We put science to work.™

Savannah River
National Laboratory®

OPERATED BY SAVANNAH RIVER NUCLEAR SOLUTIONS

A U.S. DEPARTMENT OF ENERGY NATIONAL LABORATORY • SAVANNAH RIVER SITE • AIKEN, SC

Flowsheet for Conversion of Anion Resin from Nitrate to Sulfate form for Disposal

E. A. Kyser

September 2021

SRNL-STI-2021-00106, Revision 0

SRNL.DOE.GOV

DISCLAIMER

Printed in the United States of America

Prepared for
U.S. Department of Energy

SRNL-STI-2021-00106
Revision 0

Keywords: *Anion Exchange Resin, Waste Disposal*

Retention: *Permanent*

Flowsheet for Conversion of Anion Resin from Nitrate to Sulfate Form for Disposal

E. A. Kyser

September 2021

Savannah River National Laboratory is operated by
Battelle Savannah River Alliance for the U.S. Department
of Energy under Contract No. 89303321CEM000080.

Savannah River National Laboratory®

REVIEWS AND APPROVALS

AUTHORS:

Original copy digitally signed Sept 2021.

E. A. Kyser, Actinide and Separations Science Date

TECHNICAL REVIEW:

Harris Eldridge, Actinide and Separations Science, Reviewed per E7 2.60 Date

APPROVAL:

J. M. Duffey, Manager - Actinide and Separations Science Date

T. M. Adams, Manager - Plutonium Technology Date

J. B. Schaade, Manager - SRPPF Project Engineering Date

EXECUTIVE SUMMARY

The shipment of nitrate form anion resin to WIPP is currently prohibited due to concerns about possible chemical reactions between the organic resin and the nitrate oxidizer. Conversion of spent nitrate form resin in the anion process equipment will generate a waste form that can be accepted by WIPP. This operation was previously performed in FB-Line and by SRNL. This report reviews the SRS literature on conversion of anion resin between ionic forms and compares those conditions with the ion exchange literature.

A flowsheet that uses 10 bed volumes (BV) of 1 M sodium sulfate solution to convert the resin from the nitrate form to the sulfate form is recommended for use in the SRPPF. This flowsheet uses a large excess of sodium sulfate solution to quantitatively remove the nitrate. Further optimization of the conversion operation is possible but would require development of an acceptable technique to quantify the residual nitrate at a low level to establish the effectiveness of the conversion.

TABLE OF CONTENTS

LIST OF TABLES / FIGURES

LIST OF ABBREVIATIONS

BV	Bed Volume, the apparent space that the resin in a column occupies including the interstitial space between resin beads
eq	Equivalent – in the context of ion exchange refers to one mole of electrons in the reaction
g	Gram, unit of mass
L	Liter, unit of volume
M	Molarity (moles/liter), unit of concentration
min	Minute
N	Normality (equivalents/liter), unit of concentration
rad	Radiation absorbed dose = 0.01 J/kg, unit of dose
SRNL	Savannah River National Laboratory
SRPPF	Savannah River Plutonium Processing Facility
wt %	Weight percent
WIPP	Waste Isolation Pilot Plant

1.0 Introduction

Nitrate form anion exchange resins are specifically prohibited for disposal in TRU waste. At some DOE sites, spent resin was mixed with cement to immobilize the resin in a monolith with varying success. At SRS starting in the 1980s, spent anion resin has generally been converted to a more chemically stable form or it was digested with permanganate and transferred as a slurry to the HLW tank farm. In the early years of the site it is reported that over 20 metric tons of organic resin were transferred directly to the tank farm without any attempt to digest it.[1,2] It appears that in the future conversion to a stable sulfate form could well be the favored disposal path for spent nitrate-form anion resin. This report will document the site history of converting between ionic forms (nitrate to sulfate) and will document process flowsheet conditions for performing that conversion.

2.0 Literature Review

Resin Capacity: Resin exchange capacity is typically expressed in terms of its capacity for exchangeable chloride either on a volume basis or a mass basis. Marsh reported a chloride exchange capacity[3] of 0.85 meq/mL for Reillex HPQ based on information from the manufacturer. Note that manufacturer's exchange capacity values are normally reported as minimum exchange capacity values and change with time based on usage. Marsh also reported LANL test results[4,5] as high as 3.78 meq Cl/g for samples of Reillex HPQ in the early 1990s (which is 1.33 meq/mL[6]). Marsh similarly reported capacities of polystyrene-based anion resin (including some of those in use at SRS) of 1.20 to 1.28 meq/mL. However, in the 1996-7 timeframe, changes in the manufacturing process reportedly[7] increased the anion exchange site yield of the Reillex HPQ resin by ~20%. New Reillex HPQ resin contained 40% weak base sites[4] whereas exposure to 485 Mrad (alpha) increased the weak base sites to 60% of the total while at the same time reducing the total exchange sites by only 3.5%. All resins tested showed the trend of conversion of strong base sites to weak base sites with increasing radiation dose, but Reillex HPQ both started with a higher fraction of weak base sites and retained the total exchange sites better than the quaternary amine resins with which it was compared.[4] The retention of the total exchange sites is thought to be due to the relative stability of the pyridine ring as compared to the relative ease of cleaving the quaternary amine functional group. Both strong and weak base exchange sites retain nitrate anions and can be converted to the sulfate form with sodium sulfate solution. Exchange capacity measurements on the recent lots of Reillex HPQ have not been performed but can be assumed to be on the high side of the previous reports.

History of Resin Conversion at SRS: In the early 1980s SRS personnel decided to cease the generation of additional spent nitrate-form anion resin and decided that resin should be converted to a more chemically stable form before storage as radioactive waste (unless digested with permanganate prior to discharge to

---

[1] D. D. Walker, "Organic Compounds in Savannah River Site High-Level Waste", WSRC-TR-2002-00392, Westinghouse Savannah River Company, Aiken, SC (September 30, 2002).

[2] C. H. Keilers, Jr, "Flammable Gas Generation Mechanisms for High Level Liquid Waste Facilities", X-ESR-G-00062, Rev. 1, Savannah River Remediation, Aiken SC (October 25, 2017).

[3] S. F. Marsh, "Evaluation of a New Macroporous Polyvinylpyridine Resin for Processing Plutonium Using Nitrate Anion Exchange", LA-11490, Los Alamos National Laboratory, Los Alamos, NM (April 1989).

[4] S. F. Marsh, "The Effects of In Situ Alpha-Particle Irradiations on Six Strong Base Anion Exchange Resins", LA-12055, Los Alamos National Laboratory, Los Alamos, NM (April,1991).

[5] S. F. Marsh, "The Effects of Ionizing Radiation on Reillex™ HPQ, A New Macroporous Polyvinylpyridine Resin and on Four Conventional Polystyrene Anion Exchange Resins", LA-11912, Los Alamos National Laboratory, Los Alamos, NM (November 1990).

[6] Marsh reported capacity on a mass basis with a measured density of 2.84 mL/dry resin. Resin density will be highly dependent on the drying technique.

[7] E. A. Kyser, "Plutonium Loading onto Reillex HPQ Anion Exchange Resin", WSRC-TR-2000-00372, Westinghouse Savannah River Company, Aiken, SC (Sept 26, 2000).

the HLW tank farm).[8] Holcomb issued several memos[9,10,11] describing the development of a sulfate conversion process. These memos were developed in consultation with personnel from Dow Chemical Company for Dowex 21K resin in use in FB-Line at that time. Ample references are available in the literature which describe similar conversion processes. A common factor is the use of a neutral salt solution containing an excess of the desired anion and passing that solution through the resin bed while the non-desired anion is exchanged with the desired anion and flushed from the bed. The use of non-neutral solutions would likely cause thermal effects by acid-base reactions which could pose a safety hazard. The historical flowsheet used in the SRNL has been to rinse all acidic solution from the resin bed with water and then to pass 10 bed volumes (BV) of 1 M neutral salt solution through the resin bed to convert the resin from one ionic form to another.[12] The general flowsheet has been used to convert as-received chloride form anion resin to nitrate form anion resin and then to convert used nitrate form anion resin to sulfate form anion resin for disposal. The recent chloride-to-nitrate conversion flowsheet for Reillex HPQ resin for HB-Line was documented and found that essentially all of the chloride removal occurred in the initial 3 BV (see Figure 1).[13] Generally, these conversion flowsheets involve small temperature changes (assuming pH neutral solutions are utilized) and modest resin volume changes. In 1982, when the initial JB-Line sulfate conversion was performed on Dowex 21K resin[10,11,14] no temperature increase was observed when the resin columns were converted, but when the columns were opened to manually remove the resin, resin pushed out the opening suggesting a volume change of up to 20%. Holcomb investigated the observed volume change and attributed most of this effect to radiolytic change in the resin structure rather than the sulfate conversion. Reillex HPQ resin should swell less than Dowex 21K resin (used in JB-Line) due to its resistance to radiation damage from the polyvinyl pyridine in the structure, but no data are available. Marsh investigated resin volume changes with alpha dose for both Reillex HPQ and various quaternary amine resins.[4] He observed resin mass changes on the order of 10% with alpha radiation dose up to 1000 Mrad for the quaternary amine resins compared with only 1% for Reillex HPQ resin with comparable alpha radiation dose. However, the specific volume of Reillex HPQ resin (in 7 M HNO_3) did increase by ~16% with alpha radiation dose up to 1000 Mrad. Similar specific volume changes were observed for all the resins tested. Reillex HPQ uses a divinylbenzene cross-linkage just like the polystyrene resins that were tested. The loss of cross-linkage is likely the cause of increase in specific volume with alpha radiation dose similar to that observed in the FB-Line report by Holcomb.[11]

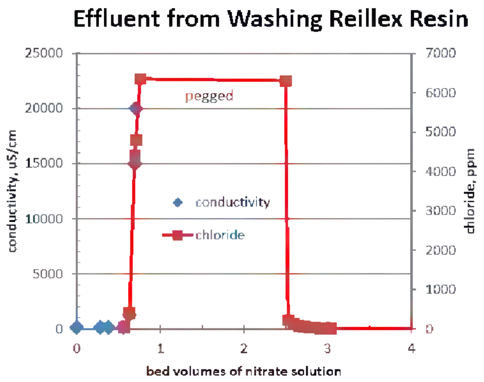

Figure 1. Chloride Concentration of Effluent during Steimke Conversion of Reillex HPO resin.[13]

Prior to the JB-Line resin conversion, a "no-load" elution was performed which removed 42 g and 8 g Pu respectively from the two columns.[14] After the sulfate conversion step, the converted resin was analyzed at less than 10 g Pu for each column.[14] Little can be concluded from the literature about the effect of a sulfate conversion on residual Pu, but conventional extended elution steps should be utilized to remove all Pu that is practical prior to the sulfate conversion process step. Holcomb's flowsheet only used approximately twice the amount of sulfate as was needed based on the stated theoretical capacity of the

---

[8] R. L Hooker, "Storage of Ion Exchange Resin on the Transuranic Waste Storage Pads", memo to J. T. Granaghan, DPST-81-582, Savannah River Laboratory, August 11, 1981.

[9] H. P. Holcomb, "Disposal of Nitrate Form Anion Exchange Resin from JB-Line", memo to E.J. Lukosius, DPSPU-81-272-133, Savannah River Plant, September 16, 1981.

[10] H. P. Holcomb, "Initial Process Conversion of JB-Line Anion Exchange Resin to Sulfate Form: Conversion Efficiency and Resin Volume Change", memo to C.W. Jenkins, DPSPU-82-272-025, Savannah River Plant, March 5, 1982.

[11] H. P. Holcomb, "Expansion of Degraded Dowex 21K Anion Exchange Resin on Conversion From Nitrate to Sulfate Form", memo to E.J. Lukosius, C.W. Jenkins, DPSPU-82-272-075, Savannah River Plant, June 18, 1982.

[12] A. Scott, personnel communication of standard laboratory practices, ~1990.

[13] J. L. Steimke, M. R. Williams, T. J. Steeper, R. A. Leishear, "Nitrate Conversion of HB-Line Reillex™ HPQ Resin", SRNL-STI-2012-00160, May 2012.

[14] DPSPU-82-60-1, Separation Technology Monthly Report, pg. 12, January 1982.

resin (44.8 equivalents sulfate per up to 20 L resin). Samples of the production resin were analyzed for completeness of conversion and Holcomb concluded that those samples still contained 0.5% nitrate, based on an indirect analysis using ion chromatography.[10] That effectiveness was accepted as sufficient at that time. Based on the Holcomb reports, it appears that the exchange from nitrate to sulfate form was highly efficient for Dowex 21K. This is likely due to the reported high selectivity for the divalent sulfate anion over the monovalent nitrate anion. One negative factor with Reillex HPQ is its higher cross-linkage which will tend to retard mass transfer and potentially slow the conversion.

In the mid-1990s the FB-Line flowsheet[15] was modified to increase the sodium sulfate solution concentration from 1 to 2 wt % while at the same time reducing the flowrate. This change reduced the volume of solution from 320 L to 250 L[16] and eliminated some complexity due to the use of a 100 L feed tank. There was recognition that at higher sodium sulfate concentrations it would be harder to justify that Pu sulfate complexation would not occur. Cleveland[17] tabulates the solubility of Pu(IV) sulfate in nitric acid solutions and this data indicates significant Pu solubility (>10 g Pu/L) below 0.25 M sulfate (ranging from 2 to 6 M HNO_3). "Extended elution" of the resin columns should result in minimal Pu inventory on the resin but the spent sulfate solutions from that conversion should not be added to tanks/streams containing significant quantities of Pu to avoid potential precipitation issues.

Flowsheets from the Ion Exchange Literature: Similar resin conversion flowsheets can be found in general ion exchange books. Kunin[18] makes general recommendations for quantitative determination of resin capacity by conversion of chloride form resin to sulfate form by use of a large volume (~70 BV) of 4 wt % sodium sulfate solution with no mention of flow rate limitations. Similarly, Harland[19] indicates that most ionic forms may be prepared by passing a large excess (5-10 BV) of an appropriate 1-2 N salt solution (or 10 wt %) at a rate of 0.3 BV/min. Since many organic resins have a total exchange capacity on the order of 1 eq/L, this amounts to an approximately 10-fold excess to quantitatively convert the resin. A key difference was Kunin's and Harland's intent to be quantitative and thus the use of a much larger excess of sulfate anion to perform the conversion over some of the other examples. Harland specifically discusses the use of sodium sulfate rather than sulfuric acid to convert anion resin to the sulfate ionic form. Table 1 contains a comparison of the various conversion flowsheets described in the literature as well as SRS documents.

---

[15] J. B. Schaade, "Anion Resin Sulfate Conversion Flowsheet Change", unnumbered memo to C. E. Armitage, Savannah River Site, December 22, 1995.

[16] Various documents state different volumes depending on whether they referred to minimum volume or the actual volume that was used.

[17] J. M. Cleveland, "The Chemistry of Plutonium", Gordon and Breach Science, New York, 1970, pg. 431.

[18] R. Kunin, "Ion Exchange Resins", John Wiley and Sons, 2nd Edition, 1958, pg. 343-7.

[19] C. E. Harland, "Ion Exchange: Theory and Practice", Royal Society of Chemistry, 2nd Edition, 1994, pg. 63-4.

Table 1. Sulfate Conversion Flowsheets.

	Vol, L	BV	Rate, L/min	mL/min/cm^2	Eq Sulfate/L Resin[20]
Holcomb JB-Line Flowsheet (1982) [9]					
Water Flush	?	?			
1 wt % (0.07 M) Na_2SO_4	320	16	0.55	1.55	2.3
Water Flush	?	?			
Dilute Caustic Flush	?				
Revised FB-Line Flowsheet (1995) [15,21]					
Water Flush	100	5	0.55		
2 wt % (0.14 M) Na_2SO_4	250	12.5	0.275	0.8	3.5
Water Flush	100	5	0.55		
Kunin (1958) [18]					
4 wt % (0.29 M) Na_2SO_4		~70	slow	gravity	~40
Harland (1994) [19]					
10 wt % (0.77 M) Na_2SO_4		10	fast	~5	15.4
SRNL (~1990) [12]					
1 M (12.7 wt %) Na_2SO_4		10	fast	<10	20
Water Flush		>3			

3.0 Application and Discussion

SRNL's historical practice has been to use 10 BV of 1 M salt solution to convert chloride form anion resin to nitrate form as well as for the conversion from nitrate to sulfate form.[12] This amount of salt is a large excess compared to the stoichiometric amount to perform the conversion. When Steimke[13] prepared the most recent batch of Reillex HPQ resin for HB-Line, he followed the conversion by using chloride test strips and found that chloride removal was essentially complete after 3 BV of 1 M $NaNO_3$ (or 3 equivalents nitrate per liter resin) using a flowrate of 2.7 mL/min/cm^2. Typical anion exchange resin contains 1 to 1.3 eq/L total anionic sites for exchange. An advantage of the use of a large excess (10 BV) is that it leaves no question about the elimination of the nitrate. Based on the FB-Line experience, the use of large excess is not necessary to achieve >99% conversion to the sulfate form. In laboratory setting, the use of a large excess does not pose the same costs as it will in SRPPF and there may be significant room for optimization of the conversion flowsheet.

While laboratory resin conversions have typically been performed at relatively high flowrates, there is an expected relationship between efficiency of conversion and flowrate. The use of lower flowrates would be expected to make more efficient use of the salt solution and still allow for essentially complete conversion of the resin. No test data exists to justify what flowrate range might be optimal, but the flowrate used during elution would be a reasonable choice. A limitation to optimizing the resin conversion is the ability to measure the small amount of remaining nitrate in the resin bed. Holcomb analyzed for additional nitrate removal by soaking the converted resin in dilute sodium sulfate solution and then analyzing the solution by ion chromatography for nitrate. Nitrate test strips (similar to the chloride test strip used by Steimke[13]) are available from laboratory supply companies and should be tested in a 1 M sodium sulfate solution to monitor the presence of nitrate in the raffinate during any optimization efforts in the laboratory. The use of Raman spectroscopy also has possible application for the direct measurement of residual nitrate in the resin matrix and is estimated to have a nitrate sensitivity on the order of 1% residual nitrate by weight.

Based on the reports on the FB-line experience with Dowex 21K and the Steimke experience converting from the chloride to the nitrate form, it appears likely that the use of as little as two to four equivalents of sulfate in the form of a 1 M sodium sulfate solution, should be sufficient to achieve 99% conversion of spent nitrate form Reillex HPQ resin to sulfate form resin for disposal. However, some testing would be

---

[20] Calculated as concentration (molarity) * Solution Volume (L) *2 eq sulfate/mole sulfate/ Resin Volume (L).

[21] J. B. Schaade, "FB-Line Anion Resin Sulfate Conversion Process", unnumbered memo to D. W. Murdoch, Savannah River Site, September 9, 1994.

needed to establish that conversion effectiveness. A post conversion nitrate measurement would be useful, but one would have to be prepared to handle a high nitrate result. If the SRPPF could remove the Pu from the resin to acceptably low levels and then prepare the resin for disposal outside the primary SRPPF facility, some handling issues might be dealt with more easily.

Additional Useful Information: For reference, Table 2 provides the concentration and density properties of sodium sulfate solution.[22,23]

Table 2. Concentrative Properties of Sodium Sulfate Solution.[22,23]

Wt %	M	g/cc
1	0.071	1.0071
2	0.143	1.0161
5	0.367	1.0436
10	0.768	1.0905
12	0.938	1.1101
12.7	1.0	1.1172
13	1.025	1.1201
15	1.204	1.1402
20	1.677	1.1907

4.0 Conclusion/Recommendation

As a process baseline, future SRS disposal of spent Reillex HPQ resin should be in the sulfate form. The use of 10 BV of 1 M sodium sulfate solution will be more than sufficient to convert the nitrate form resin to sulfate form resin. This conversion will avoid any concern about reactivity of the resin with residual nitrate salts.

Prior to startup of the SRPPF it would be desirable to optimize the excess sulfate used in the conversion process. That could be justified by demonstrating that the amount of residual nitrate remaining in the resin matrix is acceptably low with a reduced volume of sodium sulfate solution under realistic process conditions.

---

[22] "CRC Handbook of Chemistry and Physics", 62nd ed.; Weast, R.C., Ed.; CRC Press: Boca Raton, FL, 1981, pg. D-238.

[23] "Concentrative Properties of Aqueous Solutions", in CRC Handbook of Chemistry and Physics, 102nd Edition (Internet Version 2021), John R. Rumble, ed., CRC Press/Taylor & Francis, Boca Raton, FL.

Distribution:

Jeff Schaade
Thadd Adams
Laura Tovo
Michelle Bullington
Dan Burns
Lee Fox
Pat Livengood
Paul Rogerson
Lake Clark
Josh Bodkin
Quentin Price
Kerri Crawford
Ben Terry
Harris Eldridge
Jon Duffey
Kristine Zeigler
Lance Traver
Tracy Rudisill
Gene Daniel
Jarrod Gogolski
Betty Mealer
Chris Armstrong