 1-1. Summary of resin conversion experiments

Experiment	Description
N-1	Chloride to nitrate conversion using Steimke et al. flowsheet[11]
S-1	Nitrate to sulfate conversion using baseline SRPPF flowsheet
S-2	Nitrate to sulfate conversion with 2x feed volume
S-3	Nitrate to sulfate conversion with 1/4 baseline flowrate
S-4	Nitrate to sulfate conversion using higher sulfate feed concentration with sulfuric acid
S-5	Nitrate to sulfate conversion using baseline SRPPF flowsheet with resin irradiated to 100 MRad

2.0 Experimental Procedure

2.1 Chloride-Form Resin Characterization

Dry, chloride-form Reillex HPQ resin, manufactured by Vertellus (Batch 1577100008) was used for this work. This resin was supplied to SRNL by SRPPF in November 2024. The resin was dry sieved using E-11 standard 30 and 60 mesh screens (Dual Manufacturing Co.). To remove fine particles from the resin that were not separated by sieving, the resin was washed in batches with deionized (DI) water prior to nitrate conversion. The dry, sieved resin was poured into a 120-cm × 2.5-cm Bio-Rad Econo-Column to fill around 50% of the column with resin. DI water was upflowed through the column at a flowrate of approximately 100 mL/min using an FMI QD pump.

While the conversion experiments were done in downflow, washing the resin had to be done by upflowing DI water through the column. The Bio-Rad Econo-Columns have a frit with 30 μm pores at the bottom.[19] Initial testing attempting to wash the resin in downflow resulted in clogging the column frit such that flow was severely restricted and fine particles were not effectively removed from the resin beads. High velocity upflow, with no support at the top of the resin bed, results in fluidization of the resin bed. This is advantageous as it promotes suspension and transport of fine particles. When resin beads reached the top of the column, flow was stopped, the resin was allowed to settle, and then the process was repeated.

After each bed volume, a grab sample was taken, and the effluent density was measured using an Anton Paar DMA 35 density meter. Unless otherwise specified, this density meter was used to obtain all measured densities. After the effluent density appeared colorless, the pump was stopped. The washed resin was removed from column and stored in DI water as a slurry. The effluent from washing is expected to contain incompletely polymerized material and other organic and inorganic impurities, which may leach out of the resin.[11, 20] Samples of wash effluent from the beginning and end of wash cycle were analyzed for total organic and inorganic carbon and semi-volatile and volatile organic compounds. A sample of washed chloride-form resin was evaluated for particle size distribution.

Bio-Rad Econo-Columns come in standard sizes. The tolerance of the inner diameter (ID) of the columns is approximately 3 to 4% of the nominal value.[21] Precise column dimensions are critical for this work since resin bed volumes and linear velocities must be determined accurately to relate small-scale testing to the production scale. To reduce the uncertainty associated with the column ID, graduations with a resolution of 0.1 cm were added to the columns. The columns were then filled with DI water. The initial height of the water was noted, a volume of water was drained and collected, and the final height of water measured. The mass of water collected was measured and the associated volume calculated (from measured density). From the collected volume of water and change in height, the cross-sectional area and ID of the column section were calculated. This procedure was repeated for multiple column sections. The average column ID was calculated from this data and that was used to calculate the scaled flowrate for each experiment. The bed volume of resin was similarly calculated using the column ID and measured height of resin in the column. This procedure was used to characterize all columns used for quantitative experiments throughout this work.

A specific volume for the dry chloride-form resin was obtained by drying a sample of wet, washed resin to a constant mass at 60 °C using a Thermo Scientific vacuum oven (model 5831). A temperature of 60 °C has been demonstrated to minimize electrostatic effects during weighing.[20] For all resin drying in this work, unless otherwise specified, glass drying dishes pre-dried to a constant mass and stored in a desiccator were used and resin was dried to a constant mass at 60 °C and stored in desiccator. The dried resin was transferred to a 25-mL graduated cylinder. The graduated cylinder was tapped to settle the resin. The volume was measured, and the sample was weighed using a Mettler Toledo MX1203 balance. To measure the specific volume of wet chloride-form resin, the pre-weighed mass of dry chloride-form resin was slurried in DI water and transferred to a nominally 30-cm × 1.5-cm column. The resin was settled by downflowing DI water, and the BV was calculated from the settled resin bed height and experimentally determined column ID.

2.2 Nitrate Conversion

To characterize the conversion of Reillex HPQ resin from the as-received chloride form to the nitrate form, a column was packed with a slurry of washed, chloride-form resin (experiment N-1). At least 2 BV of DI water were flowed down through the column to settle the resin bed. An FMI QV model pump with a V300 stroke rate controller was used for all experiments described herein unless otherwise specified. A feed solution of 1 M $NaNO_3$ was prepared from Acros Organics 99+% ACS reagent grade sodium nitrate (Lot A0318271). The column ID was used to calculate the flowrate corresponding to a linear velocity of 2.7 cm/min, which was the linear velocity used by Steimke et al.[11] After pumping approximately 3.5 BV of 1 M $NaNO_3$ solution to the column, 3 BV of DI water were fed at the same rate. Composite cuts of effluent were taken to measure the chloride and nitrate concentrations, using Thermo Scientific Orion Versa Star Pro ion selective electrodes (ISE), and density. In general, solution volumes in this work were determined gravimetrically from a measured mass (bottle tare weights were pre-measured) and density to improve the precision of the calculated volume relative to volumetric measuring tools. A more detailed description of the method used for analyzing samples by ISE is described below in Section 2.4.2.1. Samples of each cut were subsequently analyzed by IC. The final resin bed height was measured. Resin was removed from the top half and then the bottom half of column using a transfer pipette. Care was taken to ensure all visible resin beads were removed from column. These samples were dried to a constant mass and analyzed for chlorine concentration by NAA. The specific volume of the wet nitrate-form resin was calculated using the dry nitrate-form resin mass and the resin bed volume post conversion. This nitrate conversion procedure was subsequently repeated several times at a larger scale, using nominally 100-cm × 2.5-cm columns to facilitate batch conversion of the resin.

Experimental conditions utilized for all quantitative nitrate and sulfate resin conversion experiments are described below in Table 2-1. The feed concentrations, bed volumes, and column dimensions are all nominal values. All columns used for quantitative experiments had a nominal ID of 1.5 cm. This ensured results are comparable, despite differing resin bed heights. The same linear velocities were used for the

conversion and subsequent DI water wash. Unless otherwise specified, prior to starting each conversion, at least 2 BV of DI water were used to settle the resin bed before recording the initial resin bed height.

Table 2-1. Experimental conditions for resin conversion experiments

Experiment	Feed	BV Feed	BV DI Water	Linear Velocity (cm/min)	Column Dimensions (cm x cm)	Initial Resin Bed Height (cm)	Final Resin Bed Height (cm)	Change in Resin Volume (%)
N-1	1 M $NaNO_3$	3.5	3	2.7	15 x 1.5	11.1	10.5	-5.4%
S-1	1 M Na_2SO_4	10	3	2.4	30 x 1.5	13.9	14.25	2.5%
S-2	1 M Na_2SO_4	20	3	2.4	30 x 1.5	16.9	17.3	2.4%
S-3	1 M Na_2SO_4	10	3	0.6	30 x 1.5	15.8	16.1	1.9%
S-4	2 M H_2SO_4	10	3	2.4	15 x 1.5	10	10.5	5.0%
S-5	1 M Na_2SO_4	10	3	2.4	30 x 1.5	12.1	12.2	0.8%

2.3 Sulfate Conversion

A slurry of nitrate-form Reillex HPQ resin, converted using the procedure described above in 2.2, was packed into a column. A feed solution of 1 M Na_2SO_4 was prepared from Thermo Scientific 99+% sodium sulfate decahydrate (Lot A0453240). This stock solution was divided into two bottles and used for all tests with sodium sulfate. The calculated column ID was used to determine the flowrate corresponding to a linear velocity of 2.4 cm/min, which is equivalent to the elution linear velocity at a flowrate of 0.7 L/min with a column ID of 7.6 in (SRPPF's process parameters).[1] Composite cuts of the effluent were taken and anion concentrations were measured using ISE and IC. After approximately 10 BV of 1 M Na_2SO_4 had been fed to the column, 3 BV of DI water were fed at the same flowrate. The final resin bed height was measured, and the resin was removed from column. The resin was dried to a constant mass. The specific volume of the wet sulfate-form resin was calculated using the dry sulfate-form resin mass and the resin bed volume post conversion. The dry sulfate-form resin was stored in a desiccator until a procedure for assessing nitrate concentration remaining on the solid resin could be developed.

This experiment was designed to measure anion concentrations in the effluent to develop concentration profiles as a function of BV feed transferred to the resin. The intent of this experiment was to test the baseline sulfate conversion flowsheet, using nitrate-form resin that had not been exposed to acid or radiation. Data developed from this experiment and similar experiments was not intended nor is suitable for determining the nitrate content remaining on the resin with precision. The nitrate content of the resin following this conversion was intended to be measured from a direct sample of resin, as requested by the customer. The nitrate content of the resin following conversion could feasibly be determined by a mass balance using measured effluent concentrations, but this would require starting with a measured aliquot of chloride-form resin and converting the entire aliquot to the nitrate-form followed by conversion to the sulfate form to alleviate the impact and associated uncertainties of resin specific volume changes. Additionally, minimizing the number of effluent cuts would be necessary for such an approach to reduce propagated error.

Following experiment S-1, another (S-2) was done using identical process parameters, except approximately 20 BV of 1 M Na_2SO_4 were fed to the column. This experiment was designed to determine whether nitrate was still detectable in the effluent after doubling the number of bed volumes used for the conversion and to assess the reproducibility of effluent concentration profile from the first experiment.

A third conversion experiment (S-3) was conducted using 10 BV of 1 M Na_2SO_4, at a reduced flowrate. The flowrate that was chosen, equivalent to a linear velocity of 0.597 cm/min, was approximately 25% of

the baseline flowrate. This was the lowest reproducible flowrate permitted by the pump used. The minimum linear velocity that SRPPF anticipates being able to achieve during the conversion process is around 0.342 cm/min.[22] SRPPF plans to feed the solution by gravity from a tank above the column glovebox. Flow will be manually controlled by throttling a globe valve. This experiment was designed to determine whether a lower flowrate would improve the performance with respect to nitrate removal.

After conducting three experiments using a feed of 1 M Na_2SO_4, a feed of 2 M H_2SO_4 (prepared from Fisher Scientific ACS grade, 95.0-98.0% solution, Lot 054066) was utilized for S-4. The objective was to determine whether the protonation of the weak base sites in an acidic medium would allow for sufficient charge sharing for the divalent sulfate anion to be exchanged for the monovalent nitrate anion. The increased sulfate concentration would also provide a greater driving force for mass transfer for film diffusion.[12] An increased sulfate concentration is not feasible at ambient conditions for sodium sulfate as it is already close to the solubility limit in water at a concentration of 1 M. The solubility of sodium sulfate decahydrate in water is 322.2 g/L at 20 °C.[23] The other process conditions, such as flowrate and bed volumes of feed were those described in the proposed baseline flowsheet. The composite cuts of effluent were assessed for anion concentrations and solution density. The composite cuts from the deionized water wash were additionally tested for pH, using an Oakton Environmental Express 35660-80 pH meter, to determine whether 3 BV were sufficient to remove interstitial acid after the conversion.

Exposure to radiation converts strong base sites to weak base sites.[24] Weak base sites are generally less selective for nitrate than strong base ones.[18] Therefore, the ability of the resin to exchange nitrate anions for sulfate may change relative to radiation exposure and SRPPF plans to change out their ion exchange resin after exposure to approximately 100 MRad. After conversion to the nitrate form, a column of resin was contacted with 8 M nitric acid (Sigma Aldrich ACS Reagent Grade, Lot MKCV2107) and subsequently irradiated to 100 MRad in 8 M nitric acid using a cobalt 60 irradiator. In SRPPF's process, the resin will receive the highest radiation exposure in 8 M nitric acid, as this is the expected concentration for their plutonium feed. An attempt was made to dry a sample of the irradiated nitrate-form resin to a constant mass to determine the specific volume. However, at this time, after nearly two months of drying in the oven at 60 °C and/or the desiccator, the resin has not reached a constant mass.

A fifth sulfate conversion experiment (S-5) was conducted using the nitrate-form Reillex HPQ resin that had been irradiated to 100 MRad in 8 M nitric acid. No deionized water was used to settle the resin bed prior to conversion as the resin was stored in acid and increasing the pH of the interstitial liquid prior to the conversion may result in the protonated sites dissociating.[20] The composite cuts were assessed for anion concentrations, pH, and solution density.

2.4 Characterization of Nitrate on Resin

One of the tasks described in the Technical Task Request (TTR) was to characterize the nitrate remaining on the resin after conversion to the sulfate form. A number of direct and indirect methods were explored in an attempt to accomplish this. There is no known prior experimental work/method to measure nitrate directly on anion exchange resin. The following is a summary of the methods explored during the course of this work.

2.4.1 Direct Analysis Methods

The following are methods explored to measure nitrate directly on the resin.

2.4.1.1 Combustion Analysis

Laboratory Equipment Company (LECO) TC-436 is an elemental analysis instrument that can be used to determine elemental composition of materials through combustion.[25] This method cannot distinguish

between nitrogen originating from nitrate anions and that originating in the pyridine rings of the resin. However, it is feasible that the nitrogen content of the chloride-form resin could be subtracted from the total nitrogen of a nitrate containing sample, so long as changes in resin physical properties associated with the change in anion are carefully accounted for. Samples of chloride-form Reillex HPQ resin (Vertellus, Batch 1577100008) and nitrate-form Reillex HPQ resin (Reilly Industries, Batch 80302MA) were placed in beakers with approximately 140 mL of deionized water and stirred for four hours. An older batch of nitrate-form resin was used for this scoping work as it was done prior to establishing a nitrate conversion method. After stirring, the supernate from each beaker was decanted and the resins were dried to a constant mass. The samples were stored in a desiccator and crushed into a fine powder prior to being sent for LECO TC-436 combustion analysis for nitrogen. The resins were crushed to allow for a smaller sample size to prevent saturating the instrument's detector.

2.4.1.2 Neutron Activation Analysis

Similar to LECO, NAA can quantify elemental nitrogen but cannot distinguish nitrate from other nitrogen containing compounds. As with LECO, careful accounting of changes in physical properties would be critical for this method to subtract nitrogen in the chloride-form resin, representing pyridine, from that in a nitrate containing sample. Quantification of nitrogen by NAA is difficult with traditional thermal neutron absorption techniques due to the low relative abundance of N-15 and the short half-life of N-16. A method was developed to measure the prompt gamma deexcitation from N-14.

The sample used for the scoping study was approximately 1 g of nitrate-form Reillex HPQ resin (Reilly Industries, Batch 80302MA). This was placed in a beaker with approximately 140 mL of deionized water and stirred for four hours. An older batch of nitrate-form resin was used because this scoping work was done prior to establishing a nitrate conversion method. The supernate from the beaker was decanted and the resin was dried to a constant mass. The sample was stored in a desiccator until it was ready to be analyzed. Subsequently, a 290 g sample of sieved, chloride-form Reillex HPQ resin (Vertellus, Batch 1577100008) was provided. Work was done to characterize the neutron flux, geometry for prompt gamma activation analysis, perform background measurements, and measure ammonium hydroxide, chlorine, and sulfuric acid standards.

2.4.1.3 Raman Spectroscopy / Nuclear Magnetic Resonance Spectroscopy

A study by Buscher et al. described using Raman spectroscopy as a qualitative tool for assessing organic ion exchange resins for the presence of nitrate groups.[26] This evaluation chose Raman vibrational spectroscopy over transmission or reflectance Fourier transform infrared (FT-IR) because it was more readily applicable for samples of poor optical quality, such as resin beads that have been radiolytically or chemically degraded. The nitro groups in organic molecules are generally shown in Raman spectra around 1350 cm^{-1}. This work noted that the strong base Dowex 11 resin was a much stronger Raman scatterer than the Reillex HPQ resin. It also noted that the borosilicate glass containment vessels used for characterizing the samples have low optical quality and the resin beads tended to collect in areas of the vials with the poorest optical uniformity and quality. This study suggested utilizing solid-state nuclear magnetic resonance (NMR) spectroscopy to further study the incorporation of nitro groups into a resin's structure.

Based upon Buscher et al.'s work described above, a scoping study was conducted to determine whether Raman and NMR could be used in tandem to quantify nitrate on the resin.[26] The objective was to make Raman standards by converting the chloride-form resin with isotopically labeled sodium nitrate ($Na^{15}NO_3$) and quantify the amount of ^{15}N using solid state NMR. Initial testing was done using Raman spectroscopy on two glass vials of nitrate-form Reillex HPQ resin (Vertellus, Batch 1577100008) – the resin in one sample was crushed into a powder and the resin in the other remained in bead form. SRNL does not have the capability to perform solid state NMR, but contact was made with an organization capable of performing solid state NMR.

2.4.1.4 Resin Digestion with Permanganate

The practice of digesting ion exchange resin with permanganate has been utilized historically as a disposal pathway by the Savannah River Site, specifically at H-Canyon.[6,7] A scoping study was conducted to determine whether a method could be developed to quantify the nitrate content of the resin by digesting it with permanganate and then measuring the ion concentrations in solution using IC.

Oxidation of organic compounds by permanganate can be performed under acidic or alkaline conditions.[27] The amount of oxidation that can result from one permanganate ion varies with solution pH. Flowsheets for digestion of ion exchange resin in acidic and alkaline permanganate mediums have been developed for use in HB-Line.[28] As the acidic permanganate digestion uses nitric acid, that option would not be feasible to measure the concentration of nitrate in solution from the digested resin.

Samples of the chloride, nitrate, and sulfate-form resins were dried to a constant mass. All resin was from Vertellus, Batch 1577100008. The nitrate-form resin was obtained from a batch conversion using the method described above in 2.2. The sulfate-form resin utilized for this work was the batch (S-1) converted with 10 BV of 1 M Na_2SO_4. All samples were stored in a desiccator until ready for use. The samples were crushed into fine powders and approximately 0.1 g were digested in a solution of alkaline potassium permanganate.

This solution was prepared from RICCA 5% w/v potassium permanganate (Lot 2110J32) and Sigma Aldrich 50% w/w sodium hydroxide (Lot MKCW0522). The solution pH was 8.83 at 20.6 °C, with a density of 1.0296 ± 0.001 g/mL at 21.6 °C. A ratio of 4 g potassium permanganate per mL wet nitrate-form resin was utilized for the digestions. This ratio has been shown to completely dissolve Reillex HPQ resin.[28] During the digestions, the solutions were constantly stirred using magnetic stir bars and the temperatures were maintained around 70 °C. The beakers were covered in parafilm to reduce evaporative losses. Each digestion was heated for approximately 6 hours during 2 shifts, for a total of 12 hours. At night, the heat was turned off, but the solutions were stirred.

Once the digestions were complete, the solutions were titrated with 30% w/w hydrogen peroxide (Fisher Chemical, ACS grade, Lot 185719) until no purple color remained in the solution, indicating the destruction of permanganate. Permanganate destruction was necessary because it is a strong oxidizer and would be damaging to the IC columns. Hydrogen peroxide was chosen as it can be utilized in alkaline conditions, and it does not contain any counterions that could affect the IC measurement.[27] After quenching the permanganate, the solution was filtered to separate the manganese oxide solids. The mass of the filtrate recovered, and its density were measured prior to removing samples for IC. The filter cake was analyzed using scanning electron microscopy (SEM), as described more thoroughly below.

2.4.1.5 Thermogravimetric Analysis coupled with Mass Spectrometry (TGA-MS)

Thermogravimetric analysis uses mass changes to determine the initial temperatures of chemical and physical reactions and transitions that occur as a sample is heated.[29] When interfaced with a mass spectrometer, the gases evolving from the sample can be qualitatively identified. Such coupled analysis has previously been used to characterize the decomposition of Reillex HPQ resin as it is heated. Generally, ion exchange resins decompose in stages: moisture loss, functional group decomposition, then polymer decomposition. The work by M. T. Friend et al. identified the onset temperatures for the stages of decomposition for nitric acid treated Reillex HPQ resin and untreated Reillex HPQ resin.[29] The gases that evolved during these experiments were predominantly water, nitric oxide and carbon dioxide. However, this study did not quantify the nitrate concentration on the resin.

Based upon the work by M. T. Friend et al. to characterize Reillex HPQ resin using TGA-MS, a scoping study was conducted to determine whether nitrate concentration on the resin could be quantified using

TGA-MS. Five samples of Reillex HPQ resin (Vertellus, Batch 1577100008) were tested: 2 chloride-form samples, 2 nitrate-form samples, and 1 sample of resin converted to the sulfate form with 10 bed volumes of 1 M Na_2SO_4 (S-1). Each sample was dried to a constant mass. The samples were crushed into a powder and stored in glass vials in a desiccator until ready for analysis. A calibration curve for the TGA-MS was developed using measured masses of sodium nitrate as a standard to relate intensity to the volume of NO gas evolved. The samples were analyzed using TGA-MS to determine the volume of NO gas generated.

2.4.2 Indirect / Qualitative Analysis Methods

The following are indirect or qualitative methods employed during this work to measure nitrate.

2.4.2.1 Ion Selective Electrode

Two methods were utilized to measure the concentration of ions in the effluent: ISE and IC. ISE was used to analyze samples in real-time. This facilitates quick data analysis to plan subsequent experiments and can be done for a fraction of the cost of IC. The ISE measurements were performed using a Thermo Fisher Scientific Orion Versa Star Pro pH/ISE Benchtop Multiparameter Meter with ISE module equipped with temperature probe and chloride ISE (Model: 9617BNWP) or nitrate ISE (Model: 9707BNWP).

The ISE system consists of potentiometric chemical electrodes that include an ion-selective membrane, a reference electrode, and a pH/mV meter. Potential across the membrane is developed when the specific ion-selective membrane comes into contact with a solution containing the free ion of interest. This potential is measured by the pH/mV meter and corresponds to the concentration of the ion in the solution. The activity of the analyte in the solution is significant, which is why an ionic strength adjuster solution (ISA) is often used to ensure accurate measurements. Each probe is highly selective and requires method determination in order to prepare the sample appropriately; the main idea is to adjust the ionic strength of the sample or standard.

The chloride and nitrate measurements for this work utilized a direct calibration technique that involved preparing five standard solutions that cover the expected sample range. National Institute of Standards and Technology (NIST) traceable standard solutions for chloride (1.5 M NaCl) and nitrate (1.5 M $NaNO_3$) were diluted, using a volumetric addition method, to the appropriate concentration range for the calibration curve. Quality control (QC) samples were prepared using NIST standards from different batches to prevent bias. Five calibration points from 0.0002 M to 1.5 M were used to generate a calibration curve. These standard solutions are stored in the same room as the samples to ensure consistent temperature conditions. ISA is typically used for low ionic strength samples, with concentrations less than 0.01 M for monovalent ions and less than 0.001 M for divalent ions. However, for this work, no ISA was used during the preparation of either the standard calibration samples or the actual samples. This is because the feed solutions function as an ISA. To get better detection limits and to be able to use the electrode directly in the effluent in the long term, no additives were used for these samples. Additionally, in the 1 M $NaNO_3$ or 1 M Na_2SO_4 feed solutions, none of the other ions are present in high enough concentrations to cause interference when measuring the desired ion. To ensure the measurement accuracy, the quality control sample is tested after every 6 measurements. If the QC sample measurement is off by more than 10% of the nominal value, the instrument is recalibrated before proceeding.

While no interference is observed with the 1 M $NaNO_3$ or 1 M Na_2SO_4 feed solutions, interference is observed when analyzing samples with a 2 M H_2SO_4 feed solution, which has a low pH and higher sulfate concentration. Therefore, a new calibration method is required to measure nitrate in these conditions. Calibration standards were prepared using sulfuric acid as the solvent to dilute the samples to a specific concentration. Following this, a manual calibration method was performed.

2.4.2.2 Scanning Electron Microscope

A Carl Zeiss Microscopy LLC Sigma VP field emission scanning electron microscope with an Oxford Instruments X-Max 20 silicon drift detector, a type of Electron Dispersive X-ray Spectrometer (EDS), was used to evaluate the crushed resin and the resin digestion filter cake's morphology and chemical composition, respectively. EDS collects characteristic x-rays to identify the atomic species in a sample. In ideal conditions, EDS is capable of detecting up to 0.1 wt% of a given atomic species; EDS data collected here are considered semi-quantitative as specimens with known atomic species were not used when analyzing these spectra. EDS detectors and scale bars are calibrated per manufacturing guidelines. An operating voltage of 20 kV was used for all imaging and x-ray analysis. Images are shown in Figure A-1 and Figure A-2.

2.4.2.3 Ion Chromatography

IC was utilized to measure anion concentrations in the effluent following resin conversion and also to measure concentrations after resin digestion. While ISE was used to measure concentrations in real time during the experiments, it is not a qualified analytical method, so IC was employed to verify sample concentrations afterwards. The IC method is an ISO 17025 certified method.

2.5 Quality Assurance

Requirements for performing reviews of technical reports and the extent of review are established in manual E7 2.60. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2.

3.0 Results and Discussion

3.1 Chloride-Form Resin Washing and Characterization

The density of the effluent as a function of bed volumes DI water wash is shown below in Figure 3-1. The values are shown in Table A-1. The sample at 0 BV was a grab sample that contained the first 10 mL of effluent removed from the column. The subsequent measurements are of grab samples taken at the end of each bed volume collected. After washing the sieved chloride-form resin with 10 BV of DI water, the effluent was colorless, with no visually observable small particulates. While the density of the effluent is equivalent to that of DI water at the same temperature after 1 BV, small particulates are visible until around 10 BV.

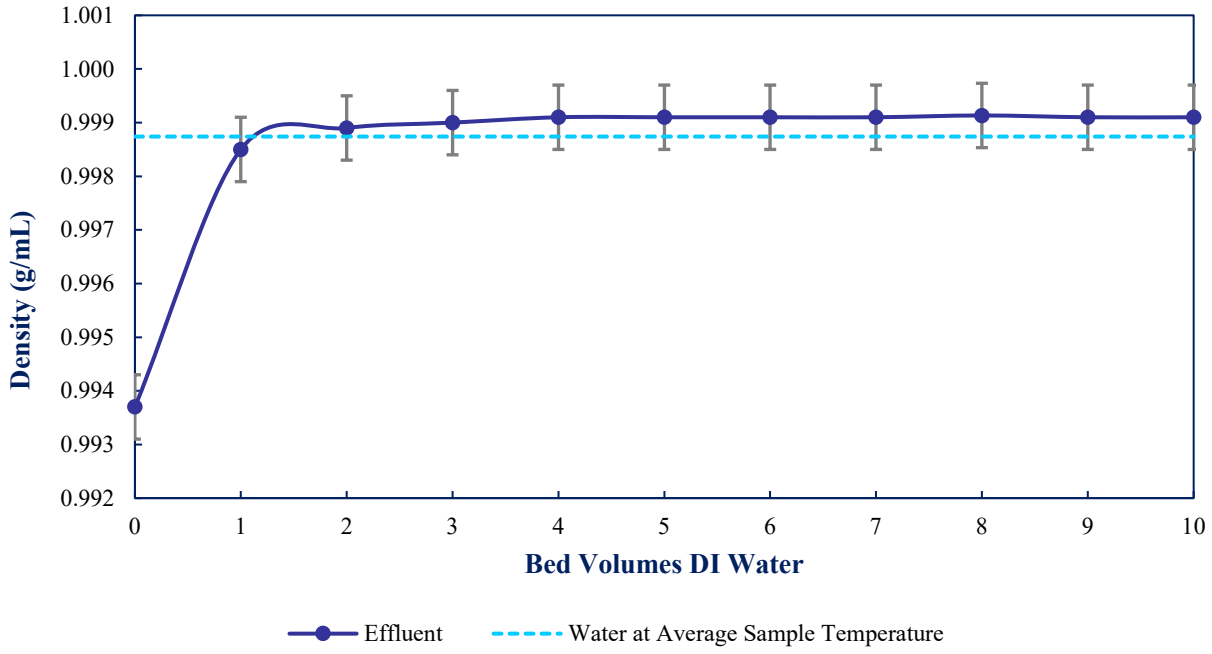

Figure 3-1. Effluent density during resin washing

The total inorganic carbon and total organic carbon (TIC/TOC) results for this work are shown below in Table 3-1. Sample 1 is a grab sample of the first liquid captured and sample 2 is one taken at the end of washing. Steimke et al. analyzed a sample of effluent by TIC/TOC from a process-scale column of chloride-form Reillex HPQ resin; after loading resin into column and rinsing with DI water, it was observed that the water near the bottom of the column had a yellow tint, which prompted this analysis.[11] This liquid was filtered through a 0.2 µm membrane before analysis. The total organic carbon was 143 µg ± 29 µg (2σ), and the total inorganic carbon was 6.40 µg ± 1.28 µg (2σ). The Steimke et al., TIC/TOC results are comparable to the ones obtained during these washing experiments after 10 BV of DI water had been upflowed through the resin bed. No filter was utilized for these experiments.

The results from volatile organic analysis (VOA) and semi-volatile organic analysis SVOA are given below in Table 3-2 and Table 3-3, respectively. The VOA done for the previous study described above measured 0.018 ± 0.007 mg/L (2σ) acetone, 0.083 ± 0.033 mg/L (2σ) 2-butanone, 0.20 ± 0.08 mg/L (2σ) tetrahydrofuran, and < 0.005 ± 0.002 mg/L (2σ) all other analytes.[11] The SVOA measured 1.6 ± 0.6 mg/L (2σ) di-isooctyladipate and < 0.10 ± 0.04 mg/L (2σ) all other analytes. None of the VOA or SVOA analytes observed in the Steimke et al. samples were detectable in the samples analyzed for this work.

Table 3-1. Total organic and inorganic carbon in wash effluent

Sample	Total Carbon (µg C/mL)	Total Organic Carbon (µg C/mL)	Total Inorganic Carbon (µg C/mL)	Two Sigma Uncertainty (%)
1	3633	3601	32.4	14
2	154	129	25.3	14

Table 3-2. VOA of wash effluent

Sample	n-Butyl Ether (mg/L)	All Other VOA Compounds (mg/L)	Detection Limit (mg/L)	Two Sigma Uncertainty (%)
1	0.28	< 0.2	1	20
2	0.26	< 0.2	1	20

Table 3-3. SVOA of wash effluent

Sample	All Other SVOA Compounds (mg/L)	Detection Limit (mg/L)	Two Sigma Uncertainty (%)
1	< 1	1	20
2	< 1	1	20

The specific volume of the washed chloride-form resin dried to a constant mass was determined to be 2.304 ± 0.007 mL/g. The specific volume of the washed chloride-form resin in deionized water on a dry mass basis was 3.39 ± 0.02 mL/g. All specific volumes can be found in Table A-2.

The washed chloride-form resin was analyzed for particle size distribution. This analysis showed that 95.05% of the particles were between 30 and 60 mesh, 4.41% were greater than 30 mesh and 0.54% were less than 60 mesh. A comparison of the particle size distribution of the chloride and nitrate forms is shown below in Figure 3-2.

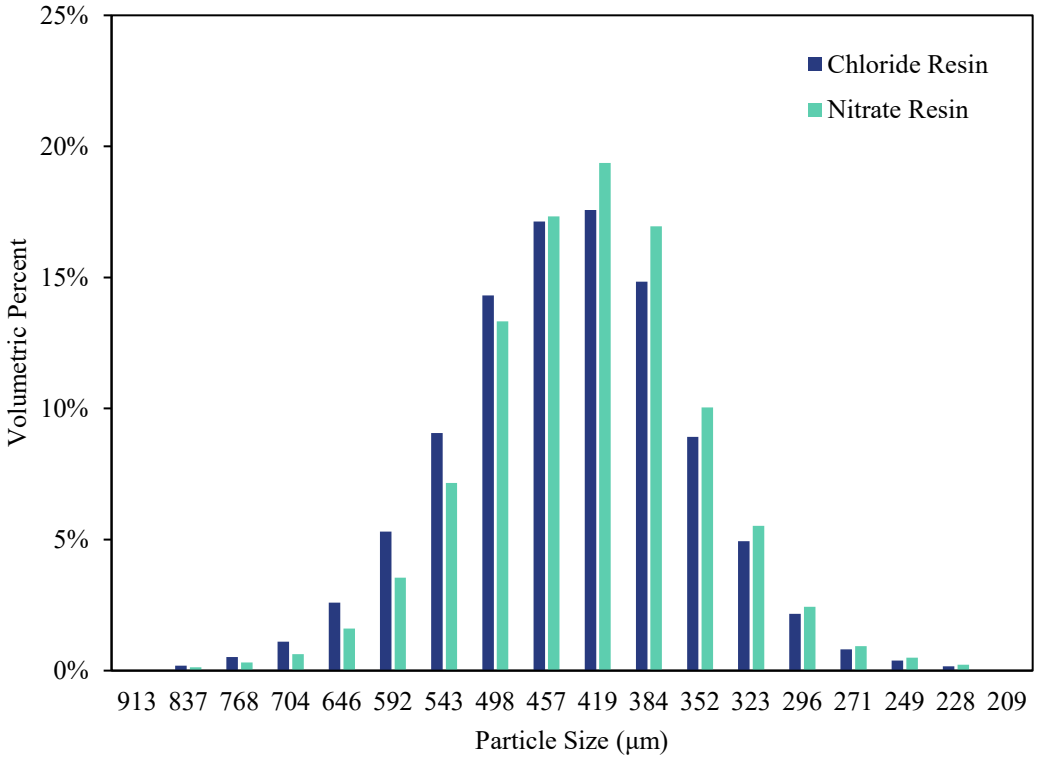

Figure 3-2. Particle size distribution for washed chloride-form resin and nitrate-form resin.

A sample of chloride-form resin that had been sieved and dried to a constant mass (but not washed) was analyzed for chlorine concentration by NAA. The measured chlorine concentration was 172,000 ± 17,200 ppm (2σ). This resin is required to have a strong base exchange capacity of at least 3.6 eq/kg dry resin (chloride form).[11, 30] This is equivalent to a chloride concentration of approximately 128,000 ppm if all active sites are occupied, assuming all chlorine present represents an exchange site as a chloride anion. In practice, the chlorine concentration may exceed this if the exchange capacity is higher than the required minimum. It is noted that there may be a bias in the chlorine content of the unwashed resin.

3.2 Nitrate Conversion

The chloride and nitrate concentrations of the effluent composite cuts, measured by IC, are shown below in Figure 3-3. The error bars represent a 20% (2σ) overall uncertainty. The sample collected for each composite cut represents the average concentration at the volumetric midpoint between bed volumes. The density of the sodium nitrate feed was 1.052 ± 0.001 g/mL. The effluent density as a function of bed volumes feed and DI water wash are shown below in Figure 3-4. The values for concentration and density are available in Table A-3 and Table A-4, respectively.

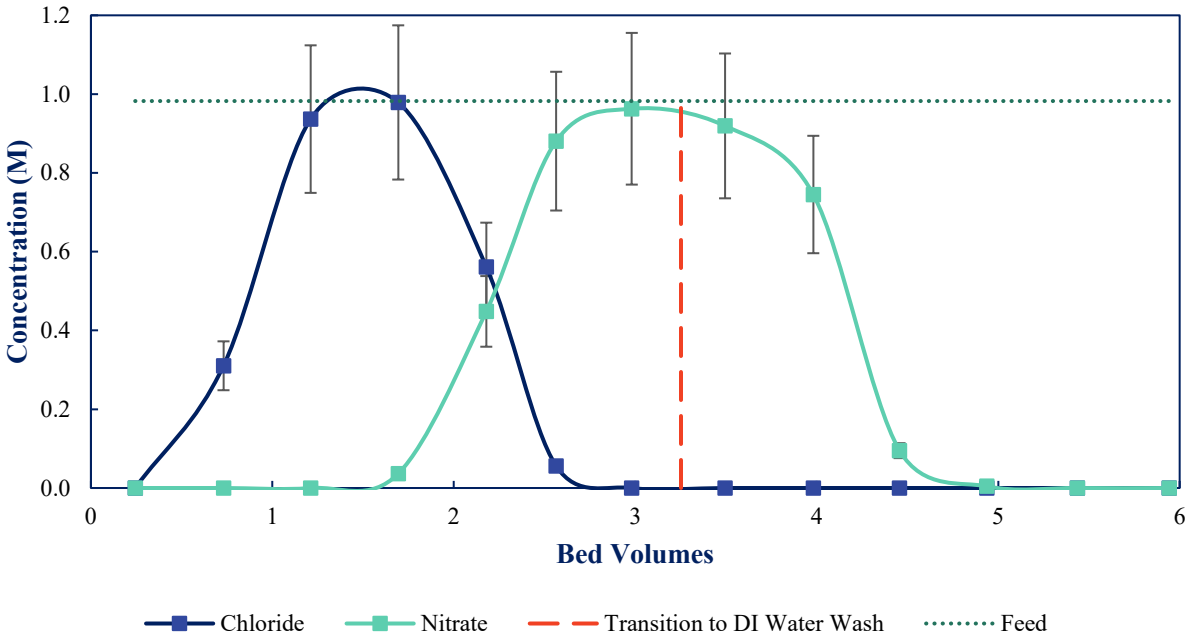

Figure 3-3. N-1 effluent anion concentrations for nitrate conversion and DI water wash measured by IC. Concentrations are shown at the volumetric midpoint of the cut.

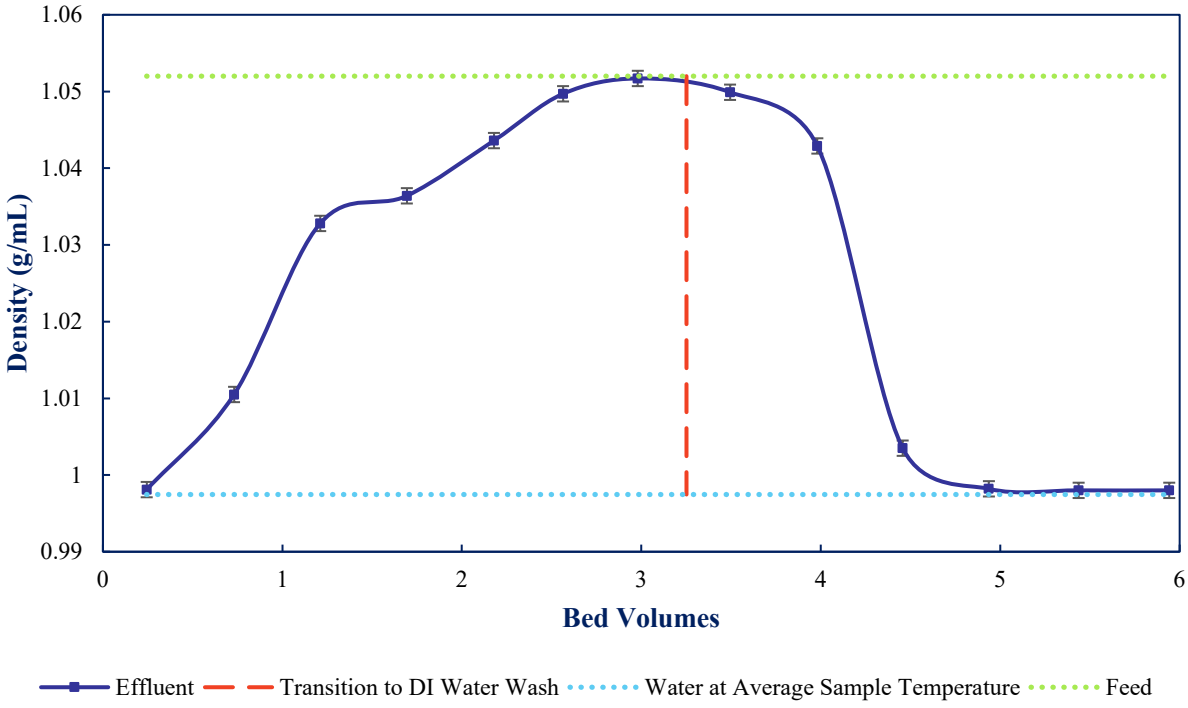

Figure 3-4. N-1 effluent density for nitrate conversion and DI water wash. Densities are shown at the volumetric midpoint of the cut.

The chloride concentration in the effluent rose rapidly and then fell as the nitrate anions displaced the chloride anions. The measured concentration of nitrate in the effluent started increasing as the chloride concentration decreased and rose to approximately equal to the feed concentration as the chloride

concentration approached zero. The densities show a similar trend – as the chloride concentration approaches zero, the density of the effluent approaches the density of the feed solution. During the DI water wash, the density approaches the density of DI water as the nitrate concentration approaches zero.

The selectivity of an ion exchange resin for one ion over another is complex and is based upon a variety of factors such as fixed ion / counterion interactions, ion / solvent interactions, water structure enforced ion pairing, and matrix charge separation.[12] For strong base anion exchange resins, the selectivity sequence for monovalent ions is generally inversely proportional to the free energy of hydration.[31] Nitrate anions have a lower free energy of hydration than chloride anions, which means they are not as strongly solvated by water as chloride anions. In concentrated electrolyte solutions, like the 1 M $NaNO_3$ feed, the direction of the exchange will still largely be determined by the counterion – chloride or nitrate – most in need of solvation.[32] However, the interactions between the counterions and the fixed ionogenic groups on the resin and between the counterions and the coions (sodium) in solution have a greater impact on selectivity as the external solution concentration increases and there is less free water available. If the coion in the external solution is a better complexing agent for the counterion in the resin phase, this can drive the exchange of ions, even if both counterions have similar affinities for the fixed cations in the resin phase. On the other hand, if one counterion has a much stronger affinity for the fixed ionogenic groups in the resin phase, the counterion may favor the resin phase, even if it is the counterion most in need of solvation.

This exchange of counterions requires that diffusion across the Nernst layer, which is a hypothetical film surrounding the resin beads where convective mass transfer diminishes, is electrically coupled.[12] This constraint requires the following conditions to be met:

zero net charge $$\boldsymbol{z_A J_A + z_B J_B = 0} \quad (1)$$

and

electroneutrality $$\boldsymbol{z_A C_A + z_B C_B = C} \quad (2)$$

where z_A and z_B are the electrovalencies of the counterions A and B, J_A and J_B are the fluxes of ion A and B, respectively, across the film layer, C_A and C_B are the concentrations of ions A and B, and C is the total external concentration. The flux can be described by Fick's first law:

flux $$\boldsymbol{J = -D\frac{dC}{dx}} \quad (3)$$

where J is the flux, D is the diffusion coefficient, C is concentration, and x is distance.

Following diffusion through the film layer, coupled transport of the counterions through the resin beads to the exchange sites is driven by the concentration gradient between the interior of the resin bead and the film interface.[12] In addition to steric factors arising from the polymer structure, there is a matrix charge distribution along the diffusion path, which slows diffusion due to the interactions between the counterions and the varying electrostatic force field. The diffusion coefficient in the resin phase is typically one to two orders of magnitude lower than those observed in the bulk solution or the film layer. Once a counterion reaches the fixed ionogenic group, a chemical reaction occurs and the counterions are exchanged. This reaction is usually very fast and is not rate controlling. Film diffusion or diffusion through the resin beads is typically the rate controlling step in ion exchange reactions.

As demonstrated in this experimental work by the rapid and complete exchange of chloride for nitrate, the Reillex HPQ resin has a high selectivity for nitrate relative to chloride for the given process conditions. This is supported by the fact that nitrate has a lower energy of hydration than chloride, driving chloride into

the bulk aqueous phase in exchange for nitrate into the resin phase. After more than 3 bed volumes of 1 M $NaNO_3$ had been fed to the column, the concentration of chloride in the effluent was less than the detection limit of 0.003 M, when measured by IC. These results are consistent with those demonstrated by Steimke et al., which indicated that the chloride concentration starts increasing sharply before one bed volume, quickly reaches a maximum, and then decreases, approaching zero before three bed volumes.[11] During that work, chloride test strips were used and the chloride concentrations during peak elution exceeded the upper limit of the test strips. Therefore, a direct comparison between the chloride concentrations for this work and the previous study cannot be made.

After drying the converted resin to a constant mass, the chlorine concentration on two samples measured by NAA was below the method detection limit (less than 88.8 ppm and 58.4 ppm). This meets SRPPF's requirement for a post-conversion chloride concentration below 250 ppm.[33] These results are similar to those measured by NAA by Steimke et al.[11]

Resin particle size distribution for the nitrate-form resin was assessed (Figure 3-2). This demonstrated that 96.61% of the particles were between 30 and 60 mesh, 2.68% were greater than 30 mesh and 0.71% were less than 60 mesh. This satisfies SRPPF's requirement for nitrate-form resin particle size.[33]

The specific volume of the wet nitrate-form resin was 2.96 ± 0.03 mL/g. This relates the volume of the nitrate-form resin in DI water to the dry nitrate-form resin mass.

3.3 Sulfate Conversion

For the baseline flowsheet test (S-1), the concentration of nitrate in the effluent composite cuts, measured by IC and ISE, is shown in Table A-3. The sample collected for each composite cut represents the average concentration between bed volumes. The density of the sodium sulfate feed was 1.118 ± 0.001 g/mL at 21.8 °C. The wet specific volume on a dry mass basis for the resin converted using this flowsheet was 3.01 ± 0.02 mL/g. However, this value is subject to change based upon flowsheet modifications that affect the fractional conversion. As shown in Table 2-1, process conditions impact resin volume changes.

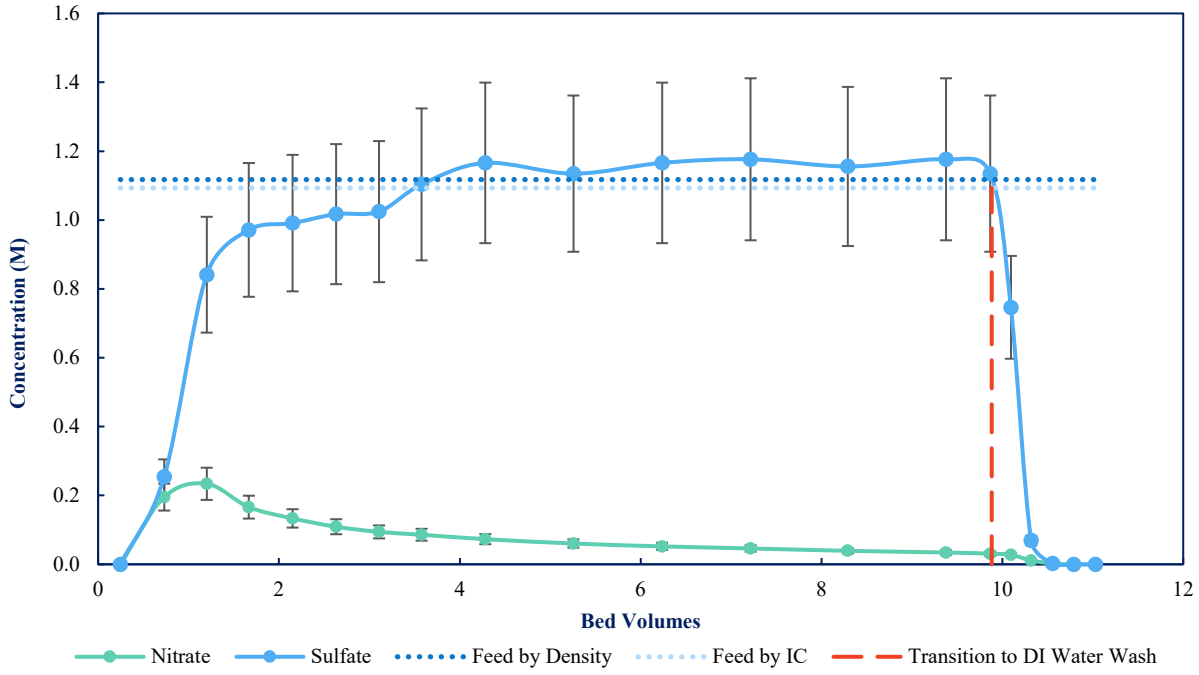

Figure 3-5. Nitrate concentration measured by IC for baseline sulfate conversion flowsheet test (S-1). Concentrations are shown at the volumetric midpoint of the cut.

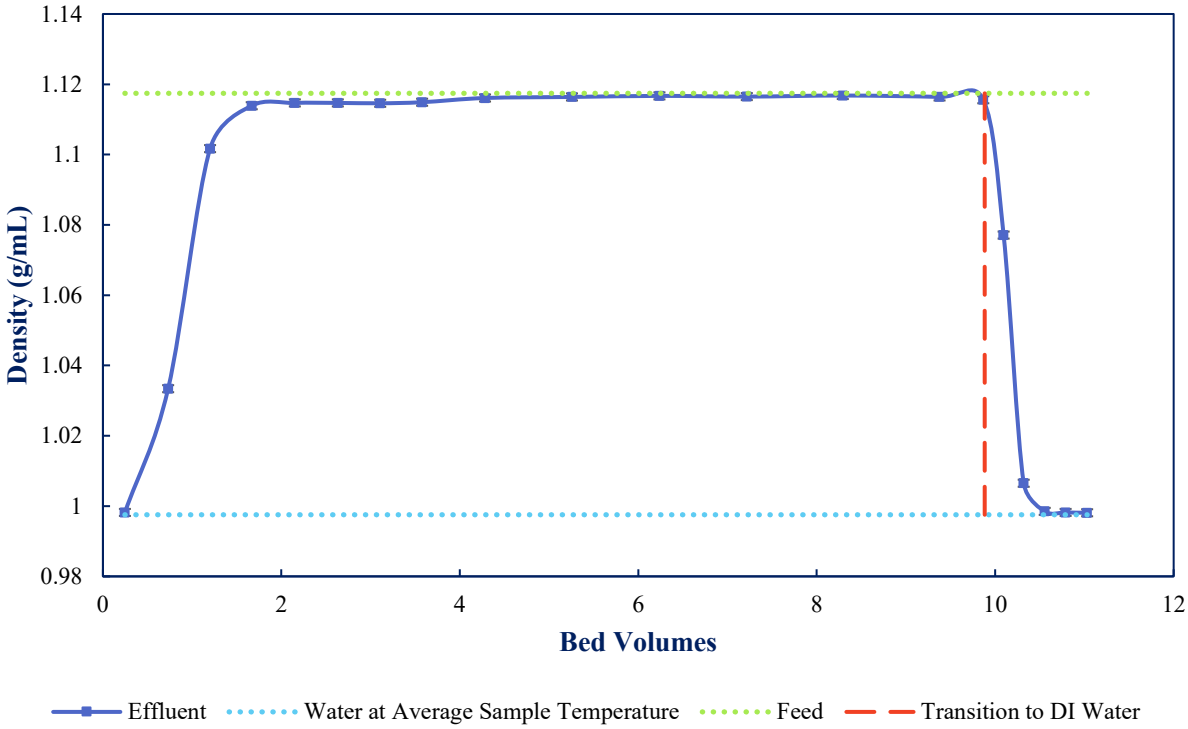

Figure 3-6. Density of effluent compared to density of feed and DI water for S-1. Densities are shown at the volumetric midpoint of the cut.

After contacting the resin with approximately 10 BV of sodium sulfate, nitrate was still measurable in the effluent, indicating that nitrate has not been completely removed from the resin by this point. The density of the effluent is within the 2σ uncertainty of the density of the feed after 4 BV, as shown in Figure 3-6. The nitrate concentration profile in the effluent, measured by IC, is shown in Figure 3-5. These experimental results are inconsistent with Kyser's conclusion based upon his literature review that, "10 BV of 1 M sodium sulfate solution will be more than sufficient to convert the nitrate-form resin to sulfate-form resin."[4] This statement may have been true if it referred to the Dowex 21K resin, which is a strong base polystyrene resin with a trimethyl benzyl ammonium functional group, rather than the Reillex HPQ resin.[12, 13] Sulfate is a divalent anion, which is generally favored by organic resins over monovalent anions, such as nitrate, due to electroselectivity and entropic factors.[31] Specifically, resins with smaller ionogenic pendant groups, like the Dowex 21K, show greater selectivity for sulfate over nitrate.[12] As the degree of crosslinking and/or the size of the ionogenic group increase(s), a resin's selectivity for divalent anions over monovalent ones decreases. These factors inhibit configurational entropy changes and prevent optimal charge sharing by a divalent anion between two fixed ionogenic groups.

Reillex HPQ is a macroporous, highly crosslinked (30% with DVB) resin with both strong and weak base exchange sites.[15] Rather than the ionogenic groups being incorporated into the resin as pendant groups on a benzene ring, they are aromatic, incorporated into the polymer structure as pyridine. The strong base sites are methylated, and the weak base sites are protonated in acidic conditions. This aromatic structure affords the resin superior resistance to attack by nitric acid via electrophilic aromatic substitution and radiation stability.[24] However, this resin's structural characteristics reduce its selectivity for sulfate over nitrate.[17] Furthermore, as only 63% of the total exchange sites are functional in neutral conditions (i.e., non-acidic), such as in 1 M Na_2SO_4, the probability of two exchange sites being close enough together to optimally share the divalent charge of the sulfate anion is reduced.[12, 15]

Similar to the conversion from chloride to nitrate, the effluent concentration of the counterion being displaced rises quickly to a maximum before 2 BV of the neutral salt feed solution has been passed through the column. However, in this case, the effluent concentration of nitrate does not rapidly approach zero – it approaches an asymptote and the rate of change decreases as the feed of 1 M Na_2SO_4 progresses. Additionally, the maximum concentration of the displaced counterion (nitrate in S-1 vs. chloride in N-1) in the effluent is lower for the sulfate conversion compared to the nitrate conversion. The initial rapid rise in the effluent nitrate concentration could be due to faster exchange at sites near the resin surface or at sites that are situated close enough to facilitate charge sharing.[12] Additionally, exchange generally occurs faster when the more mobile counterion (i.e., smaller ion) is the predominant species in the exchanger.[32]

After exchange occurs in such locations, the exchange at other sites deeper within the resin bead could occur more slowly. The varying electric field along the diffusion path may inhibit mass transfer.[12,32] The degree to which this occurs is generally proportional to the size of the diffusing counterion.[32] This effect supports the dependence of the counterion diffusivity on charge and coion concentrations. In this system (S-1), sodium is the coion, nitrate and sulfate are the counterions. The efficiency of coion exclusion from the resin matrix is dependent upon the magnitude of the Donnan potential. In concentrated external solutions, this efficiency decreases. Therefore, coion uptake into the resin matrix could be occurring whereby sodium cations pair with sulfate anions on exchange sites that are not close enough to another site to adequately share the divalent charge, forming monovalent $NaSO_4^-$.[18] However, due to the larger size of this species, the rate of mass transfer may be slowed. Furthermore, the more highly crosslinked a resin is, the lower its ability to swell.[12] The consequence of this is that a rigid and highly crosslinked resin, like Reillex HPQ, is less able to incorporate water to dilute the internal concentration to incorporate coions to facilitate the diffusion of $NaSO_4^-$ into the resin phase.

To determine whether increasing the feed solution volume could result in lower or nondetectable effluent nitrate concentrations at the conclusion of the test, another experiment (S-2) was conducted for the same

set of conditions, but the total bed volumes of feed was doubled. The concentration of anions in the effluent composite cuts are shown in Table A-7 and Figure 3-7. The error bars represent a 20% (2σ) overall uncertainty. The sample collected for each composite cut represents the average concentration between bed volumes. The density of the sodium sulfate feed was 1.118 ± 0.001 g/mL at 21.6 °C. The density of the effluent is shown in Figure 3-8.

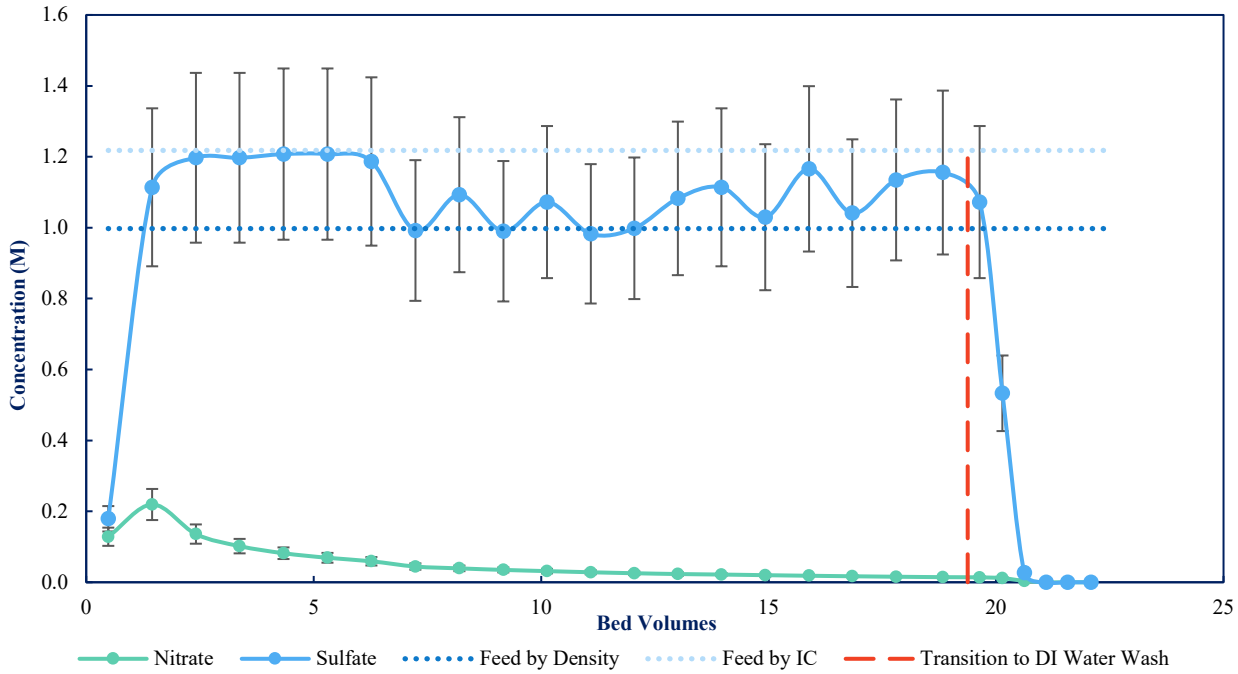

Figure 3-7. Nitrate and sulfate concentrations in effluent measured by IC for 20 BV test (S-2). Concentrations are shown at the volumetric midpoint of the cut.

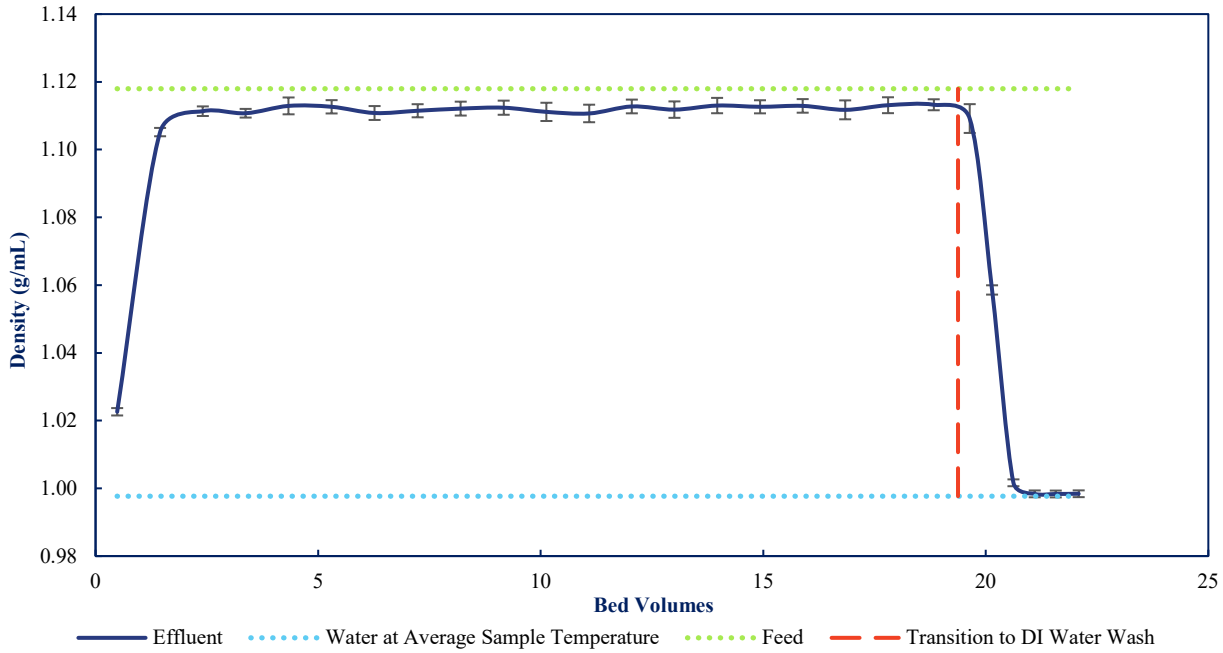

Figure 3-8. Density of effluent compared to density of feed and DI water for S-2. Densities are shown at the volumetric midpoint of the cut.

The nitrate concentration profile in the effluent for this experiment closely mirrors that shown by the data from the first experiment. A comparison of the IC and ISE data for this experiment can be found in Figure 3-9. This demonstrates that the nitrate concentrations measured by ISE follow a similar trend to the concentrations measured by IC, supporting its efficacy as a tool for real-time monitoring. Uncertainty for the ISE method utilized for this work has not yet been quantified. Therefore, only the error bars associated with the IC results are shown in the figure, which represent a 20% (2σ) overall uncertainty. This experiment demonstrates that after nearly 20 BV of 1 M Na_2SO_4 feed, nitrate is still detectable in the effluent by both methods. Therefore, the nitrate is still incorporated in the resin after ~20 BV.

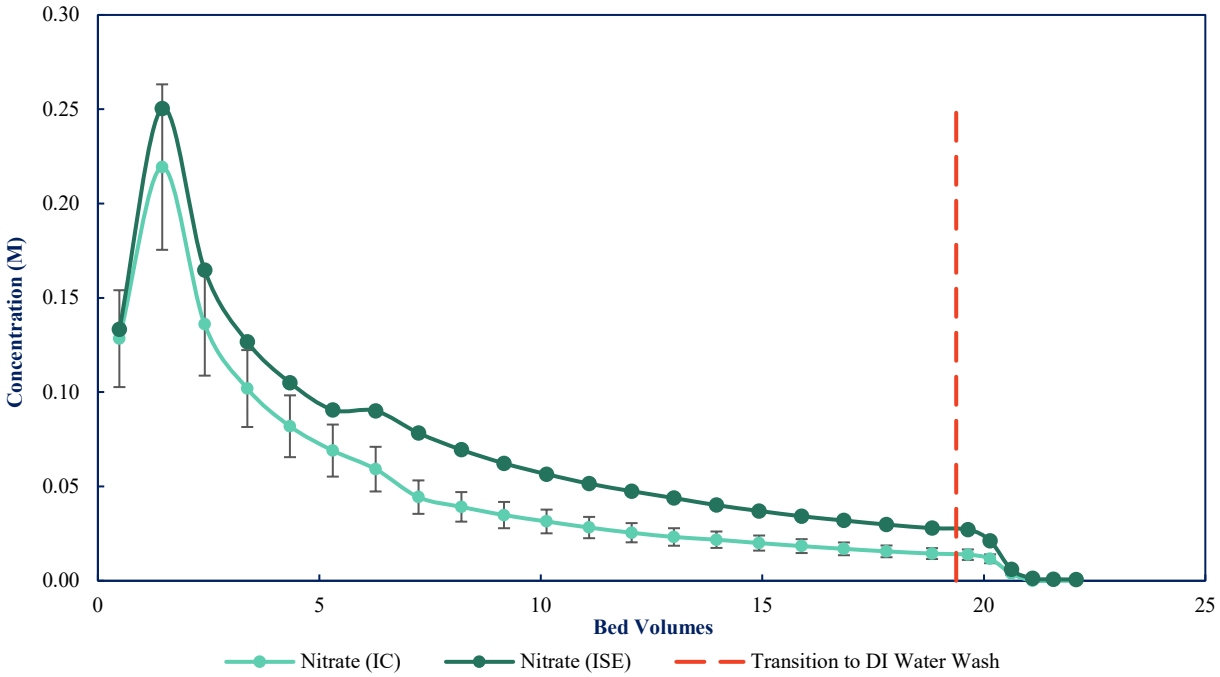

Figure 3-9. Comparison of effluent nitrate concentrations measured by IC and ISE for S-2. Concentrations are shown at the volumetric midpoint of the cut.

Based upon the results of S-2, another experiment was conducted in which the flowrate was reduced by approximately a factor of 4 (S-3). The reason for this was to increase the residence time, to determine whether allowing a longer contact time for mass transfer improved exchange performance. Generally, longer residence times provide sharper separation.[34] The concentration of nitrate in the effluent composite cuts, measured by ISE and IC, are shown in Table A-9. The sample collected for each composite cut represents the average concentration between bed volumes. The density of the sodium sulfate feed was 1.120 ± 0.001 g/mL at 19.3 °C.

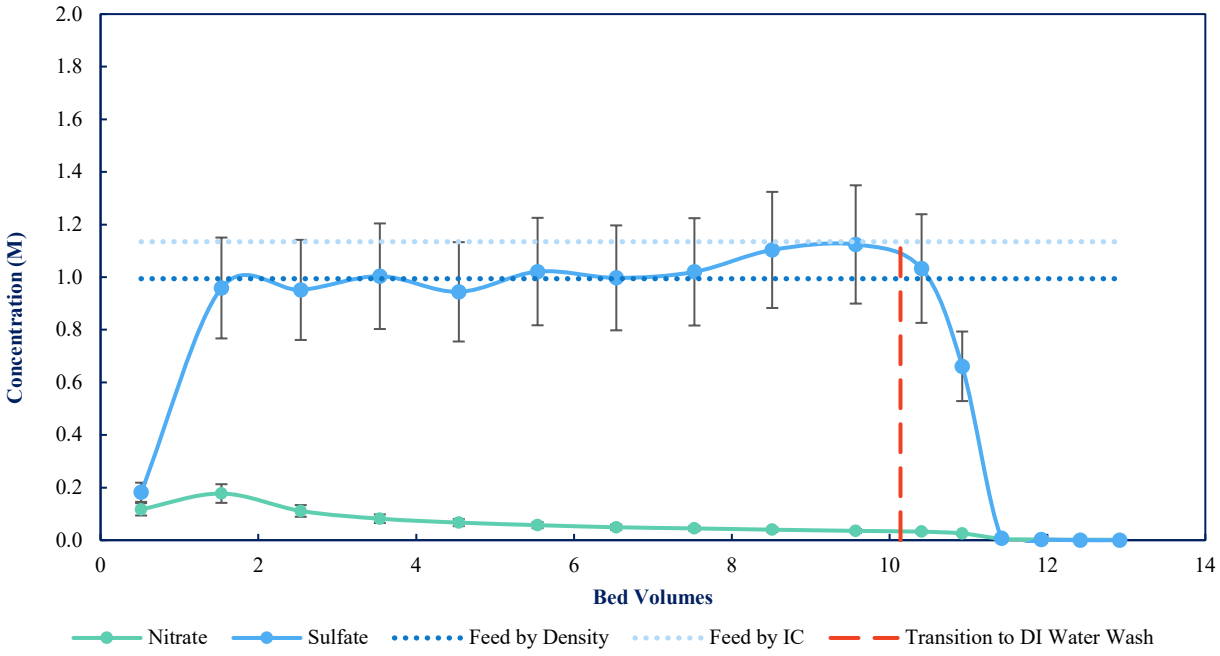

Figure 3-10. Nitrate and sulfate concentrations in effluent measured by IC for reduced flowrate test (S-3). Concentrations are shown at the volumetric midpoint of the cut.

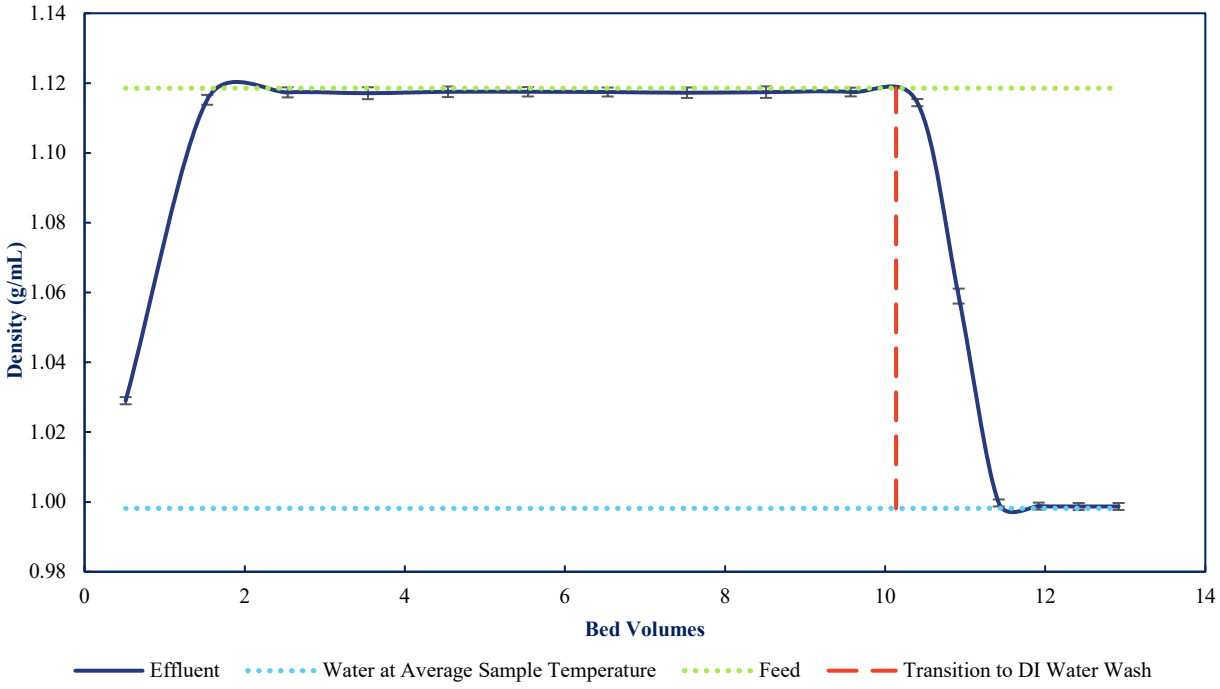

Figure 3-11. Density of effluent compared to density of feed and DI water for S-3. Densities are shown at the volumetric midpoint of the cut.

Again, after approximately 10 BV of 1 M Na_2SO_4 feed, nitrate was still detectable in the effluent. The effluent densities followed a similar trend to the previous two experiments (S-1 and S-2). The concentration profiles from the baseline flowsheet test, the 20-bed volume test, and the reduced flowrate test all show a similar trend – nitrate was still detectable in the effluent at the conclusion of the experiment, indicating that some nitrate is still sorbed to the resin. This is demonstrated in Figure 3-12, which compares the nitrate concentrations measured by ISE. For the baseline flowsheet test (S-1), composite samples were taken every half bed volume for the first 3.5 BV. This was done under the assumption that the nitrate to sulfate conversion would be complete in around 3 bed volumes, similar to the chloride to nitrate conversion and Kyser's expectation. The more frequent composite cuts are likely why the peak shown in the baseline test is slightly higher and shifted to the left compared to the other two, for which composite samples were taken every bed volume.

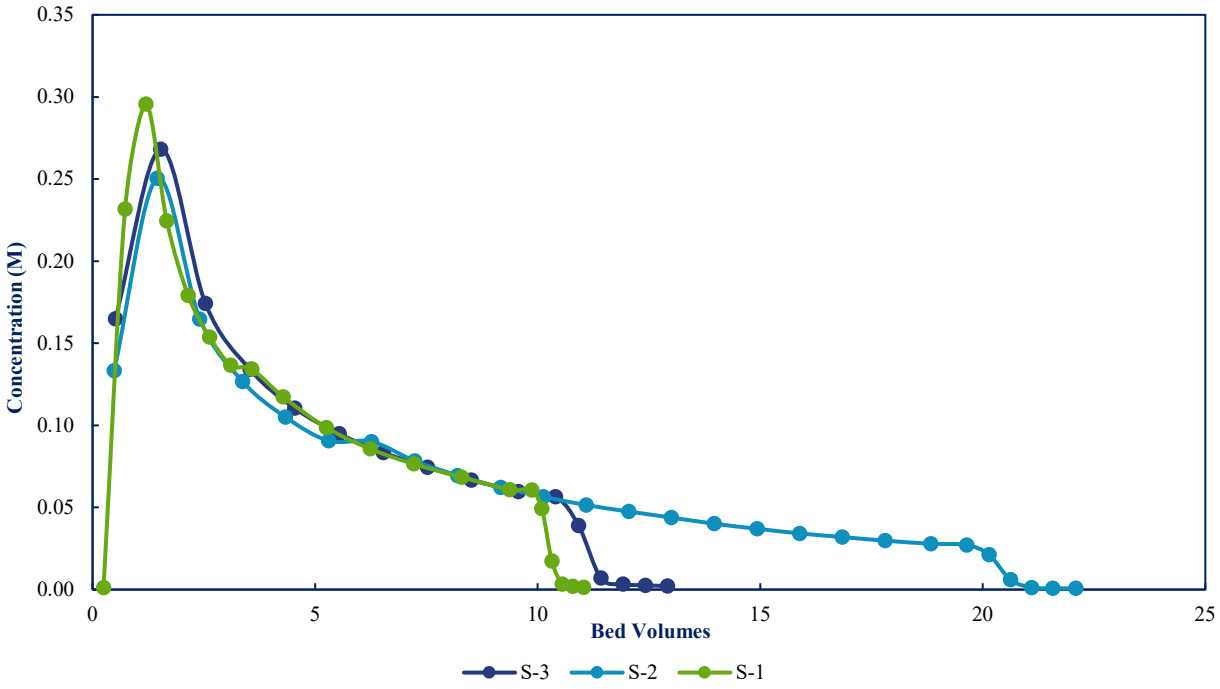

Figure 3-12. Comparison of nitrate concentrations measured by ISE for experiments S-1, S-2, S-3. Concentrations are shown at the volumetric midpoint of the cut.

Based upon the results from the first three tests, a fourth (S-4) was conducted using 2 M H_2SO_4 as the source of sulfate anions. The reason for this was to provide acidic conditions to protonate weak base sites and to provide a higher sulfate concentration. Protonating the weak base sites would create more available exchange sites, increasing the proximity of sites to allow for more favorable charge sharing. The solubility of sodium sulfate decahydrate in water is approximately 1 mol/L at 20 °C.[23] Therefore, using sulfuric acid made it possible to increase the concentration of sulfate to provide a greater driving force for mass transfer of sulfate across the film boundary into the resin.[12]

The anion concentrations in the effluent composite cuts, measured by IC, are shown in Table A-11 and Figure 3-13. The error bars represent a 20% (2σ) overall uncertainty. The sample collected for each composite cut represents the average concentration between bed volumes. The density of the sulfuric acid feed was 1.120 ± 0.001 g/mL at 19.7 °C. The effluent density profile is shown in Figure 3-14.

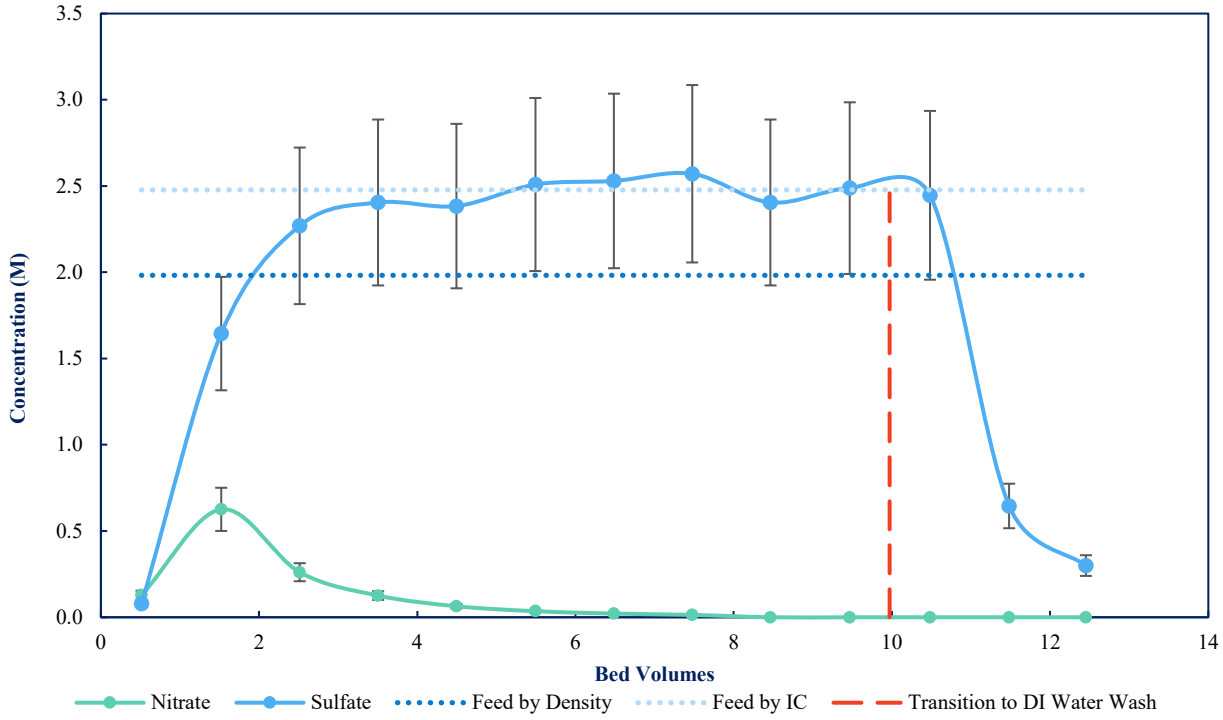

Figure 3-13. Nitrate and sulfate concentrations in effluent measured by IC for sulfuric acid test (S-4). Concentrations are shown at the volumetric midpoint of the cut.

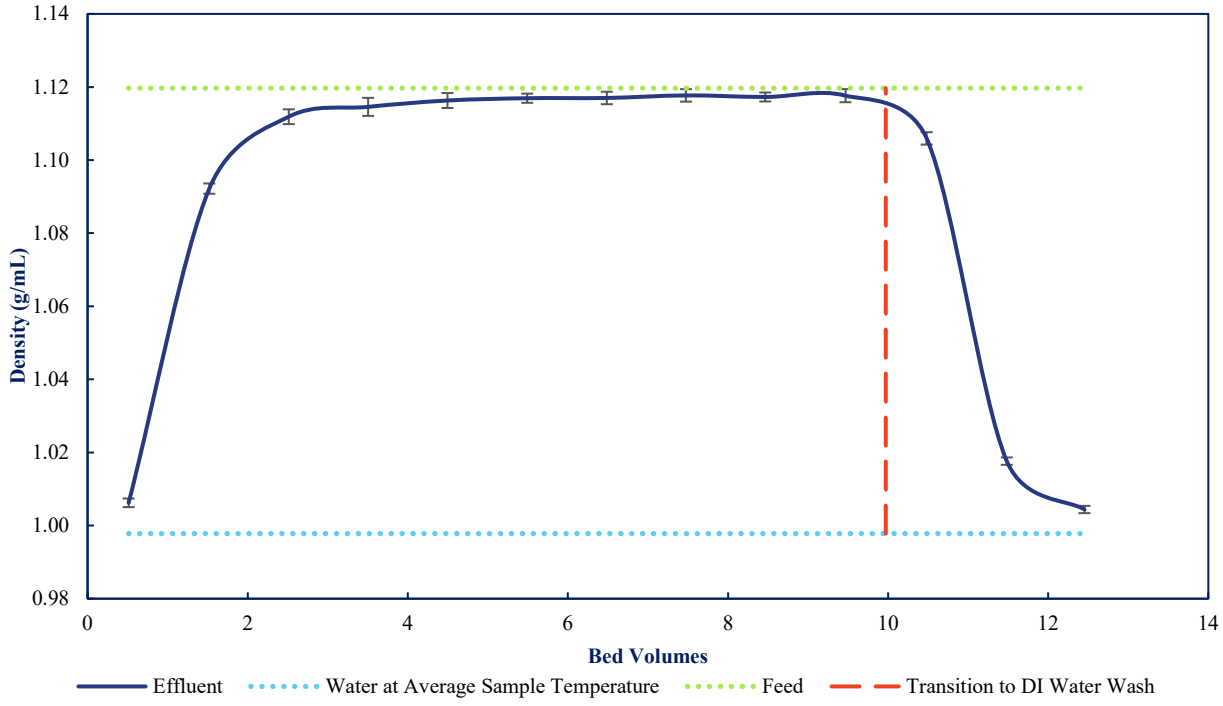

Figure 3-14. Density of effluent compared to density of feed and DI water for S-4. Densities are shown at the volumetric midpoint of the cut.

The results from S-4 demonstrate that 2 M sulfuric acid performs more favorably than 1 M sodium sulfate in terms of converting the nitrate-form resin to the sulfate form and are well supported by literature. Increasing the external electrolyte concentration by using 2 M sulfuric acid reduces the Donnan potential, making the resin more susceptible to intrusion of coions (H^+).[32] As sulfuric acid concentration increases, SO_4^{2-} anions in the bulk solution are increasingly converted to HSO_4^-, which is favored by the resin phase. As divalent sulfate has more stringent hydration requirements than monovalent hydrogen sulfate, the sulfate anions will be held more tightly in the aqueous phase and the hydrogen sulfate should better displace the nitrate counterions. The resin phase has a lower amount of free water available to solvate ions than in the aqueous phase.

Finally, nitrate-form resin that had been irradiated to 100 MRad was converted using the baseline flowsheet (S-5), with a feed of 1 M Na_2SO_4. Exposure to radiation converts strong base sites to weak base sites.[24] Weak base sites are generally less nitrate selective than strong base sites.[18] Prior to the conversion, the resin was stored in 8 M, irradiated nitric acid. Therefore, weak base sites should initially remain protonated.

The concentration of nitrate in the effluent composite cuts, measured by IC, is shown below in Table A-13 and Figure 3-15. The error bars represent a 20% (2σ) overall uncertainty. The sample collected for each composite cut should represent the average concentration between bed volumes. The density of the sodium sulfate feed was 1.110 ± 0.003 g/mL at 21.0°C. The effluent density profile is shown in Figure 3-16. Due to the high initial nitrate concentration of the interstitial liquid, which is irradiated nitric acid, with a nitrate concentration of 11.6 ± 2.3 M (2σ), the scale in Figure 3-15 makes it appear as though the nitrate concentration is zero by the end of the test. However, that is not the case.

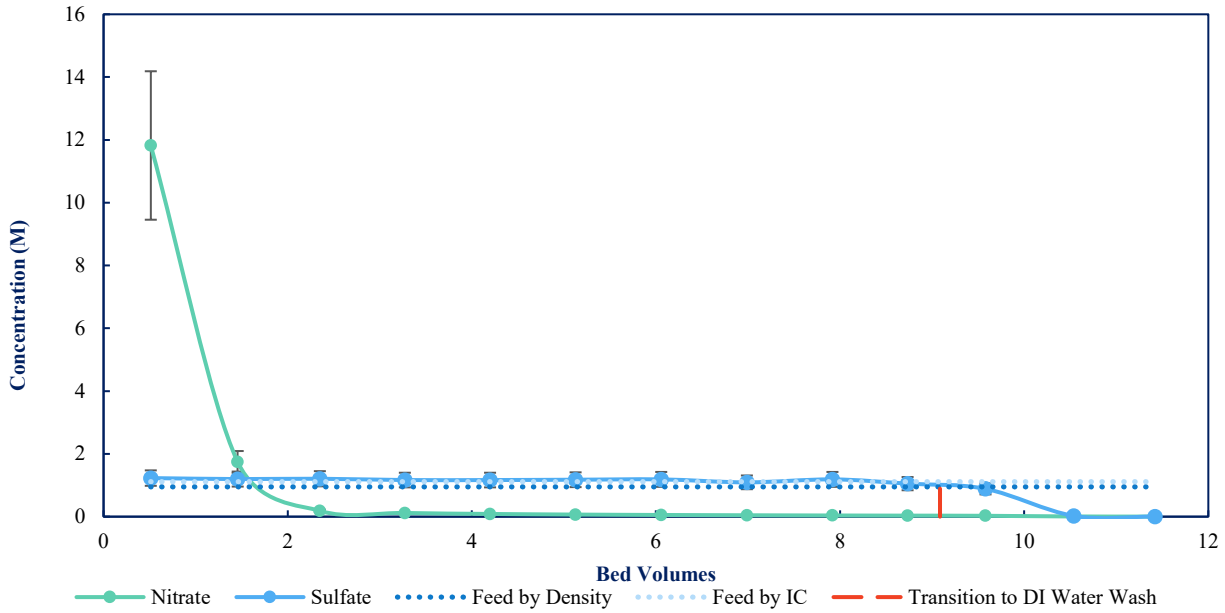

Figure 3-15. Nitrate and sulfate concentrations in effluent measured by IC for irradiated resin test (S-5). Concentrations are shown at the volumetric midpoint of the cut.

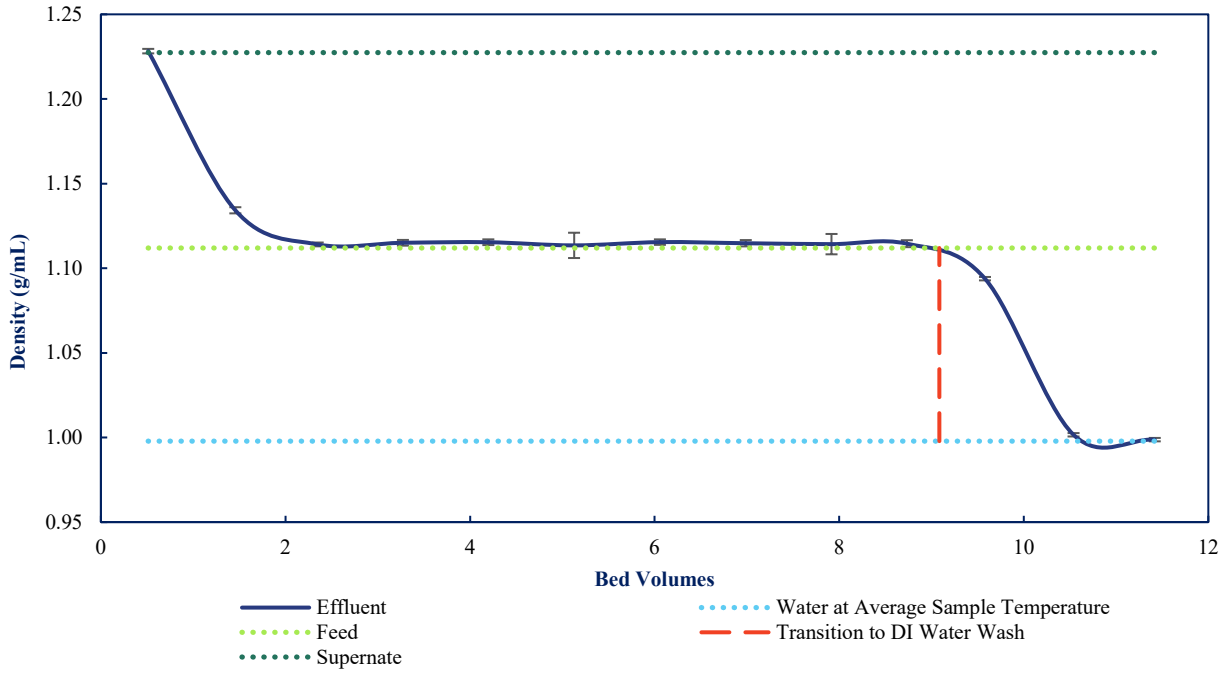

Figure 3-16. Density of effluent compared to density of irradiated nitric acid, feed, and DI water for S-5. Densities are shown at the volumetric midpoint of the cut.

While the initial effluent nitrate concentration is significantly higher for S-5 than for any of the other tests, this is likely due to high concentration of nitrate in the interstitial liquid, rather than a large quantity of nitrate being removed from the resin. The nitrate concentration of the supernate in the column prior to commencing feed was 11.6 ± 2.3 M (2σ). Based upon the effluent density and sulfate concentration, the initial interstitial liquid has been completely displaced by around 2.5 BV. After 2.5 BV, the effluent nitrate concentrations for each of the tests using sodium nitrate as the conversion reagent are within the 2σ uncertainty of each other, as shown below in Figure 3-17. This trend supports the assumption that the initial high nitrate concentration is a result of the irradiated 8 M HNO_3 being removed from the interstitial liquid. If significantly more nitrate had been removed from the irradiated resin within the first 2 BV than was removed during that same time period for any other test, it is unlikely nitrate would be detectable in all subsequent samples and at similar concentrations to tests S-1, S-2, and S-3. While the effluent pH remained acidic and increased for the duration of the conversion, it began decreasing again during the DI water wash. This may be due to the weak base ion exchange sites dissociating when the ion concentrations in the bulk solution decreased as the interstitial liquid was replaced with water. The results from S-5 demonstrate that resin irradiated to 100 MRad and exposed to nitric acid performs similarly to clean resin with respect to the concentration of nitrate measured in the effluent after 10 BV of 1 M Na_2SO_4 feed.

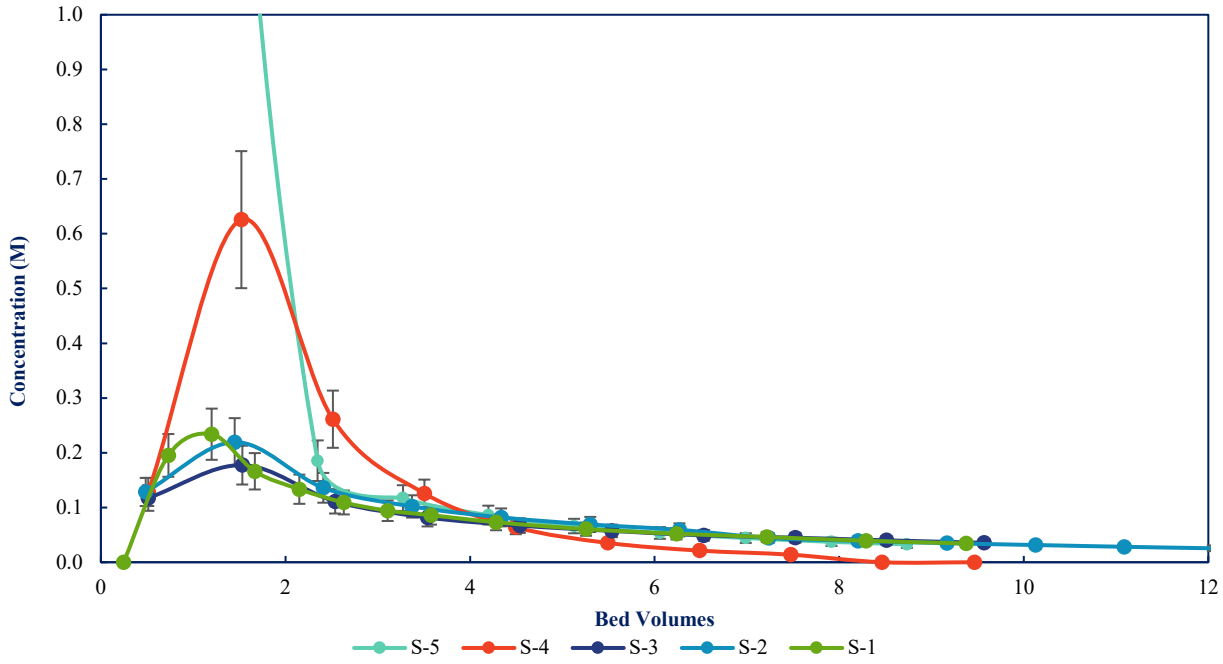

Figure 3-17. Comparison of effluent nitrate concentrations measured by IC. Concentrations are shown at the volumetric midpoint of the cut.

3.4 Nitrate Characterization

A variety of methods were tested to characterize the nitrate concentration both in the effluent during the conversion (indirectly) and on the solid resin (directly) after the conversion was complete.

3.4.1 Direct Methods

The combustion analysis using LECO TC-436 to measure nitrogen concentration resulted in inconsistent results that were nonsensical in the context of the known resin composition and had high overall uncertainty. NAA utilizing prompt gamma activation analysis to measure nitrogen had high uncertainties and required very large quantities of resin and long count times, making this method unfeasible. Utilizing the Raman spectroscopy and NMR in tandem approach was ruled out as the Raman spectroscopy equipment at SRNL could not be optimized to focus on the resin beads. The strong fluorescence background from the beads and the low optical quality of the borosilicate glass containers further complicated this. Solid state NMR using ^{15}N also has challenges and using it in this context would have yielded results that were more qualitative than quantitative. Therefore, none of these methods will be pursued further.

The resin digestion followed by IC and the TGA-MS both showed the most promise in terms of a method that could be used to measure the nitrate concentration on the solid resin. However, more method development is needed to be able to confidently quantify the nitrate concentration remaining on the resin using either method.

3.4.2 Indirect / Qualitative Methods

While SEM and ISE were not methods used to quantify nitrate on the resin, both methods were employed jointly with other analytical tools for this work. SEM served as a qualitative assessment of both the resin digestion filter cake to assess completeness of resin digestion and examining the crushed resin after

conversion for chlorine, nitrogen, and sulfur. While ISE is not a qualified analytical method, it served as a valuable tool, providing real-time results during experiments, without waiting for the IC results. While, high ion concentrations may cause interference for ISE measurements, alternative calibrations can be utilized for more accurate results.

4.0 Conclusions

While more work is needed to quantify the nitrate concentration remaining on the resin after the conversion to the sulfate form, it can be concluded that some nitrate is still sorbed on Reillex HPQ anion exchange resin after up to 20 BV of 1 M Na_2SO_4 fed at the elution linear velocity 2.4 mL/cm^2/min. This is a feed volume twice that of SRPPF's anticipated maximum of up to 10 BV. Additionally, reducing the flowrate to 25% of the baseline flowrate did not affect the removal of nitrate from the resin. Resin irradiated to 100 MRad and exposed to 8 M nitric acid yielded similar results to the other tests done with 1 M Na_2SO_4 as the conversion reagent, with respect to the effluent nitrate concentration after 10 BV of feed. Using 2 M H_2SO_4 as the conversion reagent was the only test that resulted in a nondetectable concentration of nitrate in the effluent; this occurred after 8 BV of feed were transferred to the column.

This work has validated the process for converting the chloride form of Reillex HPQ resin to the nitrate form, using 3 BV of 1 M $NaNO_3$ at a linear velocity of 2.7 mL/cm^2/min. The resin produced by this process, and used for the sulfate conversion experiments, meets SRPPF's specifications: the chloride concentration remaining on the resin after conversion was less than 250 ppm, at least 90% of the nitrate-form resin was between 30 and 60 mesh, with no more than 5% larger than 30 mesh and no more than 5% smaller than 60 mesh.[33]

5.0 Recommendations, Path Forward or Future Work

Additional work is recommended to assess the baseline sulfate conversion flowsheet. There may be value in assessing alternative reagents to optimize the conversion process. These may include, but are not limited to, sulfuric acid, and iodide sources. Burn testing through a partner, such as Southwest Research Institute (SwRI), to determine the combustibility of the converted resin as a function of volume of conversion reagent is also recommended. Furthermore, since the execution of this work, SRPPF has revised their column dimensions so future work will be scaled based upon those values. Continued method development for quantifying the nitrate concentration on solid resin, focusing on resin digestion and TGA-MS, is recommended. Once a method for converting the resin to a form that may be acceptable at WIPP has been identified, the resin drying process should be optimized.

6.0 References

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Appendix A. Tables and Figures

Table A-1. Density of effluent during resin washing

Bed Volumes	Average Density (g/mL)	Average Temperature (°C)	Density of Water at Sample Temperature (g/mL)[35]
0	0.994 ± 0.001	16.0 ± 0.2	0.9988
1	0.998 ± 0.001	16.0 ± 0.2	0.9988
2	0.999 ± 0.001	16.3 ± 0.2	0.9988
3	0.999 ± 0.001	16.4 ± 0.2	0.9988
4	0.999 ± 0.001	16.6 ± 0.2	0.9987
5	0.999 ± 0.001	16.7 ± 0.3	0.9987
6	0.999 ± 0.001	16.8 ± 0.2	0.9987
7	0.999 ± 0.001	17.0 ± 0.2	0.9987
8	0.999 ± 0.001	16.7 ± 0.2	0.9987
9	0.999 ± 0.001	16.9 ± 0.2	0.9987
10	0.999 ± 0.001	17.0 ± 0.2	0.9987

Table A-2. Resin specific volumes

Resin Form	Specific Volume (mL/g)
Dry Chloride	2.30 ± 0.01
Wet Chloride	3.40 ± 0.02
Wet Nitrate	2.96 ± 0.03
Wet Sulfate	3.01 ± 0.02

Table A-3. Anion concentrations in effluent for N-1 measured by ISE. Concentrations are shown for volumetric midpoint of composite cut. IC uncertainty is 20% at 2σ.

Bed Volumes	ISE Chloride Concentration (M)	ISE Nitrate Concentration (M)	IC Chloride Concentration (M)	IC Nitrate Concentration (M)
0.24	0.0005	0.0001	< 0.003	< 0.002
0.73	0.3156	0.0038	0.310	< 0.002
1.21	0.8934	0.0108	0.937	0.000
1.69	0.9361	0.0769	0.979	0.036
2.18	0.4937	0.5653	0.561	0.448
2.56	0.0439	0.9689	0.056	0.881
2.98	0.0017	1.037	< 0.003	0.963
Transition to DI Water Wash				
0.24	0.0000	1.016	< 0.003	0.919
0.73	0.0000	0.8823	< 0.003	0.745
1.20	0.0000	0.1095	< 0.003	0.095
1.69	0.0000	0.0052	< 0.003	0.004
2.19	0.0000	0.0019	< 0.003	< 0.002
2.69	0.0000	0.0014	< 0.003	< 0.002

Table A-4. Effluent density for N-1. Densities are shown for volumetric midpoint of composite cut.

Bed Volumes	Density (g/mL)	Temperature (°C)
0.24	0.998 ± 0.001	22.9 ± 0.2
0.73	1.011 ± 0.001	22.9 ± 0.2
1.21	1.033 ± 0.001	23.1 ± 0.2
1.69	1.036 ± 0.001	23.4 ± 0.2
2.18	1.044 ± 0.001	23.6 ± 0.2
2.56	1.050 ± 0.001	23.5 ± 0.2
2.98	1.052 ± 0.001	23.3 ± 0.2
Transition to DI Water Wash		
0.24	1.050 ± 0.001	23.2 ± 0.2
0.73	1.043 ± 0.001	23.7 ± 0.2
1.20	1.004 ± 0.001	23.4 ± 0.2
1.69	0.998 ± 0.001	23.5 ± 0.2
2.19	0.998 ± 0.001	23.5 ± 0.2
2.69	0.998 ± 0.001	23.5 ± 0.2

Table A-5. Anion concentrations in effluent for S-1. Concentrations are shown for volumetric midpoint of composite cut. IC uncertainty is 20% at 2σ.

Bed Volume	ISE Nitrate Concentration (M)	IC Nitrate Concentration (M)	IC Sulfate Concentration (M)
0.25	0.0011	< 0.002	< 0.001
0.73	0.2318	0.195	0.254
1.20	0.2957	0.234	0.841
1.67	0.2245	0.166	0.971
2.15	0.1790	0.133	0.991
2.63	0.1537	0.109	1.017
3.11	0.1366	0.094	1.024
3.58	0.1342	0.086	1.103
4.28	0.1173	0.073	1.166
5.26	0.0986	0.060	1.135
6.24	0.0857	0.052	1.166
7.22	0.0765	0.046	1.176
8.29	0.0684	0.039	1.156
9.38	0.0609	0.034	1.176
Transition to DI Water Wash			
0.24	0.0607	0.031	1.135
0.70	0.0493	0.028	0.746
1.16	0.0173	0.011	0.069
1.62	0.0033	0.003	0.002
2.09	0.0019	< 0.002	< 0.001
2.56	0.0014	< 0.002	< 0.001

Table A-6. Effluent density for S-1. Densities are shown for volumetric midpoint of composite cut.

Bed Volumes	Density (g/mL)
0.25	0.998 ± 0.001
0.73	1.033 ± 0.001
1.20	1.102 ± 0.001
1.67	1.114 ± 0.001
2.15	1.115 ± 0.001
2.63	1.115 ± 0.001
3.11	1.115 ± 0.001
3.58	1.115 ± 0.001
4.28	1.116 ± 0.001
5.26	1.116 ± 0.001
6.24	1.117 ± 0.001
7.22	1.117 ± 0.001
8.29	1.117 ± 0.001
9.38	1.116 ± 0.001
Transition to DI Water Wash	
0.24	1.116 ± 0.001
0.70	1.077 ± 0.001
1.16	1.007 ± 0.001
1.62	0.999 ± 0.001
2.09	0.998 ± 0.001
2.56	0.998 ± 0.001

Table A-7. Anion concentrations in effluent for S-2. Concentrations are shown for volumetric midpoint of composite cut. IC uncertainty is 20% at 2σ and detection limit is 100 mg/L.

Bed Volumes	ISE Nitrate Concentration (M)	IC Nitrate Concentration (M)	IC Sulfate Concentration (M)
0.49	0.1333	0.1284	0.1791
1.45	0.2504	0.2193	1.1139
2.41	0.1648	0.1360	1.1972
3.37	0.1267	0.1019	1.1972
4.34	0.1050	0.0819	1.2076
5.30	0.0906	0.0690	1.2076
6.27	0.0901	0.0592	1.1868
7.24	0.0784	0.0444	0.9921
8.20	0.0695	0.0392	1.0931
9.17	0.0623	0.0348	0.9900
10.13	0.0565	0.0314	1.0722
11.09	0.0515	0.0282	0.9827
12.05	0.0475	0.0255	0.9983
13.01	0.0439	0.0232	1.0827
13.96	0.0401	0.0218	1.1139
14.93	0.0370	0.0200	1.0296
15.89	0.0342	0.0184	1.1659
16.84	0.0320	0.0169	1.0410
17.80	0.0298	0.0156	1.1347
18.83	0.0279	0.0144	1.1555
Transition to DI Water Wash			
0.26	0.0271	0.0138	1.0722
0.77	0.0212	0.0117	0.5330
1.25	0.0060	0.0038	0.0271
1.72	0.0013	< 0.002	< 0.001
2.20	0.0008	< 0.002	< 0.001
2.71	0.0007	< 0.002	< 0.001

Table A-8. Effluent density for S-2. Densities are shown for volumetric midpoint of composite cut.

Bed Volumes	Density (g/mL)
0.49	1.023 ± 0.001
1.45	1.105 ± 0.001
2.41	1.111 ± 0.001
3.37	1.111 ± 0.001
4.34	1.113 ± 0.002
5.30	1.113 ± 0.002
6.27	1.111 ± 0.002
7.24	1.112 ± 0.002
8.20	1.112 ± 0.002
9.17	1.112 ± 0.002
10.13	1.111 ± 0.003
11.09	1.111 ± 0.003
12.05	1.113 ± 0.002
13.01	1.112 ± 0.002
13.96	1.113 ± 0.002
14.93	1.113 ± 0.002
15.89	1.113 ± 0.002
16.84	1.112 ± 0.003
17.80	1.113 ± 0.002
18.83	1.113 ± 0.002
Transition to DI Water Wash	
0.26	1.109 ± 0.004
0.77	1.059 ± 0.001
1.25	1.002 ± 0.001
1.72	0.998 ± 0.001
2.20	0.998 ± 0.001
2.71	0.998 ± 0.001

Table A-9. Anion concentrations in effluent for S-3. Concentrations are shown for volumetric midpoint of composite cut. IC uncertainty is 20% at 2σ and detection limit is 100 mg/L.

Bed Volumes	ISE Nitrate Concentration (M)	IC Nitrate Concentration (M)	IC Sulfate Concentration (M)
0.51	0.1649	0.1174	0.1822
1.53	0.2682	0.1774	0.9588
2.54	0.1742	0.1113	0.9515
3.54	0.1340	0.0818	1.0035
4.54	0.1105	0.0669	0.9442
5.54	0.0949	0.0573	1.0212
6.53	0.0835	0.0492	0.9973
7.53	0.0745	0.0448	1.0202
8.51	0.0667	0.0400	1.1035
9.57	0.0596	0.0355	1.1243
Transition to DI Water Wash			
0.27	0.0565	0.032	1.033
0.78	0.0390	0.026	0.661
1.28	0.0070	0.005	0.007
1.78	0.0033	0.003	0.003
2.28	0.0026	0.002	< 0.001
2.78	0.0021	0.002	< 0.001

Table A-10. Effluent density for S-3. Densities are shown for volumetric midpoint of composite cut.

Bed Volumes	Density (g/mL)
0.51	1.029± 0.001
1.53	1.115± 0.001
2.54	1.117± 0.001
3.54	1.117± 0.002
4.54	1.118± 0.002
5.54	1.118± 0.001
6.53	1.117± 0.001
7.53	1.117± 0.002
8.51	1.117± 0.002
9.57	1.117± 0.001
Transition to DI Water Wash	
0.27	1.114± 0.001
0.78	1.059± 0.002
1.28	1.000± 0.001
1.78	0.999± 0.001
2.28	0.999± 0.001
2.78	0.999± 0.001

Table A-11. Anion concentrations in effluent for S-4. Concentrations are shown for volumetric midpoint of composite cut. IC uncertainty is 20% at 2σ and detection limit is 100 mg/L.

Bed Volumes	IC Nitrate Concentration (M)	IC Sulfate Concentration (M)	pH
0.51	0.128	0.078	
1.52	0.626	1.645	
2.51	0.261	2.269	
3.50	0.126	2.405	
4.50	0.064	2.384	
5.49	0.035	2.509	
6.49	0.021	2.530	
7.48	0.014	2.571	
8.47	< 0.002	2.405	
9.47	< 0.002	2.488	
Transition to DI Water Wash			
0.51	< 0.002	2.4464	0.18
1.51	< 0.002	0.6454	0.83
2.48	< 0.002	0.2998	1.13

Table A-12. Effluent density for S-4. Densities are shown for volumetric midpoint of composite cut.

Bed Volumes	Density (g/mL)
0.51	1.006 ± 0.001
1.52	1.092 ± 0.001
2.51	1.112 ± 0.002
3.50	1.115 ± 0.002
4.50	1.116 ± 0.002
5.49	1.117 ± 0.001
6.49	1.117 ± 0.002
7.48	1.118 ± 0.002
8.47	1.117 ± 0.001
9.47	1.118 ± 0.002
Transition to DI Water Wash	
0.51	1.106 ± 0.002
1.51	1.018 ± 0.001
2.48	1.004 ± 0.001

Table A-13. Anion concentrations in effluent for S-5. Concentrations are shown for volumetric midpoint of composite cut. IC uncertainty is 20% at 2σ and detection limit is 100 mg/L.

Bed Volumes	IC Nitrate Concentration (M)	IC Sulfate Concentration (M)	pH
0.51	11.8216	1.2284	-0.42
1.46	1.7418	1.1972	0.50
2.35	0.1855	1.2076	2.30
3.27	0.1172	1.1659	2.68
4.20	0.0861	1.1659	2.95
5.13	0.0661	1.1763	3.04
6.06	0.0535	1.1868	3.13
6.99	0.0442	1.0931	3.26
7.92	0.0373	1.1868	3.31
8.73	0.0327	1.0514	3.34
Transition to DI Water Wash			
9.58	0.0274	0.8859	3.38
10.54	0.0060	0.0231	2.76
11.42	0.0023	0.0019	2.48

Table A-14. Effluent density for S-5. Densities are shown for volumetric midpoint of composite cut.

Bed Volumes	Density (g/mL)
0.52	1.228 ± 0.001
1.47	1.134 ± 0.002
2.36	1.114 ± 0.001
3.29	1.115 ± 0.002
4.22	1.115 ± 0.002
5.16	1.114 ± 0.007
6.09	1.115 ± 0.002
7.03	1.115 ± 0.002
7.96	1.114 ± 0.006
8.78	1.115 ± 0.002
Transition to DI Water Wash	
0.50	1.094 ± 0.001
1.46	1.002 ± 0.001
2.35	0.999 ± 0.001

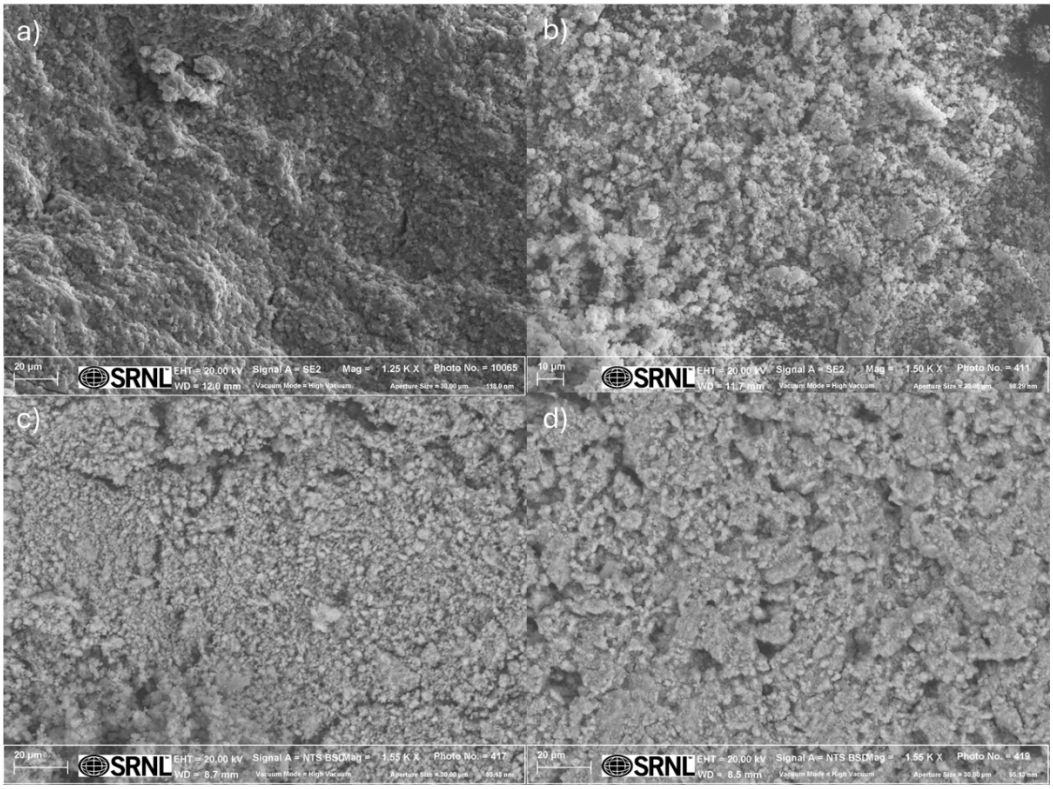

Figure A-1: SEM images of potassium permanganate digestion media a) without resin, b) chloride-form, c) nitrate form, d) sulfate form showing minimal differences in the filter cake.

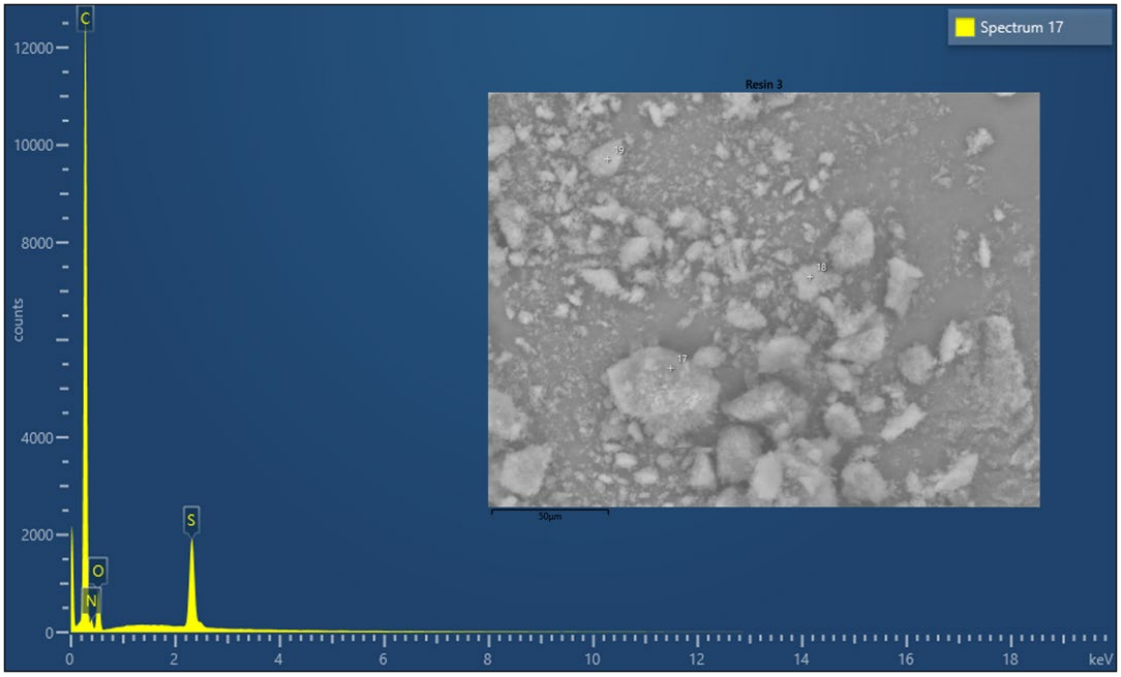

Figure A-2: SEM image of ground sulfate-form resin on carbon tape with corresponding EDS image showing S and N content on the converted resin.