Pre-conditioning and Regeneration Requirements of Ground Gel Resorcinol Formaldehyde Ion Exchange Resin

S. T. Arm
D. L. Blanchard, Jr.

January 2004

LEGAL NOTICE

Pre-Conditioning and Regeneration Requirements of Ground Gel Resorcinol Formaldehyde Ion Exchange Resin

S. T. Arm
D. L. Blanchard, Jr.

January 2004

for W. Tawoscita.

ACCEPTED FOR
WTP PROJECT USE

Test specification: 24590-PTF-TSP-RT-03-005
Test plan: TP-RPP-WTP-245, Rev. 0
Test exceptions: 24590-WTP-TEF-03-073
R&T focus area: Pretreatment
Test Scoping Statement(s): A201

Battelle—Pacific Northwest Division
Richland, Washington 99352

Completeness of Testing

This report describes the results of work and testing specified by test plan TP-RPP-WTP-245, Rev. 0 and test specification 24590-PTF-TSP-RT-03-005. The work and any associated testing followed the quality assurance requirements outlined in the test specification/plan. The descriptions provided in this test report are an accurate account of both the conduct of the work and the data collected. Test plan results are reported. Also reported are any unusual or anomalous occurrences that are different from expected results. The test results and this report have been reviewed and verified.

Approved:

Gordon H. Beeman, Manager
WTP R&T Support Project

1/20/04
Date

Summary

Battelle—Pacific Northwest Division (PNWD) is contracted to Bechtel National Inc. (BNI) on the River Protection Project-Waste Treatment Plant (RPP-WTP) project to perform research and development activities. Unit operations of the WTP process include the separation of cesium-137 by ion exchange from the liquid portion of the waste. SuperLig® 644 (SL-644) ion exchange resin was selected by the project to perform the cesium separation. However, an alternative ion exchange resin, ground-gel resorcinol formaldehyde (RF), available from Boulder Scientific (Boulder, Colorado), is currently undergoing testing.

Results and Performance Against Objectives

This investigation was conducted according to the test plan[a] in response to the test specification[b] and test scoping statement A201[c]. The test objectives were satisfied. A summary of the test objectives and how they were satisfied is provided in Table S.1.

Table S.1. Test Objective Evaluation

Test Objective	Objective met	Discussion
Establish RF resin pre-conditioning and regeneration procedures.	Yes	Preferred resin pre-conditioning and regeneration procedures are recommended based on the eight procedures tested. A single cycle resin pre-conditioning procedure is preferred, involving a wash with 0.5 M nitric acid, followed by a water rinse, and then a wash with 1 M sodium hydroxide (refer to Sections 4.0 and 5.0 for details). Either 1M or 0.25 M sodium hydroxide can be used to regenerate the resin (refer to section 5.0 for details).
Demonstrate that the selected ion exchange resin pre-conditioning and regeneration steps are sufficient to remove metals and prepare the resin for batch contact and column tests in laboratory and pilot-scale ion exchange tests.	Yes	The preferred resin pre-conditioning and regeneration procedures were selected on the basis of batch-contact and column-test performance. Therefore, the preferred procedures were demonstrated to sufficiently remove metals and prepare resin since they provided optimal equilibrium and column performance.

(a) ST Arm. 2003. Determination of Pre-conditioning and Regeneration Conditions for the Alternative Cesium Ion Exchange Resin. TP-RPP-WTP-245, Battelle, Pacific Northwest Division, Richland, WA.

(b) JJ Toth. 2003. *Preconditioning and Regeneration Tests for RF Resin.* 24590-PTF-TSP-RT-03-005, RPP-WTP project, Richland, WA.

(c) MR Thorson, RA Peterson, and GT Wright. 2002. *Alternative Ion Exchange Resin Supplemental Research and Technology Plan - Case 20.* 24590-PTF-PL-RT-02-002 (business sensitive), RPP-WTP project, Richland, WA.

Test Exceptions

Table S.2 discusses the four test exceptions, provided by Toth[a] applied to this test.

Table S.2. Test Exceptions[a]

Test Exception	Discussion
The volume of simulated LAW containing no cesium and used in the column tests shall be doubled from 25 BVs to 50 BVs. The column effluents will be measured for cesium using gamma counting. Total cesium in the column effluents shall be reported up through the total of 50 BVs.	After the single cycle cesium loading, elution and regeneration column tests require a second loading test, loading with simulated LAW containing no cesium. The second column tests described in the test plan stipulated that at least 25 BVs of LAW solution without cesium will be processed through the column or until the cesium limit in the effluent is below 0.004 mg/L. The LAW feed flow rate to the column in the second test was stipulated as 3 BV/h. However, the measurement time (required to analyze samples for cesium to confirm the LAW effluent met requirement) for cesium counting exceeds the time to conduct the column test. Counting times to confirm concentrations below 0.004 mg/L require over 4 hours. The LAW effluent measurement cannot be confirmed within the timeframe of the column test. It does not adversely impact the objectives.
The resin will be dried in a nitrogen blanket to prevent degradation.	The test plan indicates that the resin for the batch contact tests will be air-dried. Air drying may reduce the resin cesium capacity due to chemical degradation. It does not adversely impact the objectives.
Measure total organic carbon in the rinse solutions of the single cycle and dual cycle pre-conditioning tests using 0.5 M nitric acid (baseline concentration) and 0.25 M sodium hydroxide concentration (baseline concentration).	To observe resin dissolution and degradation effects of pre-conditioning, total organic carbon measurements of the rinse solutions for a single cycle pre-conditioning test can be compared to a dual cycle pre-conditioning test. The exception does not adversely impact the objectives.
The RF resin regeneration will be conducted up to 12 BVs, and the effluent regeneration solutions shall be collected and titrated for hydroxide concentration. The hydroxide concentration of the effluents will be compared to the feed conditions (either 0.25 M or 1.0 M sodium hydroxide).	In-column conditioning and regeneration tested two different regeneration solutions (0.25 M and 1.0 M) and required that the pH of the column effluent must match the pH of the column influent. This proved impracticable for the 0.25 M regeneration test, even after doubling the volume of 0.25 M sodium hydroxide regeneration solution from 6 BVs to 12 BVs. It does not adversely impact the objectives.

(a) JJ Toth. 2003. Test Exception 24590-WTP-TEF-RT-03-073, Revision 0, RPP-WTP, Richland, WA.

Results and Performance Against Success Criteria

Table S.3 discusses the success criteria provided by Toth.[a]

Table S.3. Discussion of Test Success Criteria

Success Criteria	Discussion
This test shall establish a single preconditioning process for RF cesium ion exchange material. This test shall establish a preconditioning procedure for laboratory and pilot test conditions. The effect of the preconditioning chemistry and its effect on resin loading performance shall be determined.	A single pre-conditioning process is recommended, based on the eight procedures tested, involving a wash with 0.5 M nitric acid, followed by a water rinse and then a wash with 1 M sodium hydroxide (refer to Sections 4.0 and 5.0 for details).
The test shall develop a resin preconditioning procedure that converts resin by (1) removing contaminants or metals affecting resin performance, (2) preserving resin ion exchange performance (as measured by the cesium equilibrium distribution coefficient), and (3) minimizing the use of acids and caustic.	The recommended procedure adequately removes contaminants and metals such that the resulting equilibrium performance is better than the as-received resin and the resin resulting from pre-conditioning the resin by the other tested procedures.
This test shall determine the molar requirements to convert resin from the as-received to the acid form and from the acid to the sodium form.	The absolute molar requirements were determined from the total ion exchange capacity of the resin. The ion exchange capacity and, therefore, the molar conversion requirements of the resin is 4.4 mmol/g dry-sodium-form resin.
The test shall establish laboratory column conditions for regenerating resin from the acid to the sodium form. The results shall be used for development and testing in laboratory and pilot-scale tests.	Regeneration can be accomplished with either 12 BVs of 0.25 M sodium hydroxide or 7 BVs of 1M sodium hydroxide at flow rates of 1 BV/h (refer to Section 5.0 for details).

Quality Requirements

PNWD implemented the RPP-WTP quality requirements in a quality assurance project plan (QAPjP) as approved by the RPP-WTP quality assurance (QA) organization. Testing and analytical activities were conducted in accordance with PNWD's QA project plan, RPP-WTP-QAPjP, which invoked NQA-1-1989 Part I, "Basic and Supplementary Requirements," and NQA-2a-1990, Part 2.7. These quality requirements were implemented through PNWD's Waste Treatment Plant Support Project Quality Assurance Requirements and Description Manual.

PNWD addressed data-verification activities by conducting an Independent Technical Review of the final data report in accordance with Procedure QA-RPP-WTP-604. This review verified that the reported results were traceable, that inferences and conclusions were soundly based, and that the reported work satisfied the Test Plan objectives.

(a) JJ Toth. 2003. *Preconditioning and Regeneration Tests for RF Resin.* 24590-PTF-TSP-RT-03-005, RPP-WTP project, Richland, WA.

Research and Technology Test Conditions

The test specification[a] established extensive conditions to ensure that the results are valid for RPP-WTP project needs. Due to their extensive nature, the conditions are not repeated here, but they essentially constitute the test methodology described later in this summary. The conditions, as modified by the test exceptions and test plan,[b] were satisfied.

Simulated Waste Use

The tests described by this used simulated low activity waste (LAW) and the RPP-WTP project have a contractual requirement to compare the results of such testing with those from similar tests using actual LAW. Results from actual waste testing of the batch of RF used in these tests are, as yet, unpublished. However, the concentrations of sodium, potassium, cesium and free hydroxide, the constituents most important to ion exchange performance, were prototypic at ~5 M, ~3.5 g/L, ~80 mg/L and ~1.6 M, respectively.

Test Methodology

Small batches of RF resin from combined batches BSC-187-1-0001 and BSC-187-4-0270 were pre-conditioned using seven separate procedures outlined below:

1. A ~5 mL resin bed was formed in a column. De-ionized (DI) water was then pumped through the bed for 4 hours at 14 mL/h.

2. As-received resin was soaked in 0.5 M nitric acid of volume ~5 times that of the resin in an open vessel for 2 hours with gentle swirling of the vessel contents every 20 minutes. The acid was then decanted and the wash repeated. The acid wash was followed by three separate rinses with DI water. Each rinse consisted of adding DI water of volume ~10 times that of the resin and then decanting it immediately after the resin had settled. A single wash was then performed with 0.24 M sodium hydroxide of volume ~10 times that of the resin for 2 hours with gentle swirling every 20 minutes. Three water rinses identical to those following the acid wash completed the pre-conditioning.

3. This procedure was identical to that described above, using 0.5 M nitric acid and 0.84 M sodium hydroxide.

4. This procedure was identical to that described above, using 1 M nitric acid and 0.84 M sodium hydroxide.

5. Batch pre-conditioning procedures 2 through 4 described above were each performed and then repeated.

All resins were dried under a constant flow of nitrogen gas and stored under a nitrogen headspace after pre-conditioning. Various physical properties and particle-size distributions were determined for the pre-conditioned resins.

(a) JJ Toth. 2003. *Preconditioning and Regeneration Tests for RF Resin.* 24590-PTF-TSP-RT-03-005, RPP-WTP project, Richland, WA.

(b) ST Arm. 2003. Determination of Pre-conditioning and Regeneration Conditions for the Alternative Cesium Ion Exchange Resin. TP-RPP-WTP-245, Battelle—Pacific Northwest Division, Richland, WA.

Batch-contact tests were performed to ascertain the impact of pre-conditioning procedures on the equilibrium performance. The batch-contact tests were performed by contacting approximately 0.2 g of resin with 20 mL of simulated AN-105 low-activity waste (LAW) at cesium concentrations of nominally 0.1 mg/L, 150 mg/L, and 1400 mg/L. The as-received resin and resin pre-conditioned according to the seven procedures described above were contacted in the form in which conditioned (i.e., either sodium or as-received). The contacts were performed in vials shaken in a horizontal shaker at a frequency of approximately 2 Hz for 72 hours. The vials were secured in the shaker so their length was parallel to the direction of oscillation to ensure thorough mixing of the contents. The temperature of the contacts was maintained at ambient temperature. After contacting with the resin, the simulated LAW was filtered, and the cesium-137 concentrations of the solutions were determined by gamma energy analysis (GEA).

Single-column tests were performed on the as-received resin and on two resins pre-conditioned with 0.5 M nitric acid and sodium hydroxide at concentrations of 0.24 M and 0.84 M. The apparatus consisted of an ion exchange column containing nominally 33 mL of resin expanded in 0.24 M or 0.84 M sodium hydroxide, a metering pump, pressure-relief valve, pressure gage, and two 3-way valves. The simulated AN-105 LAW was then processed followed by column rinses of 0.1 M NaOH and DI water before the resin was eluted with 0.5 M HNO_3. The resin bed was then rinsed with DI water and regenerated with either 0.24 M or 0.84 M sodium hydroxide. The columns containing the pre-conditioned resins then processed cesium-free simulated LAW to simulate a column in the polishing position in WTP. Simulated LAW effluent samples were periodically collected by directing the flow into 20-mL vials to collect nominally 5 mL of sample. The bed height and effluent bottle mass were measured during sampling events. Eluate was collected into 40-mL vials that were changed every hour to provide 30-mL fractions. Samples were analyzed by GEA for their ^{137}Cs content.

Results Summary

Pre-conditioning the resin had no adverse impact on its equilibrium performance at the cesium concentrations expected in the LAW feeds to WTP. At cesium concentrations comparable to those expected in the product from the WTP ion exchange system, pre-conditioning improved resin equilibrium performance by up to 36%. Therefore, pre-conditioning appears to improve resin selectivity, which becomes more important at low cesium concentrations.

The best equilibrium performance was achieved by pre-conditioning the resin with first 0.5 M nitric acid and then with 1 M sodium hydroxide after an intermediate water rinse. Further pre-conditioning led to deterioration in the equilibrium performance, presumably as a result of chemical degradation. There was a 28% reduction in the mass of resin upon washing the as-received resin with nitric acid, leading to an L-factor of 0.72. The mass increase factor upon completely converting the resin from the acid to sodium form (I-factor) was 1.25. The mass increase is associated with sodium and water of hydration and is, therefore, inappropriate to use in calculating ion exchange capacity. The ion exchange capacity was 0.44 mmol/g dry sodium form resin based on the analysis of the eluate arising from the column tests described below. Subjecting the resin to a single pre-conditioning cycle reduces the potassium content of the resin by a factor of ~220. The potassium is presumably residual from the resin's manufacture. Greater leaching of organic constituents from the resin occurred using 0.84 M sodium hydroxide rather than 0.24 M sodium hydroxide, but this did not appear to impair performance. There was no difference in organic leaching when using 1 M or 0.5 M nitric acid. Pre-conditioning leads to the breakage of resin particles and the formation of "fines" of average size, 300 μm. The smallest particle sizes and range occurred with the most concentrated reagents, although there was no gross generation of fines.

There was no clear preferred pre-conditioning method based on the column performance. The as-received resin provided the best column performance processing simulated LAW containing cesium at a

concentration comparable to the highest observed in the actual LAW, providing a column distribution coefficient of 220. Mass-transfer effects appeared to reduce the column-distribution coefficient below that expected from the equilibrium behavior. In addition, there appeared to be a characteristic affecting mass transfer that was impacted to a greater degree by conditioning with 1 M sodium hydroxide, compared to 0.24 M sodium hydroxide. The result was that the column-distribution coefficient achieved with resin pre-conditioned with 0.84 M sodium hydroxide was ~30% lower than that achieved with the resin pre-conditioned with 0.24 M sodium hydroxide, although equilibrium behavior predicted similar values.

Pre-conditioning had no significant impact on the elution performance. The cesium concentration in the eluate peaked upon generating 5 BVs of eluate and had reduced to less than 1% of that in the LAW feed after generating 30 BVs. Chemical analysis of the as-received resin after its regeneration showed that elution had reduced its cesium concentration by a factor of ~1000. However, the residual cesium concentration was ~20 times higher than previously observed on SL-644. Processing 50 BVs of cesium-free simulated LAW through the pre-conditioned resins led to a product containing cesium at concentrations higher than the WTP specification. However, the resin pre-conditioned with 1 M sodium hydroxide provided the lowest cesium concentrations at between 8 and 3 times the WTP specification compared to factors between 40 and 20 for the 0.24 M sodium hydroxide pre-conditioned resin. This phenomenon may have been the result of the lower bed density of the 0.84 M sodium hydroxide pre-conditioned resin, allowing greater fluid accessibility and more complete elution.

The fastest column resin conditioning and regeneration was achieved with 0.84 M sodium hydroxide. The volume of 0.84 M sodium hydroxide required to achieve a constant bed volume was approximately half that required using 0.24 M sodium hydroxide. Therefore, conditioning and regenerating with 0.24 M sodium hydroxide appears to require less raw chemicals and would lead to a smaller addition of sodium to the LAW.

Discrepancies and Follow-on Tests

The tests described in this report highlighted one test issue. For batch contact tests, mixing times should be evaluated across the range of cesium concentrations. The mixing time evaluation described by this report showed that equilibrium was not achieved at the shortest mixing time for the lowest cesium concentration, though it was achieved at the highest concentrations. The adequacy of the mixing time used in the batch-contact tests described in this report was demonstrated across the range of cesium concentrations.

Two WTP operating issues were identified.

- Column tests indicate that the cesium-137 concentration in the LAW product from ion exchange would be higher than the WTP specification as a result of it becoming contaminated with uneluted cesium-137 on the bed in the polishing position. Further tests would quantify the phenomenon and identify operating conditions to avoid it.

- The column tests also appear to indicate that the spent resin would contain cesium-137 at a concentration exceeding that established for the baseline SL-644 resin. This phenomenon is similar to that described above and is caused by insufficient elution. Further tests would identify the optimal elution conditions to minimize the residual cesium-137 concentration.

Acronyms, Abbreviations, and Definitions

BNI   Bechtel National, Inc.

BV   bed volume

CPM   counts per minute

DI   de-ionized (water)

FMI   Fluid Metering, Inc.

GEA   gamma energy analysis

HLW   high-level waste

HP   hot persulfate

IC   ion chromatography

ICP-AES   inductively coupled plasma-atomic emission spectrometry

ICP-MS   inductively coupled plasma-mass spectrometry

LAW   low-activity waste

PNWD   Battelle—Pacific Northwest Division

QA   quality assurance

QAPjP   Quality Assurance Project Plan

QC   quality control

RF   resorcinol formaldehyde

RPL ASO   Radiochemical Processing Laboratory Analytical Service Operations

RPP-WTP   River Protection Project – Waste Treatment Plant

SL   SuperLig®

TIC   total inorganic carbon

TOC   total organic carbon

WTPSP   Waste Treatment Plant Support Project

This page intentionally left blank

Contents

Figures

Tables

1.0 Introduction

1.1 Background

Battelle—Pacific Northwest Division (PNWD) is contracted to Bechtel National Inc. (BNI) on the River Protection Project-Waste Treatment Plant (RPP-WTP) project to perform research and development activities. The purpose of the RPP-WTP project is to design, construct, and commission a plant to treat and immobilize high-level waste (HLW) and low-activity waste (LAW) stored in underground storage tanks at the Hanford Site. Unit operations of the LAW treatment process include the separation of cesium-137 by ion exchange from the liquid portion of the waste. SuperLig® 644 (SL-644) was selected by the project as the baseline ion exchange resin to perform the cesium-137 separation and is available from IBC Advanced Technologies, Inc., American Fork, Utah. Kurath et al. (2000a), Kurath et al. (2000b), Arm et al (2003a), Fiskum et al. (2003a), and Arm et al. (2003b), for example, have tested this resin and shown that it satisfies the performance criteria delineated by the RPP-WTP project. However, an alternative ion exchange resin, ground gel resorcinol formaldehyde (RF), is currently undergoing testing.

The pre-conditioning and regeneration requirements for an ion exchange resin are important to understand for design and operational purposes because they can impact the chemical and physical characteristics of the resin. Evaluating the chemical and physical impacts of different pre-conditioning procedures will determine the best procedure, from those studied, for application in further laboratory and pilot-scale tests and the WTP.

1.2 Objectives

The primary objectives of this task were:

- Establish resin pre-conditioning and regeneration procedures.

- Demonstrate that the selected ion exchange resin pre-conditioning and regeneration steps are sufficient to remove metals and prepare resin for batch contact and column tests in laboratory and pilot-scale ion exchange tests.

The parameters evaluated included reagent concentration and the number of pre-conditioning cycles. This investigation was conducted according to the test plan[a] in response to the test specification[b] and test scoping statement A201[c].

(a)   ST Arm. 2003. *Determination of Pre-conditioning and Regeneration Conditions for the Alternative Cesium Ion Exchange Resin.* TP-RPP-WTP-245, Battelle—Pacific Northwest Division, Richland, WA.

(b)   JJ Toth. 2003. *Preconditioning and Regeneration Tests for RF Resin.* 24590-PTF-TSP-RT-03-005, RPP-WTP project, Richland, WA.

(c)   MR Thorson, RA Peterson, and GT Wright. 2002. *Alternative Ion Exchange Resin Supplemental Research and Technology Plan - Case 20.* 24590-PTF-PL-RT-02-002 (business sensitive), RPP-WTP project, Richland, WA.

1.3 Purpose

This report documents the testing, results, and analysis associated with the RF pre-conditioning and regeneration investigation. The purpose of the investigation was to provide information for an assessment of the best means of pre-conditioning and regenerating the RF ion exchange resin. The report is intended to aid the RPP-WTP project in establishing uniform resin pre-conditioning and regeneration procedures for laboratory and pilot scale tests.

1.4 Quality Assurance

1.4.1 Application of RPP-WTP Quality Assurance Requirements

PNWD implemented the RPP-WTP quality requirements by performing work in accordance with the PNWD Waste Treatment Plant Support Project quality assurance project plan (QAPjP) approved by the RPP-WTP Quality Assurance (QA) organization. This work was performed to the quality requirements of NQA-1-1989 Part I, Basic and Supplementary Requirements, and NQA-2a-1990, Part 2.7. These quality requirements were implemented through PNWD's *Waste Treatment Plant Support Project (WTPSP) Quality Assurance Requirements and Description Manual*. The analytical requirements were implemented through PNWD's *Conducting Analytical Work in Support of Regulatory Programs* through WTPSP's Statement of Work (WTPSP-SOW-005) with the Radiochemical Processing Laboratory Analytical Service Operations (RPL ASO).

A matrix that cross-references the NQA-1 and 2a requirements with the PNWD's procedures for this work is given in the test plan[(a)]. It includes justification for those requirements not implemented.

1.4.2 Conduct of Experimental and Analytical Work

Experiments that were not method-specific were performed in accordance with PNWD's procedures QA-RPP-WTP-1101 "Scientific Investigations" and QA-RPP-WTP-1201 "Calibration Control System" assuring that sufficient data were taken with properly calibrated measuring and test equipment (M&TE) to obtain quality results.

As specified by Toth (2003), BNI's QAPjP, PL-24590-QA00001, is not applicable since the work was not performed in support of environmental/regulatory testing, and the data will not be used as such.

The applicable quality control (QC) parameters for chemical analysis are delineated in the test plan[(a)]. Blank spike and/or Lab Control Sample QC failures would result in re-analyzing the sample for the particular analyte for which the spike failed. Matrix spike and/or duplicate analysis QC failures would not result in re-analyzing the sample but probable reasons for the failure would be discussed in the analytical report to be stored in the project files. A qualitative impact assessment of the failure on the results would be discussed in the report.

Analytical processes were performed in accordance with the requirements in the PNWD's *Conducting Analytical Work in Support of Regulatory Programs* and WTPSP's Statement of Work (WTPSP-SOW-005) with the RPL ASO. Cesium-137 tracer used in the batch contacts and column tests was counted using a GEA system consisting of a multi-channel analyzer and a suitable detector, such as a high purity germanium detector. Counting was performed according to the procedure *Gamma Energy Analysis*

(a)   ST Arm. 2003. *Determination of Pre-conditioning and Regeneration Conditions for the Alternative Cesium Ion Exchange Resin.* TP-RPP-WTP-245, Battelle—Pacific Northwest Division, Richland, WA.

(GEA) and Low Energy Photon Spectroscopy (LEPS), PNL-ALO-450 when activity concentrations are required for reporting. The procedure *Routine Research Operations*, RPL-OP-001 was used to control counting when relative activity concentrations (e.g. in calculating equilibrium distribution coefficients and column breakthrough profiles) was required for reporting. Absolute counting efficiency and energy calibration were not required since the analysis is comparative. The GEA instrument was monitored for consistent operation by counting cesium-137 control standards both before and after one day's analysis sequence. The instrument background was counted once per day the system was used.

Additional equipment that was used included a ruler, thermometer, clock and balances.   The thermometer for monitoring the batch-contact temperature, ruler and timepiece are standard laboratory equipment for use as indicators only. Balances are calibrated annually by a certified contractor, QC Services, Portland, Oregon.

1.4.3   Internal Data Verification and Validation

PNWD addressed internal verification and validation activities by conducting an Independent Technical Review of the final data report in accordance with PNWD's procedure QA-RPP-WTP-604. This review verified that the reported results are traceable, that inferences and conclusions are soundly based, and the reported work satisfies the Test Plan objectives. This review procedure is part of PNWD's *WTPSP Quality Assurance Requirements and Description Manual*.

Analytical completeness of 98% for the analytes of interest measured by the RPL ASO was calculated according to the formula:

$$\%C = 100 \times \left(\frac{N_v}{N_p} \right) \tag{1.1}$$

where,   %C = percentage completeness
  N_p = total number of planned measurements
  N_v = number of valid measurements as defined by the task

The analysis was incomplete due to a resin wash sample, identified in section 3.1.1, being inadvertently mislaid.

2.0   Test Design and Operation

This section describes the process for preparing simulated AN-105 LAW, preparing reagents, and preparing and storing ion exchange resin. It also describes the resin conversion methods, batch-contact procedure, and the ion exchange column test set-up.

2.1   Overview

The tests described by this report involved pre-conditioning small quantities of as-received RF resin following seven separate procedures and then evaluating the impacts of those procedures on resin physical properties and performance. Resin performance was evaluated by determining and comparing equilibrium distribution coefficients and by single-column tests.

2.2   Physical Properties and Conversion Methods

2.2.1   Conversion Methods

As-received RF resin from combined batches BSC-187-1-0001 and BSC-187-4-0270 from Boulder Scientific (Boulder, Colorado) was pre-conditioned using seven separate procedures outlined below all at ambient temperature of 22 ± 2°C.

2.2.1.1   As-received Resin (Procedure #1)

The resin was received dry and split into working batches with the aid of an open-pan riffle sampler (Model H-3980, Humboldt Manufacturing, Co., Norridge, IL). These tests used resin from a 500 g batch that was stored in a glass bottle back-filled with nitrogen when not in use. The bottle was shaken before samples of resin were extracted. The test plan[a] identifies this procedure as RT-03-005-01.

2.2.1.2   DI Water Rinse (Procedure #2)

Approximately 1.3 g of as-received resin was slurried into a column of 10-mm diameter with DI water to form a bed of volume ~5 mL. DI water was then pumped through the bed for 4 hours at 14 mL/h, or 2.8 BV/h. Note that a lower flow rate than the 6 BV/h specified by Arm[a] was inadvertently used. The resin was then extracted from the column and dried under a continuous nitrogen gas stream. The resin was stored in a bottle with a nitrogen headspace. The test plan [a] identifies this procedure as RT-03-005-02.

2.2.1.3   Single 0.5 M Nitric Acid and 0.25 M Sodium Hydroxide Washes (Procedure #3)

A 50g sample of as-received resin was soaked in 420 mL of 0.5 M nitric acid in an open vessel for 2 hours with gentle swirling of the vessel contents every 20 minutes. The acid was then decanted, to generate a supernate designated acid #1, and the wash repeated, generating acid #2. The acid wash was followed by three separate rinses with 840 mL of de-ionized (DI) water. Each rinse consisted of adding DI water and then decanting it immediately after the resin had settled. A single wash was then performed with 840 mL of 0.25 M sodium hydroxide for 2 hours with gentle swirling every 20 minutes. The caustic supernate was designated caustic #1. Three water rinses identical to those following the acid wash completed the pre-conditioning. The resin was split in half and one half dried under a continuous

---

(a)   ST Arm. 2003. *Determination of Pre-conditioning and Regeneration Conditions for the Alternative Cesium Ion Exchange Resin.* TP-RPP-WTP-245, Battelle—Pacific Northwest Division, Richland, WA.

nitrogen gas stream and stored in a bottle with a nitrogen headspace. This procedure is identified as RT-03-005-03 in the test plan.[a]

2.2.1.4   Single 0.5 M Nitric Acid and 1 M Sodium Hydroxide Washes (Procedure #4)

This procedure was identical to that described in Section 2.2.1.3 except that 1 M instead of 0.25 M sodium hydroxide was used. The test plan [a] identifies this procedure as RT-03-005-04.

2.2.1.5   Single 1 M Nitric Acid and 1 M Sodium Hydroxide Washes (Procedure #5)

This procedure was identical to that described in Section 2.2.1.4 except that 1 M instead of 0.5 M nitric acid was used. The test plan [a] identifies this procedure as RT-03-005-05.

2.2.1.6   Dual 0.5 M Nitric Acid and 0.25 M Sodium Hydroxide Washes (Procedure #6)

The pre-conditioning procedure described in Section 2.2.1.3 was performed on the remaining half of the resin from procedure #3 (maintaining the same ratio of resin mass and solution volume) before it was dried under a continuous nitrogen gas stream and stored in a bottle with a nitrogen headspace. The two acid supernates and the caustic supernate were designated acid #3, acid #4 and caustic #2, respectively. This procedure is identified as RT-03-005-06 in the test plan.[a]

2.2.1.7   Dual 0.5 M Nitric Acid and 1 M Sodium Hydroxide Washes (Procedure #7)

The pre-conditioning procedure described in Section 2.2.1.4 was performed on the remaining half of the resin from procedure #4 (maintaining the same ratio of resin mass and solution volume) before it was dried under a continuous nitrogen gas stream and stored in a bottle with a nitrogen headspace. This procedure is identified as RT-03-005-07 in the test plan.[a]

2.2.1.8   Dual 1 M Nitric Acid and 1 M Sodium Hydroxide Washes (Procedure #8)

The pre-conditioning procedure described in Section 2.2.1.5 was performed on the remaining half of the resin from procedure #5 (maintaining the same ratio of resin mass and solution volume) before it was dried under a continuous nitrogen gas stream and stored in a bottle with a nitrogen headspace. This procedure is identified as RT-03-005-08 in the test plan.[a]

2.2.2   Physical-Properties Determination

2.2.2.1   F Factors

The F factor indicates the loss in mass from drying the resin at 50°C under vacuum to constant mass and is defined by the equation

$$F = \frac{m_d}{m_i} \tag{2.1}$$

where m_d is the mass of resin dried at 50°C under vacuum, and m_i is the initial mass of dry resin (dried under ambient conditions). Samples of between 0.2 g and 0.3 g were extracted from resins dried under ambient conditions and further dried under house vacuum (~550 mm mercury) at 50°C until the weight changed less than 1% over 24 hours. Exceptions to this method were the resins used in the column tests, which were dried at 50°C but at atmospheric pressure since a vacuum pump was not available to evacuate

---

(a)   ST Arm. 2003. *Determination of Pre-conditioning and Regeneration Conditions for the Alternative Cesium Ion Exchange Resin.* TP-RPP-WTP-245, Battelle—Pacific Northwest Division, Richland, WA.

the oven used for radioactive material. Thus, the product of the F factor and mass of resin dried under ambient conditions (for which the F factor is determined) gives the absolute resin mass. Therefore, the F factor was determined every time the resin mass was required to facilitate comparative analyses on a consistent basis.

2.2.2.2 L and I Factors

L and I factors were determined for the pre-conditioning procedures outlined in Section 2.2.1 using approximately 6 g of as-received resin for each procedure. The processed resin was dried under a constant flowing nitrogen gas stream after completing each DI water rinse cycle. The dried resin was weighed, and samples were extracted for F-factor determination.

The L factor indicates the loss in mass from acid washing the as-received resin (corrected for water loss) and is determined from the equation

$$L = \frac{(m_H F_H)}{(m_i F)} \tag{2.2}$$

where F_H is the F factor for the acid-form resin of mass m_H, m_i is the initial mass of the as-received resin, and F is the F factor of the as-received resin.

The I factor defines the mass increase upon conversion from the acid to the sodium forms and is determined from the following equation

$$I = \frac{m_{Na} F_{Na}}{m_H F_H} \tag{2.3}$$

where m_{Na} and F_{Na} are the mass and F-factor of the nitrogen dried sodium-form resin.

Equivalent I-factors were also determined indirectly from the solution sodium consumption. In this case, the I-factor is determined by the equation

$$I = \frac{22.99 \times V \times ([Na]_i - [Na]_f)}{m_H F_H} + 1 \tag{2.4}$$

where V is the conditioning solution volume and $[Na]_i$ and $[Na]_f$ are the initial and final sodium concentrations, respectively.

The sodium concentration in the eluate from the column test was also used to calculate an equivalent I-factor by the equation

$$I = \frac{m_{Na} F_{Na}}{m_{Na} F_{Na} - V_e [Na]_e} \tag{2.5}$$

2.3

2.2.2.3 Bed Densities

The bed density, ρ_b, were derived from the equation

$$\rho_b = \frac{mF}{V_b} \tag{2.6}$$

where m and F are the mass and associated F-factor of the resin, and V_b is the wet-bed volume.

Bed densities were derived during the column tests and in the course of determining the L and I factors. The latter determination was accomplished by loading ~6g of wet resin into a measuring cylinder and lightly tapping it to settle the resin before recording the volume. The accuracy is ~±10% since measurements were taken to the nearest mL.

2.2.2.4 Particle-Size Distribution

An approximate 15g sample of as-received resin was wet sieved in a sieve shaker (by Retsch Inc. Newtown, PA) at a vibration amplitude setting of 40 for 20 minutes using sieves of nominal aperture 212 µm, 300 µm, 355 µm, 400 µm, 500 µm, and 600 µm. A continuous flow of DI water at a rate of approximately 1 L/minute was maintained throughout the sieving operation. After sieving, the sieves were dried under ambient conditions in air before the resin fractions were transferred to separate bottles. These fractions were then dried at 50ºC under house vacuum until their weights changed by less than 1% over 24 hours.

The particle-size distribution of resin prepared according to the procedures outlined in Sections 2.2.1.3, 2.2.1.6, and 2.2.1.8 was also assessed. Approximately 15 g of resin was first dry-sieved through a sieve of nominal aperture of 212 µm using the sieve shaker at vibration amplitude setting of 40 for 20 minutes. The smaller-sized fraction was then dried at 50ºC under house vacuum until its weight changed by less than 1% over 24 hours before its particle-size distribution was determined using a laser spectrometer. The larger sized fraction was wet-sieved in the sieve shaker at vibration amplitude setting of 40 for 20 minutes using sieves of nominal aperture of 212 µm and 300 µm. As before, the sieves were dried under ambient conditions in air before the resin fractions were transferred to separate bottles and dried at 50ºC under house vacuum until their weights changed by less than 1% over 24 hours.

2.3 Simulated AN-105 LAW Preparation

Tests were performed using a simulated LAW since using actual waste would have proved unacceptably expensive and impractical from a supply standpoint for the scale of the test.

The LAW currently stored in Tank 241-AN-105 (AN-105) was selected as that to simulate and test since processing of the LAW in this tank is scheduled for the WTP, and it is representative of the Envelope A type waste that will constitute the majority of the feed to the WTP. Several gallons of the simulated LAW at a sodium concentration of nominally 5 M were prepared by Noah Technologies Inc. (San Antonio, TX) in two batches under sub-contracts 7526 and 8432. The batches of simulated LAW were analyzed by ion chromatography (IC), inductively coupled plasma-atomic emission spectrometry (ICP-AES), hot persulfate (HP) oxidation, furnace oxidation and titration. Table 2.1 compares the actual analyte concentrations with their targets. In general, the actual concentrations are acceptably consistent with the targets. Silver and calcium concentrations were significantly below their targets presumably due to their precipitation as chloride compounds. This phenomenon of the simulated AN-105 LAW was observed before by Arm et al. (2003b). The densities of batches 1 and 2 were measured at 1.234 g/mL and 1.228 g/mL, respectively.

Cesium was omitted from these batches and added as cesium nitrate by PNWD staff to the concentrations desired for the test and are provided later in the report. Cesium concentrations were determined by inductively coupled plasma-mass spectrometry (ICP-MS).

Table 2.1. Simulated AN-105 LAW Composition

Analyte	Main Reagent Used	Analysis Method	Concentration (mg/L)[a,b]		
			Target	Batch 1	Batch 2
Aluminum	Aluminum trihydroxide	ICP-AES	18,600	18,500	18,400
Cadmium	Cadmium nitrate	ICP-AES	1.54	*2.3*	*1.7*
Calcium	Calcium nitrate	ICP-AES	18.7	<5.6	<5.6
Chromium	Sodium chromate	ICP-AES	629	637	645
Lead	Lead nitrate	ICP-AES	24.9	*22*	<2.9
Magnesium	Magnesium nitrate	ICP-AES	2.53	<3.1	<3.1
Molybdenum	Potassium molybdate	ICP-AES	38.4	43.3	43.3
Phosphorus	Sodium phosphate	ICP-AES	87.1	94.8	93.7
Potassium	Potassium nitrate	ICP-AES	3,480	3,520	3,500
Selenium	Selenium nitrate	ICP-AES	0.463	*7.5*	*10*
Silicon	Sodium meta-silicate	ICP-AES	98.6	131	*120*
Silver	Silver nitrate	ICP-AES	7.63	<0.62	<0.62
Sodium	Various	ICP-AES	115,000	115,000	115,000
Zinc	Zinc nitrate	ICP-AES	4.73	7.26	*1.7*
Boron	Boric acid	ICP-AES	23.9	27.8	27.3
Inorganic carbon	Sodium carbonate	HP	1,170	1,380	1,310
Chloride	Sodium chloride	IC	4,250	3,840	3,650
Fluoride[c]	Sodium fluoride	IC	88.9	*120*	*110*
Hydroxide (free)	Sodium hydroxide	Titration	39,100[e]	26,550	25,700
Nitrate	Sodium nitrate	IC	71,300	75,500	73,800
Nitrite	Sodium nitrite	IC	52,000	51,800	54,700
Sulfate	Sodium sulfate	IC	360	409	376
Glycolic acid	Glycolic acid	HP	928[d]	900[d]	880[d]
Acetate	Sodium and ammonium acetate				
Formate	Sodium formate				
Oxalate	Sodium oxalate				
Total carbon	Sodium carbonate, acetate, formate and oxalate and glycolic acid	Furnace oxidation	2,100	2,190	2,130

(a) Results in normal type have errors likely <15%, but those in italics are within ten times their detection limit with errors likely exceeding 15%.
(b) Reported results satisfy the WTP project quality control criteria unless otherwise noted.
(c) Results are upper-bound values due to interferences from co-eluting anions (e.g., formate and acetate) during analysis.
(d) Concentrations are for total organic carbon.
(e) The target free hydroxide concentration is likely high because some of that added as sodium hydroxide would have become associated with other metals, particularly aluminum. Aluminum exists in solution associated with four hydroxide groups whereas it was added as the trihydroxide compound. The target concentration decreases to 27,400 mg/L accounting for the aluminum, which is close to the reported measured values.

2.4 Reagent Preparation

All reagents were "reagent grade." Solutions of nominally 0.1 M, 0.25 M, and 1 M sodium hydroxide were prepared by dissolving the required mass of sodium hydroxide pellets in DI water. The solutions of nominally 0.25 M and 1 M sodium hydroxide were analyzed by titration and returned actual hydroxide concentrations of 0.24 M and 0.84 M, respectively.

Solutions of 0.5 M and 1 M nitric acid were prepared by diluting the 68 to 70 wt% nitric acid commercial stock with DI water.

2.5 Batch-Contact Procedure

Batch-contact tests were performed in triplicate to ascertain the impact of the pre-conditioning procedure on the equilibrium performance of the resin. The batch-contact tests were performed by contacting approximately 0.2 g of resin, measured to an accuracy of 0.001 g, with 20 mL of simulated AN-105 LAW at cesium concentrations of nominally 0.1 mg/L, 150 mg/L, and 1400 mg/L.

The resin was weighed and contacted in either the as-received or conditioned forms. Note that the conditioned form was nominally sodium but the procedures using 0.24M sodium hydroxide only partially converted the resin from the acid form. The simulated LAW was transferred to 40-mL contact vials by pipette, and the actual volume was determined from the net mass and density. The vials were backfilled with nitrogen to provide an inert gas headspace before sealing. The contact vials containing the resin and simulated LAW were shaken in a horizontal shaker at a frequency of approximately 2 Hz. The vials were secured in the shaker so their length was parallel to the direction of oscillation to ensure thorough mixing of the contents. A fan blowing across the shaker was used to maintain the temperature of the contact vials at ambient temperature ($24\pm2^{\circ}C$). Contact time was 72 hours for most of the vials, but a select number were also contacted for 36 and 120 hours to assess the extent of equilibration at 72 hours.

After contacting with the resin, the simulated LAW was filtered, and the cesium-137 concentrations of the solutions were determined by gamma energy analysis (GEA). The batch-distribution coefficients (K_d) were determined from the relationship,

$$K_d = \frac{(C_0 - C_1)}{C_1} \frac{V}{M}$$

(2.7)

where C_0 and C_1 = initial and final cesium-137 concentrations (CPM/mL)
             V = volume of simulated LAW (mL)
             M = mass of ion exchange resin in fully converted sodium form (g)

The mass of ion exchange resin in the fully converted sodium form was derived from the as-received resin mass by the equation

$$M = m_i \times F \times L \times I_f$$

(2.8)

where I_f is the I-factor for the resin fully converted to the sodium form. The mass of ion exchange resin in the fully converted sodium form was derived from the conditioned resin mass by the equation

$$M = \frac{I_f}{I_c} \times m_c \times F_c$$

(2.9)

2.6

where I_c, m_c, and F_c are the I-factor, mass, and F-factor of the conditioned resins, respectively.

2.6 Ion Exchange Column Test Setup

Figure 2.1 provides a process schematic of the apparatus. The apparatus consisted of an ion exchange column containing nominally 33 mL of RF resin expanded in 0.24 M or 0.84M sodium hydroxide supported by a screen with 50 μm openings. Other constituents of the apparatus included a metering pump, pressure relief valve, pressure gage (indicated by "P") and two 3-way valves.

The column was a Spectrum Chromatography Spectra/Chrom® column manufactured from glass with plastic plungers on the ends that could be adjusted to control the distance between the top of the resin bed and the column feed, although no adjustments were made while processing. The internal diameter of the column was 2.5 cm, providing a height to diameter ratio of 2.7. All solutions were pumped down flow through the bed such that a head of fluid was always present between the top bed surface and plunger.

The pump was a Fluid Metering, Inc. (FMI) piston pump with the flow rate controlled from outside of the fumehood using an FMI stroke-rate controller. The pump was pre-calibrated using water, and it provided pumping rates between approximately 30 mL/h and 150 mL/h.

The pressure-relief valve was set to open at a pressure of 10 psi, which was below the maximum operating pressure of the column. The valves were used to eliminate air from the system, isolate the column from the pump, and prevent the column from draining while the pump was stopped. The equipment and fittings were connected using $^1/_{16}$-in. internal-diameter polyethylene tubing.
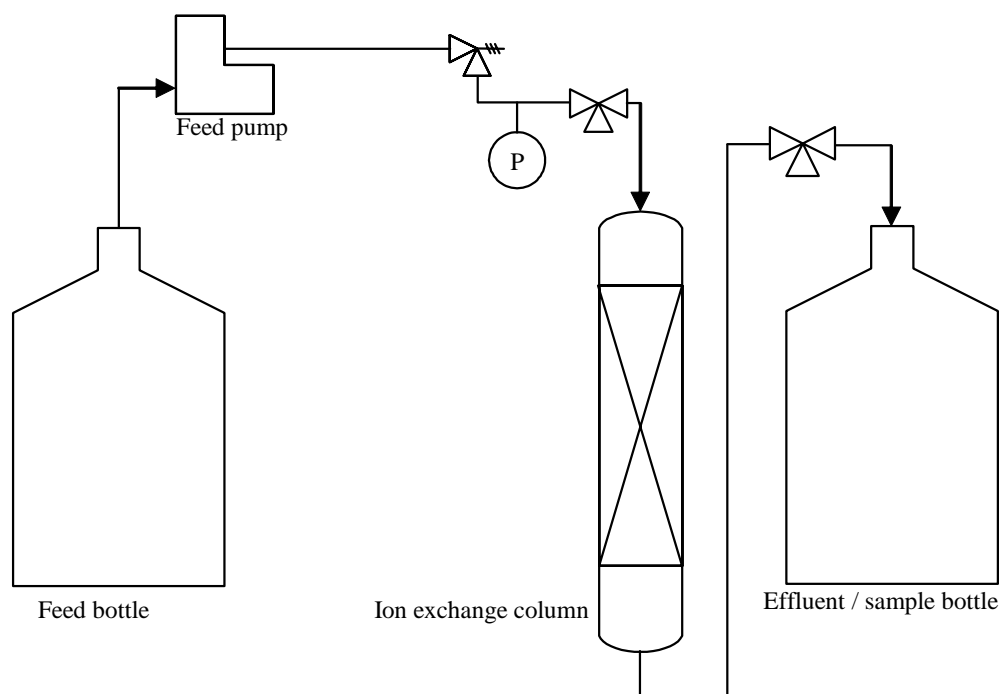
Figure 2.1. Schematic of RF Column Test Process

3.0   Pre-Conditioning Process Test Results and Discussion

This section describes 1) chemical consumption (sodium and acid), resin leaching and supernate characterization, 2) bed densities and I and L factors, and 3) particle-size analysis.

3.1   Chemical Consumption and Supernate Characterization

3.1.1   Sodium Consumption

Supernates from the sodium hydroxide washes of Procedures #3 through 8 were analyzed by titration to determine their hydroxide concentrations and thereby their sodium concentrations since the proton released upon exchange with the sodium ion forms water with the free hydroxide in solution.

The hydroxide concentrations of supernates from Procedures #3 and #6 (i.e., those using 0.24 M sodium hydroxide) were 0.11 M and 0.13 M, respectively, providing an average of 0.12 M, which compares to a feed concentration of 0.24 M. Sodium consumption is then 2.9 mmol/g of dry sodium-form resin, providing an I-factor 1.07 according to equation 2.4. Supernates from the 0.84 M sodium hydroxide washes of Procedures #4, #7, and #5 contained hydroxide at concentrations of 0.54 M, 0.54 M and 0.56 M, respectively. The supernate from the final caustic wash of Procedure #8 was inadvertently mislaid but probably is the same as that from Procedure #5 given the patterns observed from Procedures #3 through #7. The average supernate hydroxide concentration from the 0.84 M sodium hydroxide washes is 0.55 M, to provide a sodium consumption of 6.3 mmol/g of dry sodium-form resin and an I-factor of 1.17.

There is presumably an equilibrium established between the solution and resin for sodium since the 0.24 M sodium hydroxide solution provided insufficient sodium to fully convert all of the resin, indicated by the difference between the I-factors of 1.07 and 1.17, but not all of the sodium from that solution was consumed.

The post-caustic wash-water rinse composites from Procedures #3 and #6 were also analyzed for pH. The composite of the water rinse performed following the first caustic wash returned a pH value of 11.5 (0.0032 M hydroxide) while that from the second caustic wash provided a value of 10.1 (1×10^{-4} M hydroxide), indicating that the water rinse diluted the hydroxide by a factor of up to 1900.

3.1.2   Acid Consumption

Supernates from the acid washes of Procedures #3 through 8 were potentiometrically analyzed to determine pH. Note that there is likely significant uncertainty (~$\pm$0.5 pH) associated with pH values less than unity since the pH probe is not designed to operate at such pH values. For example, the pHs of the 0.5 M nitric acid and 1 M nitric acid reagents were 0.6 and 0.4, respectively, compared to theoretical values of 0.3 and 0.0.

Table 3.1 tabulates the pHs of the acid-wash supernates. Acid washes #1 and #2 were performed consecutively on the as-received resin. The pH of the second wash was always lower than that of the first but also appeared to be always higher than the initial reagent pH. The same pattern was repeated on the third and fourth washes conducted after the post-caustic wash rinse except that the pH of the initial reagent and second 1 M nitric acid wash were identical. Therefore, acid washing appeared complete only on Procedure #8 using 1 M nitric acid. However, conclusions should be drawn with care since most of the pH measurements were less than unity.

Table 3.1. pH of Acid Wash Supernates

Procedure	pH			
	Acid #1[a]	Acid #2[a]	Acid #3[b]	Acid #4[b]
3 / 6	1.4	1.2	1.3	0.8
4 / 7	1.2	0.8	1.0	0.7
5 / 8	0.6	0.5	0.5	0.4
(a) Supernate from acid washing as-received resin.				
(b) Supernate from acid washing sodium form resin.				

The post-acid wash-water rinse composites from Procedures #3 and #6 were also analyzed for pH. Both composites returned pH values of 2.2 (0.0063 M acid), indicating that the water rinse effectively diluted the acid by a factor of ~15.

3.1.3 Resin Leaching

3.1.3.1 Organic and Inorganic Carbon

Supernates from all acid and caustic washes and water rinses from Procedure #6 were analyzed for their total organic carbon (TOC) and total inorganic carbon (TIC) contents. Table 3.2 shows the TIC and TOC concentrations in the acid and caustic pre-conditioning reagents against which the concentrations in the supernates should be compared. TOC concentrations were generally below detection (<4 mg/L) except for the 1 M nitric acid reagent at 11 mg/L. TIC concentrations in the caustic reagents were somewhat above detection.

Table 3.2. TIC and TOC Concentrations in Conditioning Reagents

0.5 M Nitric Acid		1 M Nitric Acid		0.24 M Sodium Hydroxide		0.84 M Sodium Hydroxide	
TOC	TIC	TOC	TIC	TOC	TIC	TOC	TIC
<4	[a]	11	[a]	<4	6	<4	14
(a) Not applicable since carbonate would be destroyed in the acid matrix.							

Table 3.3 presents the TOC concentrations in the acid- and caustic-wash supernates. TOC concentrations in the supernate from the first acid wash were ~1 g/L, and there appeared to be no correlation with the acid concentration. TOC concentrations decreased to ~300 mg/L in the second acid wash. TOC concentrations in the supernates from the first caustic wash were an order of magnitude lower than in the previous acid-wash supernates. The TOC concentrations in the 0.84 M sodium hydroxide were double those in the 0.24 M sodium hydroxide, which indicates that the higher caustic strength leached more of the resin. TOC concentrations in the subsequent acid and caustic washes were of the same order as in the first caustic-wash supernate and showed no patterns. Therefore, the first two acid washes appear to remove the majority of the soluble organic constituents.

Table 3.3. TOC Content of Acid and Caustic Washes

Procedure	TOC Concentration (mg/L)					
	Acid #1	Acid #2	Caustic #1	Acid #3	Acid #4	Caustic #2
3 / 6	950	270	26	16	26	10
4 / 7	990	260	50	20	18	12
5 / 8	910	300	50	16	22	Not measured

The TIC concentrations of the caustic washes are shown in Table 3.4. No inorganic carbon was detected in the acid-wash supernates, presumably because it was destroyed in the acid matrix. The TIC concentrations in the caustic supernates were ~100 mg/L and appeared not to be correlated with sodium hydroxide concentration. TIC concentrations in the second caustic wash were somewhat lower than in the first. The inorganic carbon is presumably associated with a metal, such as potassium, that is residual from the resin's manufacture.

Table 3.4. TIC Content of Caustic Washes

Procedure	TIC Concentration (mg/L)	
	Caustic #1	Caustic #2
3 / 6	75	68
4 / 7	110	88
5 / 8	66	Not measured

Table 3.5 presents the TOC and TIC concentrations in the composites of the water-rinse supernates. The organic content and the inorganic carbon content of these supernates are probably associated with residues of the previous acid or caustic washes. For example, the TOC content of the supernate from the post-acid #2 rinse is a tenth of the concentration in the actual acid-wash supernate and would represent 2% of the acid wash remaining in the slurry before rinsing. Likewise, the TOC and TIC concentrations in the composite supernate of the post caustic #1 rinse both represent 2.5% of the previous wash remaining in the slurry before rinsing.

Table 3.5. TOC and TIC Concentrations in DI Water Rinse Supernates from Procedure #6

TOC Concentration (mg/L)							
Post Acid #2[a]		Post Caustic #1[a]		Post Acid #4		Post Caustic #2	
TOC	TIC	TOC	TIC	TOC	TIC	TOC	TIC
26	<3	7	19	<4	<2	<4	39
(a) Supernates from procedure #3 (procedure #3 is a subset of #6).							

3.1.3.2 Potassium

The as-received resin was believed to be loaded with potassium residual from its manufacture. To confirm this belief, a sample of the as-received resin was digested and the digestate analyzed by ICP-AES. The analysis showed the as-received resin to be loaded with potassium at a concentration of 173 mg/g resin dried under ambient conditions. The analysis also indicated the presence of sodium at a concentration of 0.907 mg/g resin dried under ambient conditions (indicative only value). Analysis of Resin #3 showed the potassium concentration to have reduced to 0.780 mg/g after a single wash cycle with 0.5 M nitric acid and 0.25 M sodium hydroxide. Note that the error associated with this concentration is likely greater than 15% because it is less than the estimated sample quantitation limit of 4.89 mg/g. Therefore, washing once with 0.5M nitric acid and 0.25M sodium hydroxide reduced the potassium concentration on the resin by a factor of ~220. Analysis of Resin #3 also provided an indicative only concentration for sodium of 59.9 mg/g.

3.2   Bed Densities and I and L Factors

The dry bed densities in water of the pre-conditioned resins are presented in Table 3.6. In general, the acid-form resin-bed density appeared independent of the acid concentration in the pre-conditioning reagent and averaged 0.49 g/mL. The average acid-form resin-bed density inferred from the column tests described later in Section 5.6 was 0.44 g/mL. The difference between these values of ~10% is probably not significant. In contrast, the sodium-form resin-bed density was generally lower after pre-conditioning with 0.84 M sodium hydroxide than with 0.24 M sodium hydroxide. The density after pre-conditioning with 0.24 M sodium hydroxide is ~0.5 g/mL, which is close to that measured for the acid-form resin and possibly indicates that the resin was not completely converted to the sodium form. Indeed, the average bed density of 0.43 g/mL measured here for resins pre-conditioned with 1 M sodium hydroxide is identical to that measured for the presumed fully converted resins in the column tests reported later in Section 5.4.

Table 3.6. Dry Bed Densities for Pre-Conditioned Resins

Procedure	Dry Bed Density in Water (g/mL)	
	Acid Form	**Sodium Form**
#3	Not measured	0.50
#4	Not measured	0.41
#5	Not measured	0.40
#6	0.52	0.51
#7	0.45	0.35
#8	0.50	0.56

Table 3.7 shows that the L-factor is independent of the nitric acid concentration since both Procedures #3 and #5 using 0.5 M and 1 M nitric acid, respectively, provided L-factors of 0.72. Note that the L-factor for Procedure #4 was not measured since it used the same nitric acid concentration as Procedure #3. L-factor determinations for Procedures #6, #7, and #8 are not applicable since the resins were subjected to Procedures #3, #4, and #5 as the first part of performing them.

I-factors for resin pre-conditioned with 0.24 M sodium hydroxide solution (Procedures #3 and #6) averaged 1.11 while those for resin pre-conditioned with 0.84 M sodium hydroxide averaged 1.25 with a standard deviation of 0.028, or 2.3%. Note that the I-factors recorded in Table 3.7 for Procedures #6, #7, and #8 are the averages derived from converting the sodium-form resin produced from the respective single-wash procedure to the hydrogen form and then conversion to the sodium form.

Table 3.7. L and I Factors for Pre-Conditioned Resins

Procedure	#3	#4	#5	#6	#7	#8
L-factor	0.72	Not Measured	0.72	Not Applicable	Not Applicable	Not Applicable
I-factor	1.11	1.24	1.26	1.11	1.25	1.26

The I-factors can be used to calculate the equivalent concentration of sodium on the resin. For Procedures #3 and #6, using 0.24 M sodium hydroxide, the equivalent concentration of sodium on the resin is 4.3 mmol/g dry sodium-form resin while it is more than doubled to 8.7 mmol/g dry sodium-form resin for procedures using 0.84 M sodium hydroxide. Section 5.5 provides a capacity of 3.9 mmol/g dry sodium-

form resin based on the column test in which the resin was presumed fully converted to the sodium form. The resin capacities derived from the I-factors, sodium consumption (Section 3.1.1), Resin #3 analysis, and column eluate analysis described in Section 5.5 are summarized in Table 3.8.

There appears to be good agreement between the I-factors determined for Procedures #3 and #6 and that derived from the column test. However, comparison of the capacities derived from the batch pre-conditioning results suggest that the volume and concentration of 0.24 M sodium hydroxide used in Procedures #3 and #6 was insufficient to convert all of the ion exchange sites to the sodium form. This is further confirmed by the lower sodium concentration found on the resin following pre-conditioning with 0.24 M sodium hydroxide compared to that derived from the column eluate analysis. In addition, in the column tests described later in Section 5.2, the #7 resin volume remained constant upon further 0.84 M sodium hydroxide conditioning in the column whereas the #6 resin expanded further when conditioned with 0.24 M sodium hydroxide, again indicating incomplete conversion during pre-conditioning. Comparison of the bed densities from the batch pre-conditioning and column tests, described above, also suggests incomplete conversion. Thus, the 0.84 M sodium hydroxide appears to have been sufficient to convert all of the resin to the sodium form, and 1.25 represents the true I-factor.

Table 3.8. Summary of Derived Resin Capacities and I-factors

Procedure	Method of Calculation	I-Factor	Derived Apparent Sodium Capacity (mmol/g dry sodium form resin)
#3 and #6 using 0.24 M sodium hydroxide	Sodium consumption	1.07[a]	2.9
	Mass increase	1.11	4.3
#3 using 0.24 M sodium hydroxide	Sodium concentration (indicative only)	1.06[b]	2.6
#4, #5, #7, and #8 using 0.84 M sodium hydroxide	Sodium consumption	1.17[a]	6.3
	Mass increase	1.25	8.7
0.24 M sodium hydroxide conditioning in column test	Eluate analysis	1.11[b]	4.4
(a) Derived value based on hydroxide analysis.			
(b) Derived value based on sodium analysis			

The discrepancies between the derived capacities should be addressed. The capacity derived from the I-factor of 1.25 is assumed artificially high due to the sodium on the resin being hydrated, the water of which would not be evaporated under vacuum at 50°C. Assuming the correct capacity to be 4.4 mmol/g, then the I-factor of 1.25 would represent the mass increase associated with an average 1.3 moles of water for every mole of sodium, which is not unreasonable considering that the hydration number of the sodium ion in water is generally quoted between eight and four. The resin structure would then replace some of those water molecules once the sodium is bound onto the resin. Therefore, use of the I-factor to calculate ion exchange capacities is inappropriate because it includes water of hydration as well as sodium.

The reason for the discrepancy between the capacities derived from the eluate analysis and sodium consumption is not known at present. One possibility is that the slightly acidic water remaining in the slurry after the prior water rinse neutralized some of the hydroxide content of the wash to form sodium nitrate. This phenomenon would have led to the derivation of artificially high sodium-consumption values since they are inferred from the change in hydroxide concentration. However, this appears unlikely since the volume of the post-acid wash-water rinse remaining after decantation would need to have been unreasonably high.

The best measure of the ion exchange capacity is from the column eluate analysis, from which a value of 4.4 mmol/g dry sodium form resin is derived.

3.3   Particle-Size Analysis

Resin #1 was wet-sieved with sieves ranging in size from 600 μm to 212 μm. The results tabulated in Table 3.9 show that ~58% of the as-received resin has a particle size less than 600 μm.

Resins conditioned according to Procedures #3, #6, and #8 were first dry-sieved with a 212-μm sieve, and then the fractions retained were wet-sieved using 212-μm and 300-μm sieves. The results presented in Table 3.10 clearly show that Procedure #8 using the more concentrated solutions generated more fine material than Procedures #3 and #6. There is not sufficient difference between the results from Procedures #3 and #6 to quantify the impact of multiple washes, but there is clearly no gross generation of fine particles.

Table 3.9. Wet Sieved Particle-Size Analysis of As-Received Resin

Sieve Size (μm)	Weight % of Resin Retained
212	0.57
300	1.5
355	10
425	14
500	32
600	42

Table 3.10. Particle-Size Analysis of Pre-Conditioned Resins

	Weight % of resin retained		
Sieve size (μm)	Procedure #3	Procedure #6	Procedure #8
<212 (dry sieved)	0.20	0.28	0.76
212	0.52	0.39	2.3
300	99	99	97

Dry resin passing through the sieve of mesh size 212 μm was dispersed in water and analyzed in a Malvern Mastersizer 2000 laser spectrometer. Comparison of the data should be tempered considering the uncertainty associated with the statistical significance of differences between the resins. Ideally, the pre-conditioning procedures and resin analyses would be performed multiple times to reduce the uncertainty. The results for the resins conditioned according to Procedures #3, #6, and #8 are graphically presented in Figure 3.1, and some statistics derived from the results are presented in Table 3.11. Approximately 50 vol% of the finest particles has sizes greater than 212 μm. This is presumably attributable to the ~60% expansion of the dry resin when wetted and the non-spherical nature of the material permitting needle-like particles to pass through the 212 μm sieve. The apparently large particles associated with the relatively long tail of resin #3 may be the result of contamination from the sieving operation. Note that very few large particles would be needed to have a significant impact on a volume – based distribution. Comparison of the results from Procedures #3 and #6 show the effect of double

compared to single conditioning cycles. Conditioning the resin in two cycles reduces the size and size range of the fines and so provides greater differentiation between the two size distributions. The use of the more concentrated reagents in Procedure #8 also reduced the size and size range of the finest particles, perhaps associated with a greater osmotic shock.
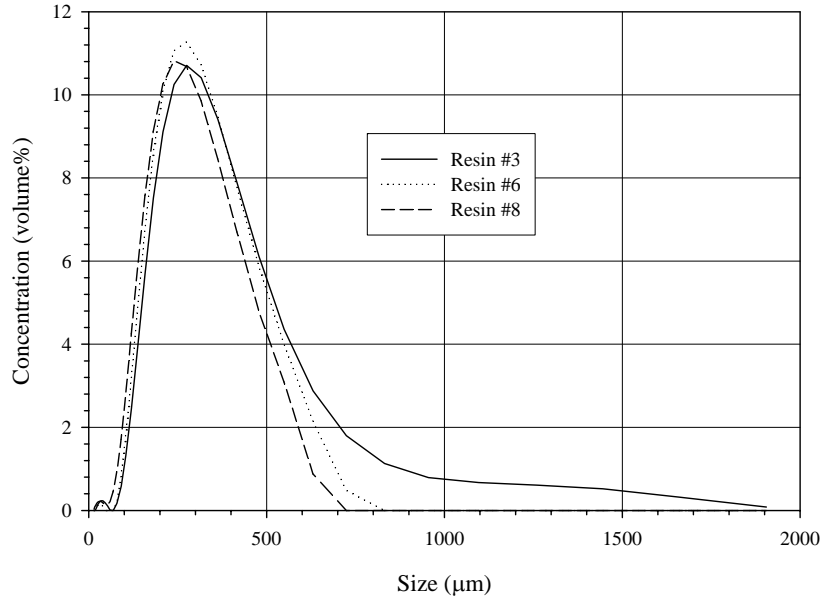
**Figure 3.1. Particle-Size Distributions of Resin of Size Less than
212 μm Conditioned with Procedures #3, #6, and #8**

Table 3.11. Pre-Conditioned Resin Fines Size Statistics

Parameter	Procedure #3	Procedure #6	Procedure #8
Maximum size (μm) of the smallest 10 vol%	160	152	131
Maximum size (μm) of the smallest 50 vol%	304	281	257
Minimum size (μm) of the largest 10 vol%	604	505	465

4.0   Batch-Contact Test Results

This section describes the affect of the mixing time, the number of pre-conditioning cycles on batch performance, the pre-conditioning reagent, and in-column water washing on the resin equilibrium performance in contact with simulated AN-105 LAW. All equilibrium distribution coefficients are reported on a fully converted sodium form mass basis to account for mass changes occurring during pre-conditioning.

4.1   Mixing-Time Evaluation

The batch contacts described in this section were largely mixed for 72 hours. However, selected contacts were performed with mixing times of 36 hours and 120 hours to ascertain the effectiveness of mixing for 72 hours in achieving chemical equilibrium. Resin #6 (pre-conditioned twice with 0.5 M nitric acid and 0.24 M sodium hydroxide) was used for this study. Figure 4.1 illustrates the effect of mixing time on the batch performance of Resin #6. The mixing time of 72 hours is evidently adequate to achieve chemical equilibrium since data for the mixing times of 72 and 120 hours are essentially identical. A mixing time of 36 hours appears not to be adequate to achieve equilibrium since the batch-distribution coefficient is ~15% lower for the abbreviated time compared to the reference or extended mixing times at the lowest cesium concentration.
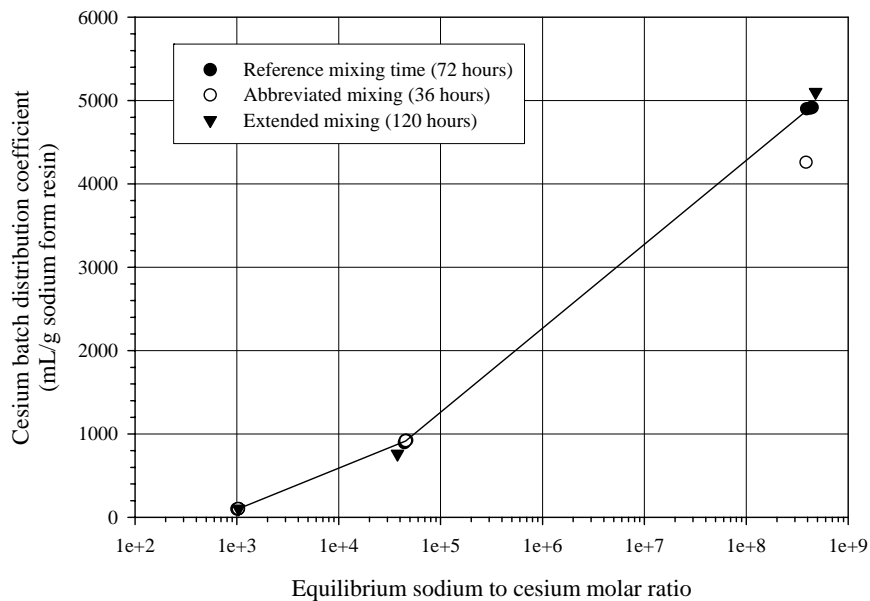

Figure 4.1. Effect of Mixing Time on the Batch Performance of Procedure #6

4.2   Effect of the Number of Pre-Conditioning Cycles on Batch Performance

The effect of the number of pre-conditioning cycles is illustrated in Figure 4.2, Figure 4.3, and Figure 4.4 for resins pre-conditioned with 0.5 M nitric acid/0.25 M sodium hydroxide, 0.5 M nitric acid/1 M sodium hydroxide, and 1 M nitric acid/1 M sodium hydroxide, respectively. The results show no significant impact of pre-conditioning or the number of pre-conditioning cycles except at the lowest cesium concentrations.

At the lowest cesium concentration, the effect of pre-conditioning is always to improve the equilibrium performance of the resin by between 13% and 36%. At least some of this improvement is probably due to the lower concentration of potassium on the pre-conditioned resin. Section 3.1.3.2 gives the potassium concentration on the as-received resin at 173 mg/g so that the 0.2 g of resin used in the batch contact would have contained ~35 mg of potassium. In comparison, the 20 mL of simulated LAW would have contained ~70 mg so that the contribution from the resin is significant. However, the effect of pre-conditioning the resin twice, compared to once, is actually to reduce the equilibrium performance for resins pre-conditioned with 0.5 M nitric acid by up to 10%. Note that the reduction is consistent, although the difference is small. For resin pre-conditioned with 1 M nitric acid, the effect of pre-conditioning the resin twice, compared to once, is to improve the equilibrium performance by ~6%.

The effect of pre-conditioning the resin, therefore, appears to improve its selectivity since this parameter becomes more important at low cesium concentrations, by washing residual potassium from the resin. However, the equilibrium performance presumably deteriorates in performing a second cycle due to chemical degradation. Chemical degradation may be the result of oxidation from oxygen dissolved in the pre-conditioning reagents since Arm et al. (2003b) have observed a similar phenomenon for the resin SL-644. A single pre-conditioning cycle appears, therefore, to be preferred when the reagents are saturated in oxygen.

Resin performance may have improved for that pre-conditioned with 1 M nitric acid due to the lower concentration of oxygen dissolved in the reagent, leading to the resin undergoing less chemical degradation so that the net effect was to improve selectivity. Therefore, multiple pre-conditioning cycles may improve resin equilibrium performance if the pre-conditioning reagents are de-aerated.
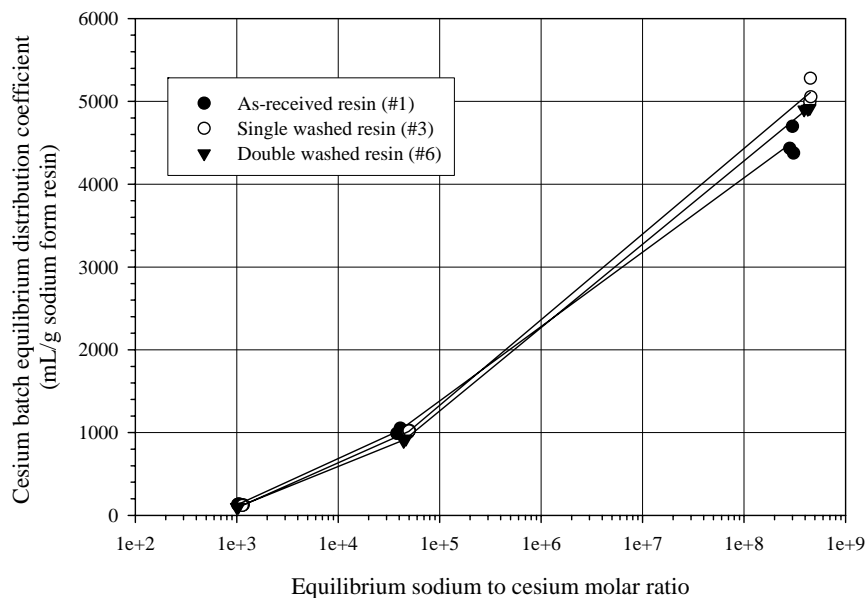
Figure 4.2. Batch-Equilibrium Performance of Resins Pre-Conditioned with 0.5 M Nitric Acid and 0.25 M Sodium Hydroxide
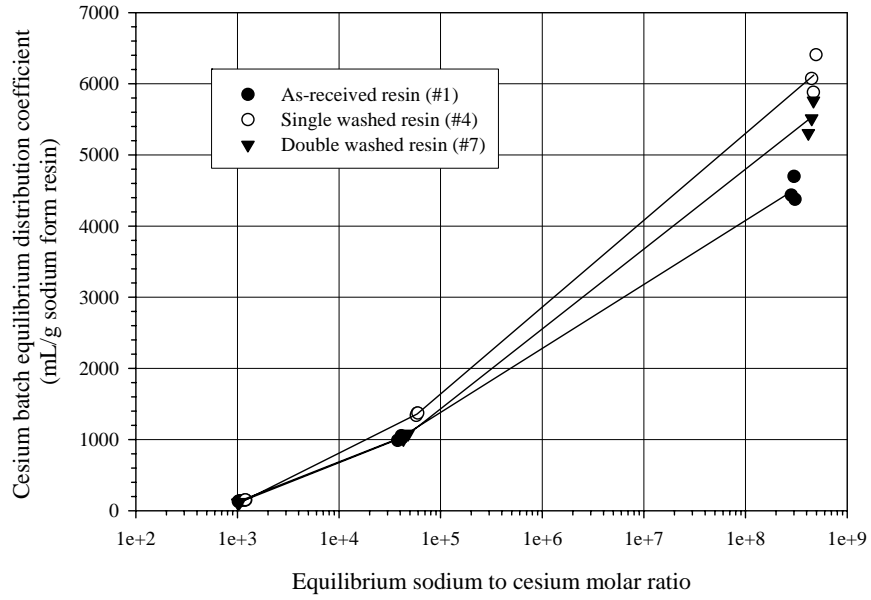
Figure 4.3. Batch-Equilibrium Performance of Resins Pre-Conditioned with 0.5 M Nitric Acid and 1 M Sodium Hydroxide
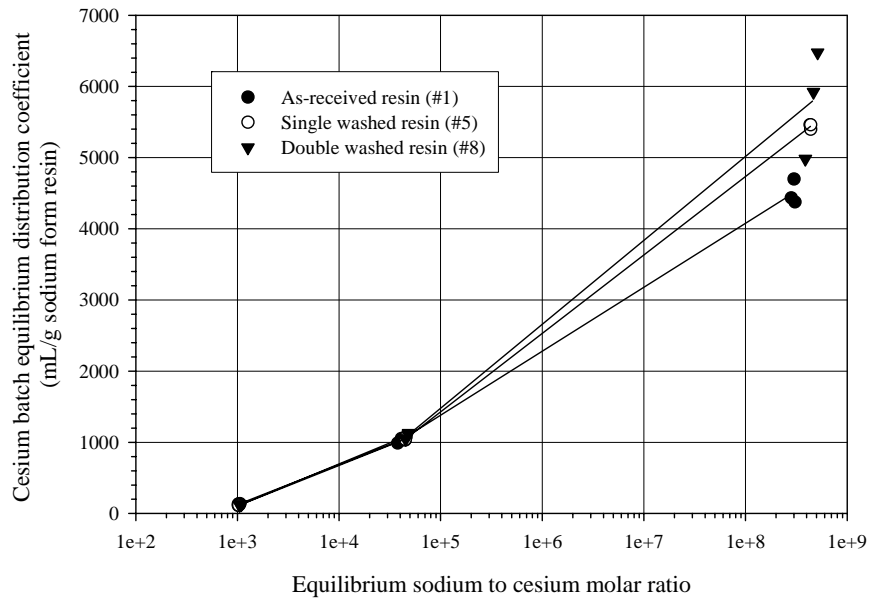
Figure 4.4. Batch-Equilibrium Performance of Resins Pre-Conditioned with 1 M Nitric Acid and 1 M Sodium Hydroxide

4.3   Effect of Pre-Conditioning Reagent

The effect of a pre-conditioning reagent on the equilibrium performance of resins pre-conditioned in a single cycle is presented in Figure 4.5. Figure 4.5 again shows the insignificant impact of pre-conditioning except at the lowest cesium concentrations.

Both acid and caustic pre-conditioning appears necessary to effect the improvement because pre-conditioning with 1 M sodium hydroxide yields improved performance compared to 0.25 M sodium hydroxide pre-conditioning when both also use 0.5 M nitric acid as the acidic pre-conditioning reagent. Therefore, 1 M sodium hydroxide is the preferred caustic pre-conditioning reagent.

Comparison of the performance of resins pre-conditioned with 0.5 M and 1 M nitric acid reagents shows the former to provide the best performance. Selectivity presumably deteriorates at the highest nitric acid concentration due to nitration of the resin. Therefore, 0.5M nitric acid is the preferred acid pre-conditioning reagent.
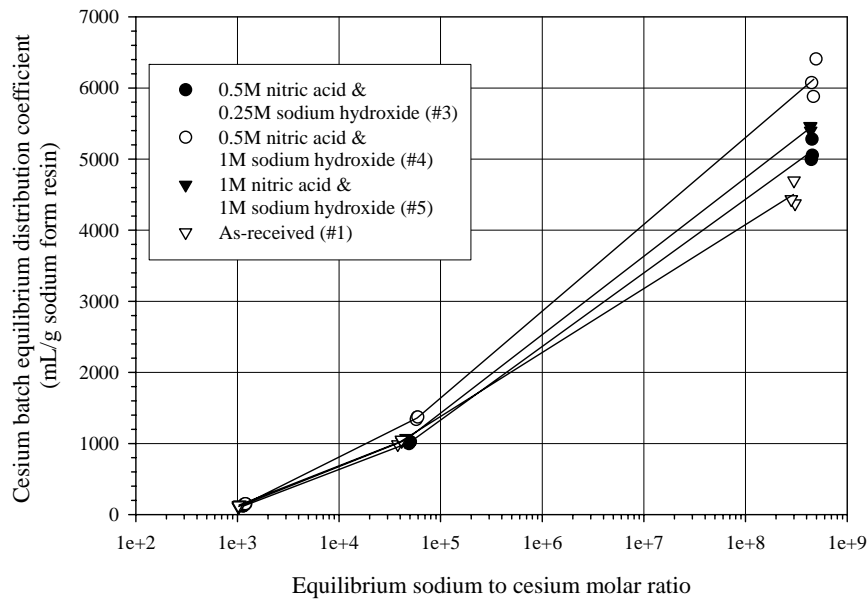

Figure 4.5. Batch-Equilibrium Performance of Resins Pre-Conditioned in a Single Cycle

4.4 Effect of In-Column Water Washing

Resin #2 had been pre-conditioned by washing it with DI water in a column at a flow rate equivalent to 3 bed volumes (BV)/h for 4 hours so that ~4 mL of dry resin was contacted with ~60 mL of water (~15:1 volume ratio). Figure 4.6 shows that the effect of performing this operation appeared to significantly degrade the resin across the studied range of cesium concentration, leading to reductions in the equilibrium distribution coefficient of between 4 and 6 times compared to the as-received resin. The reasons for such deterioration in the resin are not clear. Oxygen solubility in water is similar to that in 0.5 M nitric acid and 0.25 M sodium hydroxide at ~0.2 mmol/L, and so resin would have been exposed to actually less oxygen than in a single pre-conditioning cycle. Maybe air leaked through the screw cap of the bottle during the 2 months that it was stored and the resin degraded, or it was inadvertently opened.
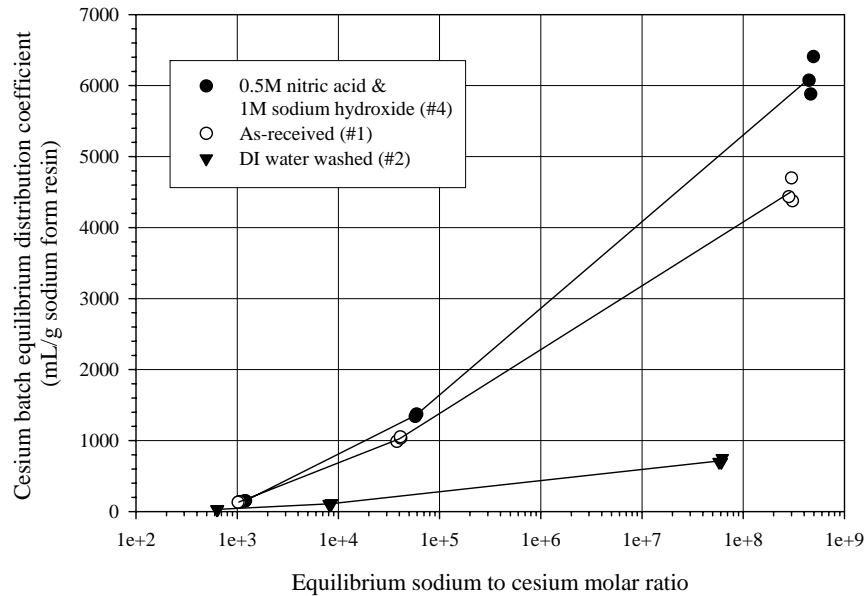

Figure 4.6. Effect of In-Column Water Washing on Batch Equilibrium Performance

5.0 Column-Test Results

This section presents the results from the column tests performed on the as-received resin (Resin #1) and resins pre-conditioned with dual cycles of 0.25 M sodium hydroxide/0.5 M nitric acid (Section 2.2.1.6, Resin #6) and 1 M sodium hydroxide/0.5 M nitric acid (Section 2.2.1.7, Resin #7) with simulated AN-105 LAW.

5.1 Bed-Volume Definition

Solution volumes and flow rates are reported relative to the resin bed volume of sodium-form resin measured in the conditioning operation immediately before processing simulated LAW. The nominal bed volume was 33 mL, providing a height to diameter ratio of 2.7.
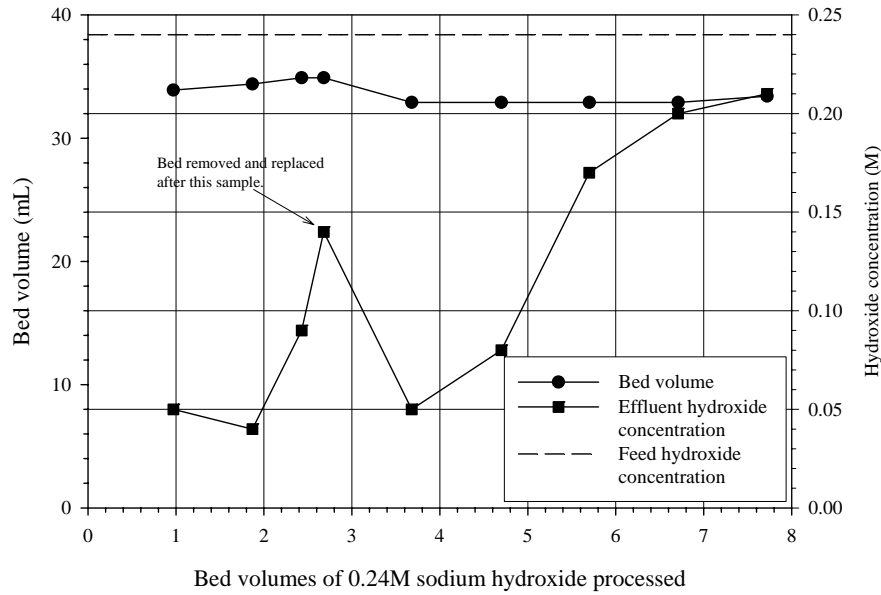
5.2 Resin Conditioning

The ion exchange resin was slurried into the column using DI water and then conditioned with sodium hydroxide solution pumped through the apparatus at 3 BV/h to process 12 BVs or until the pH of the effluent became equal to that of the feed as measured by pH paper. Effluent was collected in fractions of the same volume as the resin bed volume (~33 mL). The column tests were performed at ambient temperature, or $22\pm3^{\circ}$C.

The as-received resin was conditioned with approximately 260 mL (~7.8 BVs) of 0.24 M sodium hydroxide. As shown in Figure 5.1, the effluent hydroxide concentration increased after the second BV had been processed while the resin bed volume increased from 34 mL to 35 mL, which was probably due to the change from a near neutral to caustic chemical environment. However, the resin bed was removed from the column after approximately the third BV because a high feed pressure indicated a blockage in the apparatus. Once removed, the resin bed was rinsed with approximately 2 BVs of DI water to remove fines since these were initially but erroneously considered to be the cause of the feed high pressure. A blockage in the exit line from the bed was actually found to be the cause and subsequently removed. Sufficient resin was added back to the column to make up a bed of volume 33 mL, and conditioning was continued.

The low-effluent hydroxide concentration immediately following bed replacement shown in Figure 5.1 is attributable to water being displaced from the column. However, as before, the effluent hydroxide concentration increased after the second BV had been processed following replacement of the bed while the resin bed volume remained constant. The rate of increase in the effluent hydroxide concentration appeared to reduce as conditioning proceeded, and the concentration in the final sample, after processing ~5 BVs of solution since bed replacement, was 0.21 M (88% of the feed concentration of 0.24 M).

Resin #6 was conditioned with approximately 470 mL (~12 BVs) of 0.24 M sodium hydroxide. The resin bed expanded from 33 mL to 38 mL, as Figure 5.2 shows, and 5 mL was removed upon completion of conditioning. The effluent hydroxide concentration gradually increased to a constant value of 0.20 M, or 83% of the feed concentration. The increasing resin bed volume and the more gradual increase in the hydroxide concentration, compared to the result from conditioning the as-received resin, suggest that the resin was consuming sodium and had not been totally converted to the sodium form during pre-conditioning. The reason why the effluent hydroxide never attained that of the feed is not known, but the observation is consistent with that from conditioning the as-received resin. However, the resin appears to

5.1

have been totally converted because the resin bed volume remained constant for ~4 BVs after having increased for the first 8 BVs.

Figure 5.1. Conditioning As-Received Resin (Procedure #1) with 0.24 M Sodium Hydroxide
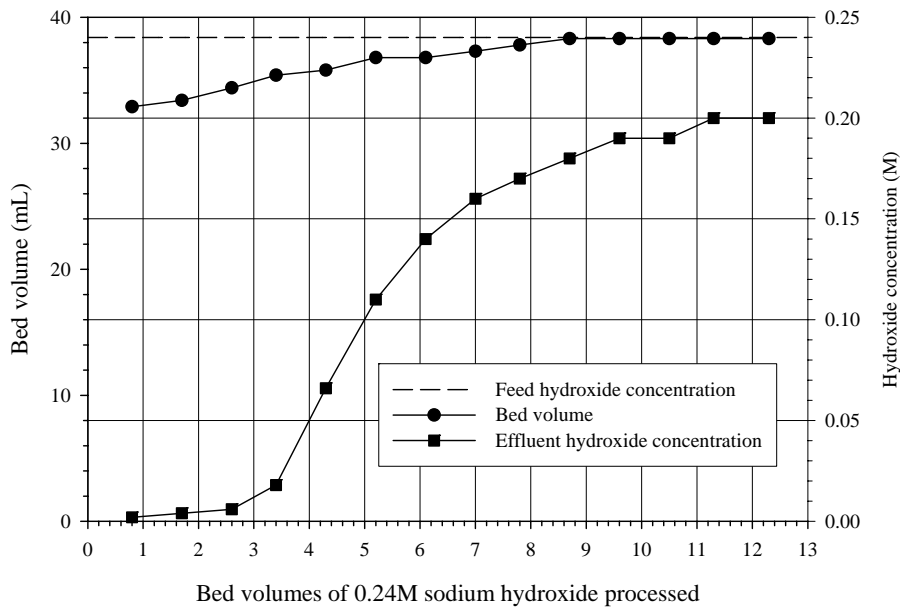
Figure 5.2. Conditioning Resin #6 with 0.24 M Sodium Hydroxide

Resin #7 was conditioned with approximately 240 mL (~7 BVs) of 0.25 M sodium hydroxide. The resin bed expanded from 33 mL to 34 mL, as Figure 5.3 shows. The small increase in the resin bed volume was again probably due to the change from a near neutral to caustic chemical environment since other results indicate the resin to have been totally converted to the sodium form during pre-conditioning. The effluent hydroxide-concentration profile is similar to that observed from conditioning the as-received

resin, attaining a constant value of ~0.8 M (95% of the feed concentration) after processing ~5 BVs of solution. Once again, the final hydroxide concentration (~0.8 M) was a little below that of the feed (0.84 M) as observed for the as-received resin and Resin #6.
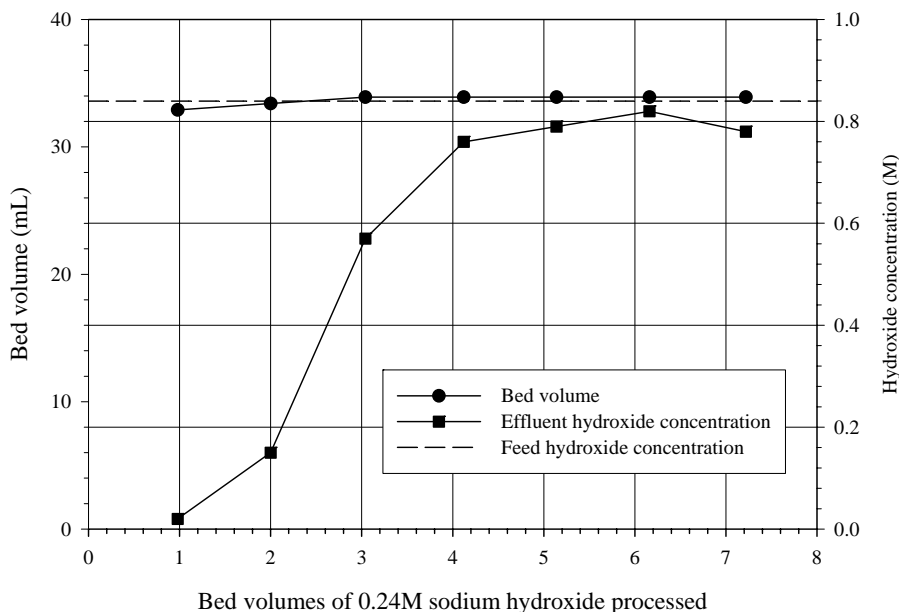
Figure 5.3. Conditioning Resin #7 with 0.84 M Sodium Hydroxide

5.3 Simulated AN-105 LAW Processing

Up to 260 BVs of simulated AN-105 LAW was processed through the column at nominally 3 BV/h. The column test with Resin #1 processed simulated LAW from Batch 1 in Table 2.1 and containing 78.5 mg/L of cesium. Batch 2 simulated LAW was processed by Resins #6 and #7 with the feeds containing 77.6 mg/L and 76.6 mg/L of cesium, respectively. Table 5.1 provides the simulated LAW processing details and shows that the BVs increased by ~3% (or ~1 mL) from the values attained during conditioning, except Resin #7, which decreased by ~3%. In addition, the table also shows that Resin #7 separated less cesium than Resins #1 or #6. The resin performance characteristics are further revealed with reference to Figure 5.4.

Figure 5.4 shows that initial breakthrough of 1% occurred after Resins #1 and #6 had processed ~140 BVs of simulated LAW, but after ~90 BVs for Resin #7. The column-distribution coefficient is the number of BVs processed at 50% breakthrough and provides a measure of resin capacity. The Resin #1 breakthrough profile was visually extrapolated to 50% breakthrough to provide a column-distribution coefficient of 220. Column-distribution coefficients of 210 and 150 were exhibited by Resins #6 and #7, respectively.

The breakthrough and batch-contact results can be compared. In theory, the product of the dry bed density and equilibrium distribution coefficient provides the column-distribution coefficient. The sodium-to-cesium molar ratios in the column feeds were 8480, 8570, and 8680 for Resins #1, #6, and #7, respectively. Therefore, the expected column-distribution coefficients are 300, 260, and 270, based on the results in Section 4.0 and the dry bed densities in Table 5.1 for Resins #1, #6, and #7, respectively. The equilibrium-distribution coefficients appear to overestimate the column-distribution coefficients by

36%, 24%, and 80% for Resins #1, #6, and #7, respectively. This phenomenon perhaps indicates that mass-transfer effects are significant and are reducing the effective capacity of the resin below equilibrium. In addition, the batch-contact results indicate that Resins #6 and #7 should have provided nearly identical performances when actually the column-distribution coefficient of Resin #7 was ~30% lower that of Resin #6. The reason for the difference is uncertain at present, but may be because some mass-transfer-affecting characteristic was impacted to a greater degree by conditioning with 1 M sodium hydroxide, resulting in a lower effective capacity. Further resin physical-property testing and microscopic analysis may be required to explain the phenomenon.

Table 5.1. Simulated LAW Processing Details

Parameter	Conditioning procedure		
	#1	**#6**	**#7**
Volume (mL)	7080	8430	6940
Volume (BVs)	210	260	200
Flow Rate (mL/h)	100	100	100
Flow Rate (BV/h)	3	3	3
Bed Volume (mL)	34	34	33
Dry Bed Density (g/mL)	0.46	0.46	0.41
Percentage of Feed Cesium Recovered in Effluent	3.8	6.7	31
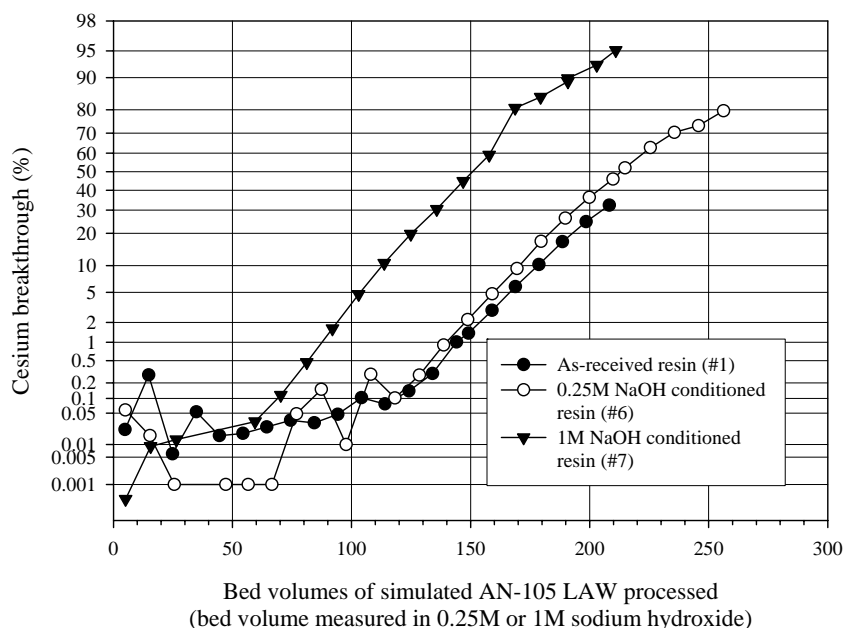
Figure 5.4. Breakthrough Profiles from As-Received and Pre-Conditioned Resins

5.4   Column Preparation for Elution

The columns were rinsed with nominally 3 BVs each of 0.1 M sodium hydroxide to displace simulated LAW (feed displacement) and DI water to displace 0.1 M sodium hydroxide (pre-elution rinse) at 3 BV/h before they were eluted. The feed displacement and pre-elution rinse process details specific to each resin are provided in Table 5.2. The BVs essentially remained the same as their values when processing simulated LAW for the two pre-conditioned resins, although the Resin #1bed volume increased by 3 mL

(~9%). The reason for the relatively large increase in the as-received resin (#1) bed volume is uncertain. It appears to be related to nitric acid pre-conditioning since all resins had by now been contacted with caustic solutions, albeit at different concentrations, and only the as-received resin had not been contacted with nitric acid.

Table 5.2. Feed Displacement and Pre-Elution Rinse Process Details

Operation	Parameter	Conditioning procedure		
		#1	#6	#7
Feed Displacement (0.1 M sodium hydroxide)	Volume (mL)	110	100	120
	Volume (BVs)	3	3	3.5
	Flow rate (mL/h)	100	100	120
	Flow rate (BV/h)	3	3	3.5
	Bed volume (mL)	37	35	34
	Dry bed density (g/mL)	0.42	0.44	0.41
	Recovered percentage of feed cesium	0.2	0.5	0.8
Pre-Elution Rinse (DI water)	Volume (mL)	100	100	120
	Volume (BVs)	3	3	3.5
	Flow rate (mL/h)	100	99	120
	Flow rate (BV/h)	3	3	3.5
	Bed volume (mL)	37	34	34
	Dry bed density (g/mL)	0.42	0.46	0.41
	Recovered percentage of feed cesium	0.0	0.0	0.1

Figure 5.5 shows the profile of hydroxide concentration in the effluents from feed displacement and the pre-elution water rinse for processing resin #6. The concentration dropped sharply during feed displacement to a value of 0.23M as the simulated LAW was displaced from the column. The hydroxide concentration reduced more slowly during the pre-elution water rinse to a final value of 0.09M. The rinse volume appears to have been inadequate to displace the feed displacement since the final hydroxide concentration was close to that in the feed displacement feed (0.1 M). The gradual reduction in the hydroxide concentration is indicative of mixing within the column, particularly in the fluid head above the bed since otherwise step changes in the concentration would be exhibited.
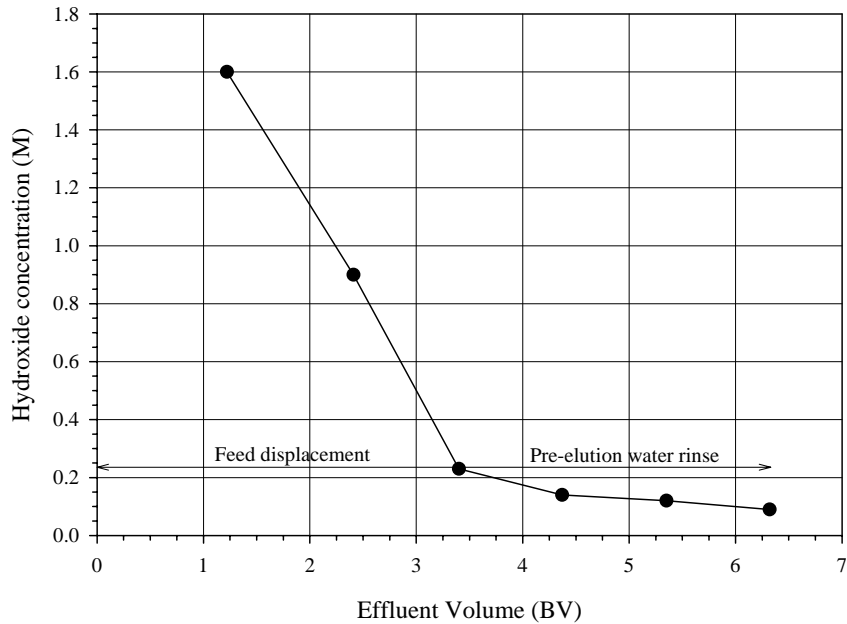
Figure 5.5. Hydroxide Concentration Profile During Feed Displacement and the Pre-Elution Water Rinse of Resin #6

5.5 Elution

The resins were eluted with nominally 30 BVs of 0.5 M nitric acid at a nominal flow rate of 1.4 BV/h. Eluate was collected in fractions of volume equivalent to a BV to obtain elution profiles expressed in terms of the eluate to simulated LAW feed cesium concentration ratios. Table 5.3 provides the process details specific to each resin and shows that the greatest quantity of cesium was recovered from Resin #6. The eluate from processing Resin #1 was analyzed and found to contain 1.35 g/L of sodium and 158 mg/L of potassium (potassium concentration for indication only). The sodium and potassium eluate concentrations and the cesium recovery shown in Table 5.3 indicate a resin capacity of 4.4 mmol/g of sodium-form resin based on the resin mass reported in Section 5.9.

Table 5.3. Elution Process Details

Parameter	Resin		
	#1	**#6**	**#7**
Volume (mL)	1040	1030	1070
Volume (BVs)	31	30	32
Flow Rate (mL/h)	47	47	48
Flow Rate (BV/h)	1.4	1.4	1.4
Final Bed Volume (mL)	29	27	26
Dry Bed Density (g/mL)	0.43	0.46	0.43
Percentage of Feed Cesium Recovered in Eluate	90.3	92.3	86.2
Quantity of Cesium Recovered in Eluate (mmoles)	3.8	4.5	3.6

Figure 5.6 through Figure 5.9 provide the elution, resin bed volume, and pH profiles of the as-received and pre-conditioned resins. The eluate to simulated LAW feed cesium-concentration ratios peak at ~100 when ~5 BVs of eluate were generated, and the ratio of the eluate to the simulated LAW-feed cesium concentration remains above 0.1 for ~10 BVs for every resin. The peak in the ratio of the eluate to the simulated LAW-feed cesium concentration approximately coincides with the resin attaining a constant

5.6

bed volume after reducing to 29 mL from 37 mL (22% reduction) for Resin #1 and to ~27 mL and 26 mL from 34 mL for Resins #6 and #7 (21% reduction), respectively. Figure 5.7 shows the peak in ratio of the eluate to the simulated LAW-feed cesium concentration to coincide with the eluate pH, attaining a constant value of ~0.7, or that presumably of the feed eluant. Note that there is likely significant uncertainty associated with pH values less than unity since the pH probe is not designed to operate at such pH values. The final pH of ~0.7 corresponds to an acid concentration of 0.2 M, which is considered close, given the measurement uncertainties, to the expected concentration of 0.5 M (pH of 0.3).

All of the elution profiles exhibit tailing and, in fact, appear to attain a steady final eluate to simulated LAW-feed cesium concentration ratio. Final ratios of the eluate to simulated LAW-feed cesium concentration were 0.005, 0.003, and 0.001 for Resins #1, #6, and #7, respectively, after generating ~31 BVs of eluate. Resins #1 and #6 exhibit peaks in their ratios of eluate to simulated LAW-feed cesium concentration at ~22 BVs, with the former resin exhibiting a much longer peak than that of the latter. All three resins, therefore, exhibit similar elution performance.
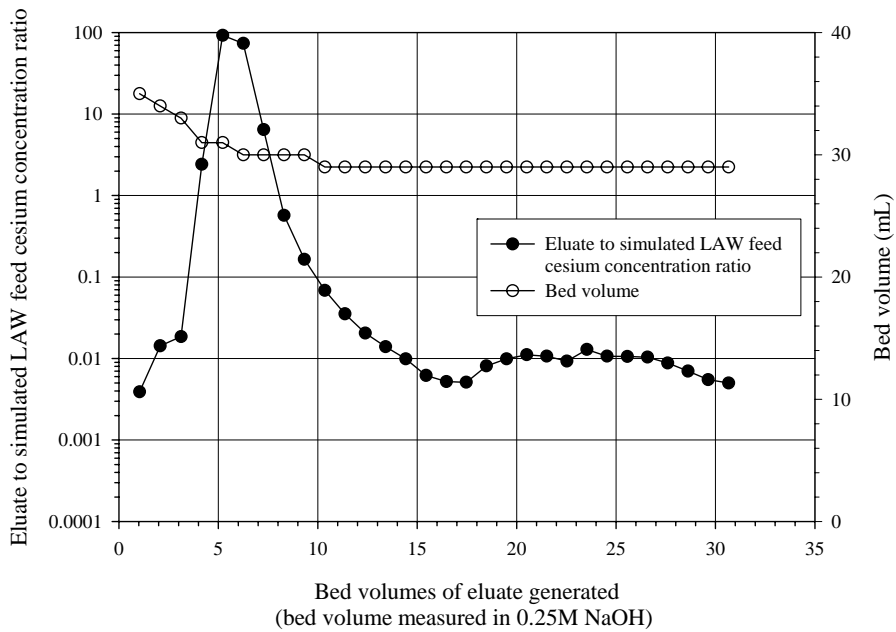
Figure 5.6. Elution and Bed Volume Profile of As-Received Resin
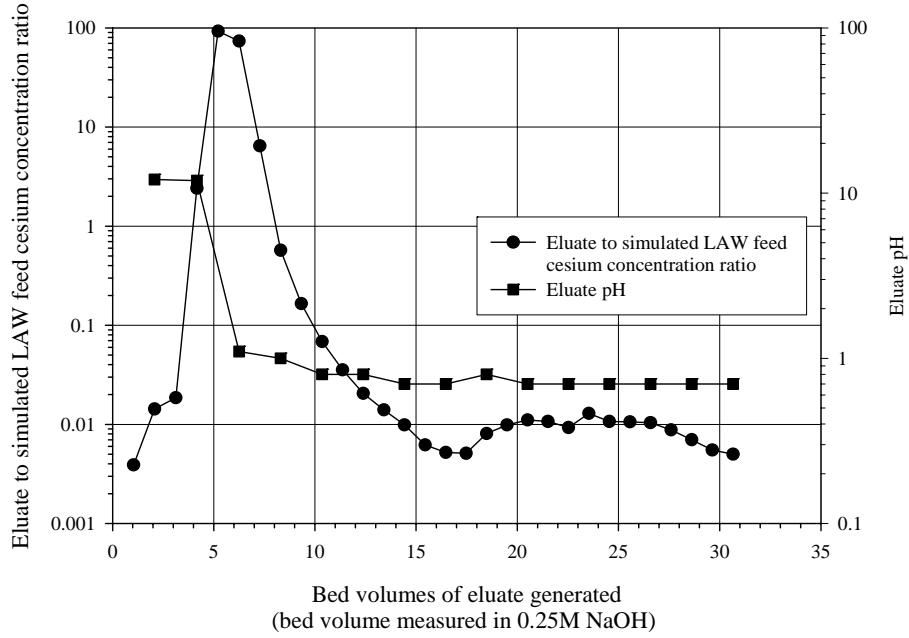
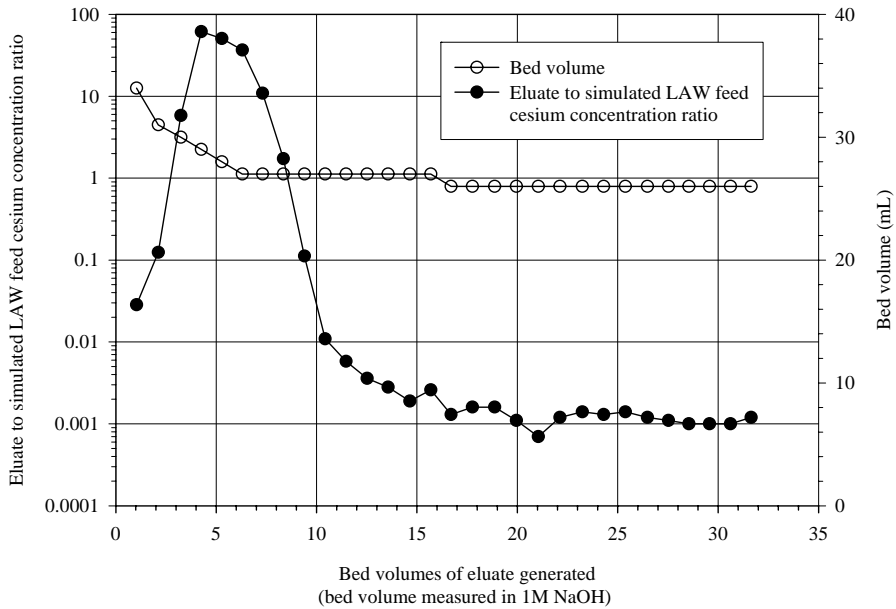**Figure 5.7. Elution and Eluate pH Profiles of As-Received Resin**
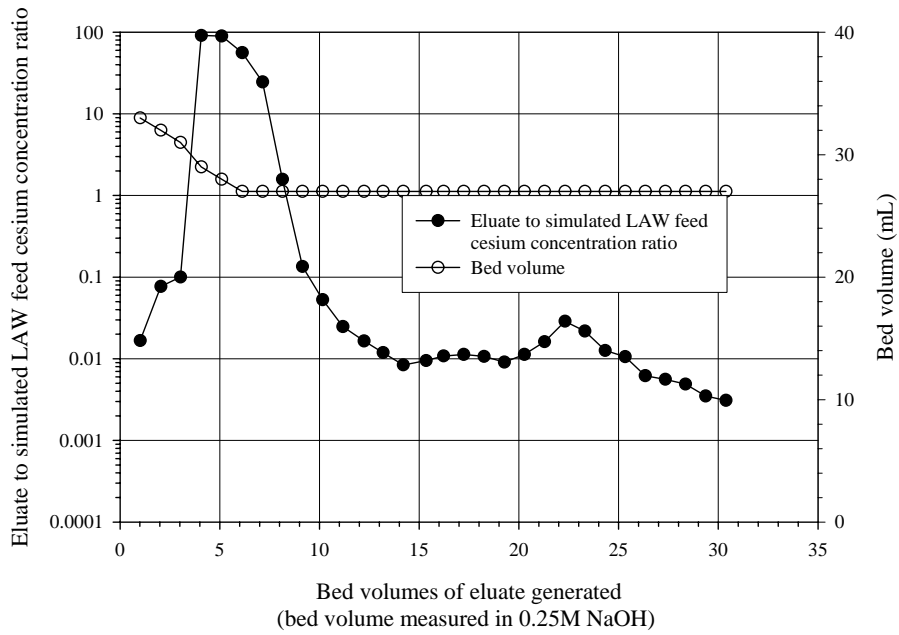
Figure 5.8. Elution and Bed Volume Profile of 0.25 M Sodium Hydroxide Pre-Conditioned Resin

Figure 5.9. Elution and Bed Volume Profile of 1 M Sodium Hydroxide Pre-Conditioned Resin

5.6   Post-Elution Rinse

The columns were rinsed with nominally 3 BVs of DI water at nominal flow rates of 3 BV/h to displace eluate. The process details specific to each resin are provided in Table 5.4 and show that the resin bed volume remained essentially the same as its final value attained during elution. Effluent was collected in fractions of the same volume as the resin bed volume expanded in the conditioning reagent (~33 mL), and those generated from rinsing the as-received resin were analyzed for pH. The effluent pH remained nearly constant at 0.7 and 0.8 in the first two fractions but then increased to 1.8 in the last fraction, indicating a residual acidity of ~0.02 M when the operation was terminated.

Table 5.4. Post-Elution Rinse Process Details

	Resin		
Parameter	**#1**	**#6**	**#7**
Volume (mL)	100	98	120
Volume (BVs)	3	3	3.5
Flow Rate (mL/h)	100	98	120
Flow Rate (BV/h)	3	3	3.6
Final Bed Volume (mL)	30	27	25
Dry Bed Density (g/mL)	0.42	0.46	0.45
Recovered Percentage of Feed Cesium	0.0	0.0	0.0

Note that total cesium recoveries of 91%, 97% and 87% are derived from Table 5.2, Table 5.3 and Table 5.4 for resins #1, #6, and #7, respectively. These recoveries are considered to be within the bounds of experimental uncertainty.

5.7 Resin Regeneration

The ion exchange resins were regenerated with sodium hydroxide solution pumped through the apparatus at 3 BV/h. Regeneration was to continue until the effluent hydroxide concentration was within 10% of that of the feed. An initial indication of the changes in hydroxide concentration was provided using pH paper, and regeneration terminated once the paper indicated that the pH of the effluent and feed were equal. Effluent was collected in fractions of the same volume as the resin bed volume (~33 mL), and samples were analyzed by potentiometric titration to determine the hydroxide concentration.

Resins #1 and #6 were regenerated with approximately 400 mL (~12 BVs) of 0.24 M sodium hydroxide. The resin bed volume and effluent hydroxide concentration profiles are shown in Figure 5.10 and Figure 5.11. The resin beds expanded by approximately 17%, from 30 mL to 35 mL and from 28 mL to 33 mL for the Resins #1 and #6, respectively, attaining constant values after processing ~10 BVs of solution in both cases. The effluent was initially slightly acidic as the post-elution rinse water was displaced, and then the hydroxide concentration increased to approximately 0.15 M when regeneration was terminated. The pH paper proved inadequate in determining feed and effluent hydroxide-concentration equality. The effluent hydroxide concentration appears not to have attained a constant value, although the resin bed volume appears to have done so. The effluent hydroxide-concentration profiles cannot be extrapolated with certainty to provide a total volume required for complete hydroxide breakthrough because the rate of increase appears to decrease. However, a linear extrapolation of the profiles indicate that ~16 BVs of 0.24 M sodium hydroxide would have been required for complete hydroxide breakthrough for both resins.
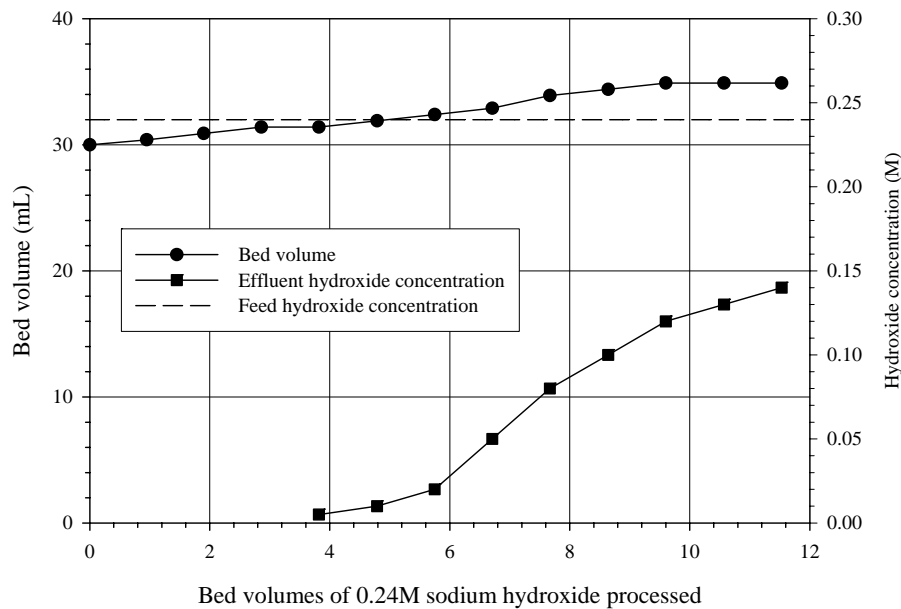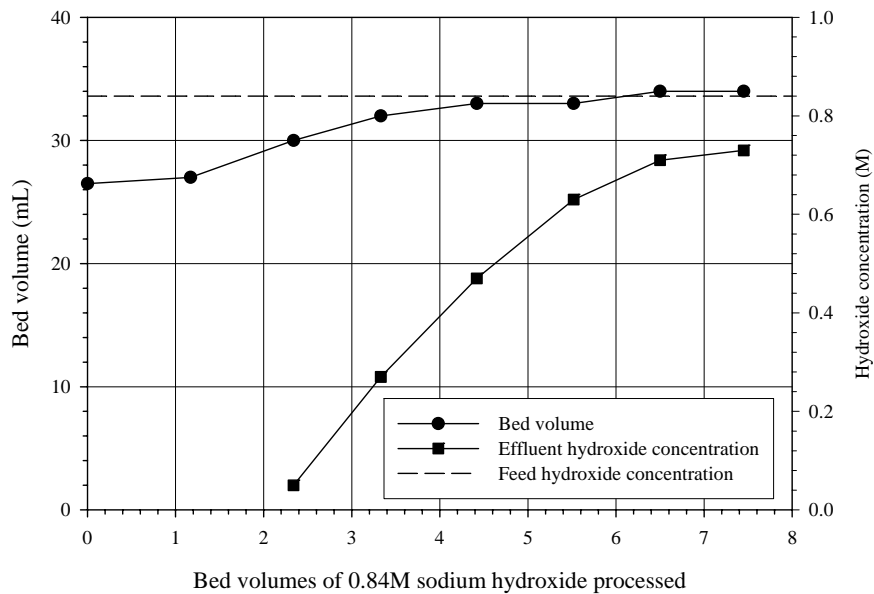

Figure 5.10. Regeneration of Resin #1 with 0.24 M Sodium Hydroxide
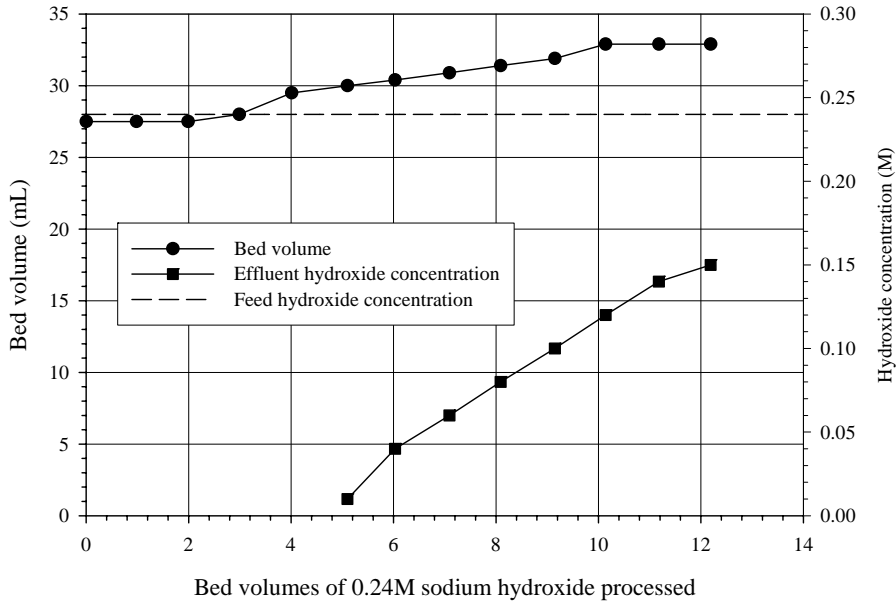
Figure 5.11. Regeneration of Resin #6 with 0.24 M Sodium Hydroxide

Resin #7 was regenerated with approximately 250 mL (~7 BVs) of 0.84 M sodium hydroxide, and the resin bed expanded from 26 mL to 34 mL or by ~30%, as Figure 5.12 shows, attaining a constant value after processing ~4 BVs of solution. The effluent hydroxide concentration increased sharply after the post-elution rinse water had been displaced and appears to have attained a nearly constant value of ~0.75 M or ~0.09 M less than the feed after processing 8 BVs.

Figure 5.12. Regeneration of Resin #7 with 0.84 M Sodium Hydroxide

Note that the effluent became caustic after processing ~2 BVs of 0.84 M sodium hydroxide compared to nearly 4 BVs of 0.24 M sodium hydroxide. This was probably due to the greater capacity of the 0.84 M

solution to neutralize the mildly acidic post-elution rinse water remaining in the column. Therefore, there appears to be significant mixing of feed with the existing solution in the head of fluid above the bed so that the concentration of hydroxide entering the bed is also increasing. This phenomenon may account for the bed attaining a constant volume before the effluent hydroxide concentration since the latter would continue to increase due to the mixing effect, although the resin was presumably fully converted as indicated by the constant resin bed volume.

The volume of 0.84 M sodium hydroxide required to achieve constant resin bed volume was approximately half that required by 0.24 M sodium hydroxide. Therefore, using 0.24 M sodium hydroxide to regenerate the resin would require less raw chemicals and would lead to a smaller addition of sodium to the LAW. However, final down-selection of regeneration reagent needs also to consider its impact on column performance when processing LAW in both lead and polishing positions.

5.8 Cesium-free Simulated LAW Processing

Cesium-free simulated AN-105 LAW was processed at 3 BV/h through the columns containing the pre-conditioned resins previously used to process simulated LAW containing cesium to assess the removal of cesium remaining on the resin after elution. Resins #6 and #7 processed approximately 1650 mL (~50 BVs) and 1590 mL (~50 BVs) of solution, respectively. The BVs remained essentially the same as their final values attained during regeneration. Samples of effluent were collected and analyzed by GEA to ascertain their cesium-137 concentrations. The cesium-133 concentration was determined from the cesium-137 to cesium-133 ratio in the feed used in the breakthrough test.

Figure 5.13 illustrates the breakthrough of cesium-133 for Resins #6 and #7 compared to the concentration of 0.004 mg/L equivalent to the Envelope A contract limit for cesium-137 of 0.087 mCi/L, assuming that the total cesium concentration in Envelope A LAW is four times that of cesium-137. The figure shows that the cesium concentrations in the effluents from both resins exceeded the limit, indicating that a freshly eluted column placed in the polishing position would fail to produce an adequately decontaminated LAW product. Effluents from Resin #6 contained cesium at concentrations between 40 and 20 times the limit while those from Resin #7 were between 8 and 3 times, although the concentrations in the effluents from both resins were decreasing when the operation was terminated.

The worse performance of Resin #6 may have, at least in part, been due to the presumed higher concentration of cesium on the resin. However, the concentrations of cesium on the resins upon completion of LAW processing were close at 0.29 mmol/g of dry sodium-form resin and 0.26 mmol/g dry sodium-form resin for Resins #6 and #7, respectively, based on the quantities of cesium recovered in the eluate given in Table 5.3 and the resin masses in Section 5.9. A more probable reason may be the greater porosity of the #7 resin bed, as indicated by the lower dry-bed densities, both at the start of elution (Table 5.2) and after (Table 5.3) since a lower density would favor more efficient elution as the resin structure is more accessible. Note that the molar ratio of sodium to cesium in the cesium-loaded simulated LAW was ~8500, which is comparable to the value for actual AZ-102 LAW of 8850 found by Fiskum et al. (2003b), so these results are applicable to processing actual waste, albeit for the highest cesium concentration. These results appear to suggest that resin elution beyond 30 BVs would be required before the eluted column is placed in the polishing position in the WTP since the product would otherwise become unacceptably contaminated.
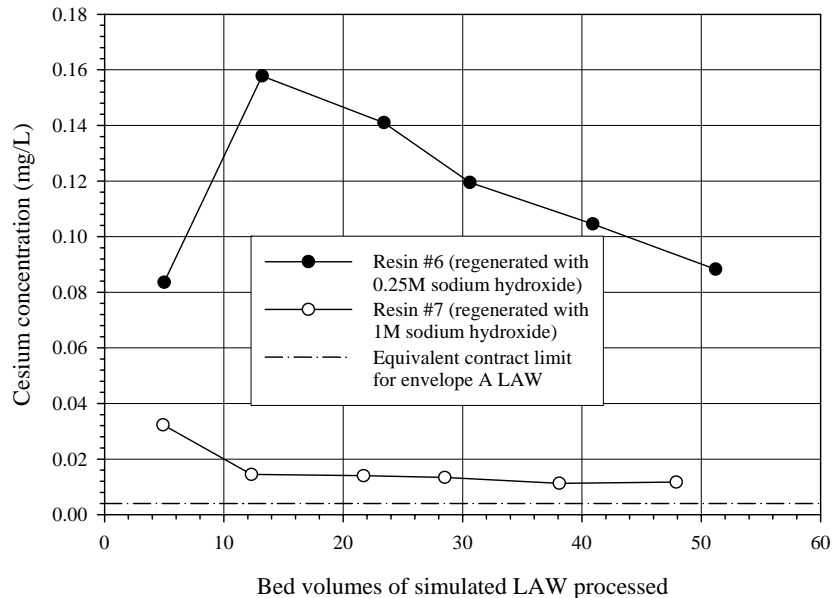
Figure 5.13. Cesium Breakthrough Processing Cesium-Free Simulated AN-105 LAW

5.9 Final Rinsing, Bed Removal, and Residual Cesium Analysis

The columns containing pre-conditioned resin were rinsed with nominally 3 BVs each of 0.1 M sodium hydroxide to displace simulated LAW (feed displacement) and DI water to displace 0.1 M sodium hydroxide (pre-elution rinse) at 3 BV/h before the resin was removed. Resin #1 was removed from the column after rinsing with DI water. The resins were dried in air under ambient conditions to a free-flowing state, and then samples were further dried at 50°C at atmospheric pressure. The final bed weights, which were used to determine bed densities, are provided in Table 5.5; initial weights were not measured.

Table 5.5. Final Sodium Form Resin Bed Weights

Resin	Bed Weight Dried at 50°C and Atmospheric Pressure (g)
#1	15.6
#6	15.5
#7	14.0

Resin #1 was digested and the digestate analyzed by ICP-MS for cesium. The equivalent cesium concentration on the resin was determined to be 31.6 µg/g or 0.23 µmol/g. Elution had therefore reduced the cesium concentration on the resin by a factor of ~1000. If the resin had been processing waste containing cesium of which a quarter was cesium-137, the ratio found by Kurath et al. (2000a) and Kurath et al. (2000b) for Envelope A AW-101 and Envelope C AN-107 LAW samples, then the residual activity would have been 0.69 mCi/g (325 Ci/m^3). Hassan et al. (2001) found that the fraction of cesium-137 in the total cesium in an Envelope B AZ-102 LAW sample was a third. If this value were assumed, then the residual cesium-137 activity would have been 0.92 mCi/g (430 Ci/m^3). These concentrations are factors of >20 higher than that of the 30 µCi/g derived by Arm et al. (2003b) for SL-644 resin having been cycled 25 times with simulated AN-105 LAW. In addition, these values are between the Hanford Site Solid Waste Acceptance Criteria (McDowell 2002) Category 1 and 3 limits (5.5×10^{-3} Ci/m^3 and 12,000

Ci/m^3, respectively) indicating that the spent resin from WTP would have to be dispositioned in high-integrity containers. Again, note that the molar ratio of sodium to cesium in the cesium-loaded simulated LAW was ~8500, which is comparable to the lowest value for actual AZ-102 LAW of 8850 found by Fiskum et al. (2003b), so these results are applicable to processing actual waste, albeit for the highest cesium concentration. Therefore, further elution beyond 30 BVs would appear required for the same residual cesium-137 contents of the RF and SL$^{®}$644 resins.

6.0   Conclusions

- Pre-conditioning the resin had no adverse impact on its equilibrium performance at the cesium concentrations expected in the LAW feeds to WTP. At cesium concentrations comparable to those expected in the product from the WTP ion exchange system, pre-conditioning improved resin equilibrium performance by up to 36%. Therefore, pre-conditioning appears to improve resin selectivity, which becomes more important at low-cesium concentrations.

- The best equilibrium performance was achieved by pre-conditioning the resin with first 0.5 M nitric acid and then with 1 M sodium hydroxide after an intermediate water rinse. Further pre-conditioning led to deterioration in the equilibrium performance, presumably as a result of chemical degradation.
    - There was a 28% reduction in the mass of resin upon washing the as-received resin with nitric acid, leading to an L-factor of 0.72.
    - The mass increase factor upon completely converting the resin from the acid to sodium form (I-factor) was 1.25.
    - Subjecting the resin to a single pre-conditioning cycle reduces the potassium content of the resin by a factor of ~220. The potassium is presumably residual from the resin's manufacture and is significant in impairing the equilibrium performance of the as-received resin.
    - Greater leaching of organic constituents from the resin occurred using 1 M sodium hydroxide rather than 0.25 M sodium hydroxide, but this did not appear to impair performance. There was no difference in organic leaching when using 1 M or 0.5 M nitric acid.
    - Pre-conditioning leads to the breakage of resin particles and the formation of "fines" of 300 μm average size. The smallest particle sizes and range occurred with the most concentrated reagents, although there was no gross generation of fines.

- There was no clear preferred pre-conditioning method based on the column performance.
    - The as-received resin provided the best column performance processing simulated LAW containing cesium at a concentration of 78 mg/L, comparable to the highest observed in the actual LAW, providing a column-distribution coefficient of 220. Mass-transfer effects appeared to reduce the column performance below that expected from the equilibrium behavior. In addition, there appeared to be some mass-transfer-affecting characteristic impacted to a greater degree by conditioning with 1 M sodium hydroxide, compared to 0.25 M sodium hydroxide. The result was that the column-distribution coefficient achieved with resin pre-conditioned with 1 M sodium hydroxide was ~30% lower than that achieved with the resin pre-conditioned with 0.25 M sodium hydroxide, though equilibrium behavior predicted similar values.
    - Pre-conditioning had no significant impact on the elution performance. The cesium concentration in the eluate peaked upon generating 5 BVs of eluate and had reduced to less than 1% of that in the LAW feed after generating 30 BVs. Chemical analysis of the as-received resin after its regeneration showed that elution had reduced its cesium concentration by a factor of ~1000. However, the residual cesium concentration was ~20 times higher than previously observed on SL-644.
    - Processing 50 BVs of cesium-free simulated LAW through the pre-conditioned resins previously used to process simulated LAW containing cesium led to a product containing cesium at concentrations higher than the WTP specification. However, the resin pre-conditioned with 1 M sodium hydroxide provided the lowest cesium concentrations at between 8 and 3 times the WTP specification compared to factors between 40 and 20 for the 0.25 M sodium hydroxide pre-conditioned resin. This phenomenon may have been as a result of the lower bed density of the 1

M sodium hydroxide pre-conditioned resin, allowing greater fluid accessibility and more complete elution.

- The fastest column resin conditioning and regeneration was achieved with 1 M sodium hydroxide. The volume of 1 M sodium hydroxide required to achieve a constant resin bed volume was approximately half that required using 0.25 M sodium hydroxide, although analysis is complicated by the mixing effect associated with the head of fluid above the bed. Therefore, conditioning and regenerating with 0.25 M sodium hydroxide appears to require less raw chemicals and would lead to a smaller addition of sodium to the LAW. However, the contribution of the conditioning and regeneration reagent selection compared to the resin pre-conditioning procedure to column performance needs to be better understood to facilitate a final down-selection.

7.0   Recommendations

7.1   Pre-conditioning Procedure

Procedure #4 is the recommended pre-conditioning procedure considering the overall performance of the conditioned resin in batch contact and column tests. Procedure #4 involves washing the as-received resin twice with 0.5M nitric acid before rinsing it three times with DI water. The resin is then washed with 1M sodium hydroxide once and again rinsed three times with DI water.

7.2   Regeneration Procedure

Regeneration can be either accomplished with 12 BVs of 0.25M sodium hydroxide to minimize reagent use and the addition of sodium to the LAW, or 7 BVs of 1M sodium hydroxide to minimize processing time. However, the column performance of resin pre-conditioned according to the recommended procedure in section 7.1 and regenerated with 0.25M sodium hydroxide requires verification.

8.0   References

Arm ST, DL Blanchard, PK Berry, SJ Bos, SA Bryan, JR DesChane, GS Klinger, AV Mitroshkov, KB Olsen, BM Rapko, RL Russell, RL Sell. *Radiation Stability Testing of SuperLig® 639 and SuperLig® 644 Resins.* 2003a, PNWD-3239, Battelle—Pacific Northwest Division, Richland, WA.

Arm ST, DL Blanchard, SK Fiskum and DR Weier. 2003b. *Chemical Degradation of SuperLig®644 Ion Exchange Resin.* PNWD-3315, Battelle—Pacific Northwest Division, Richland, WA.

Fiskum SK, DL Blanchard Jr., MJ Steele and JJ Wagner. *Analysis of SuperLig® 644 Resin Used in Hanford Tank Waste Processing.* 2003a, PNWD-3353, Battelle—Pacific Northwest Division, Richland, WA. See also references therein.

Fiskum SK, ST Arm and DL Blanchard, Jr. 2003b. *Small Column Ion Exchange Testing of SuperLig®644 for Removal of ^{137}Cs from Hanford Waste Tank 241-AZ-102 Concentrate (Envelope B).* PNWD-3267, Battelle—Pacific Northwest Division, Richland, WA.

Hassan NM, WD King, DJ McCabe, and ML Crowder. 2001. *Small-Scale Ion Exchange Removal of Cesium and Technetium from Envelope B Hanford Tank 241-AZ-102*, WSRC-TR-2000-00419, Westinghouse Savannah River Company, Aiken, SC.

Kurath DE, DL Blanchard, and JR Bontha. 2000a. *Small Column Ion Exchange Testing of Superlig 644 for Removal of ^{137}Cs from Hanford Tank Waste Envelope A (Tank 241-AW-101)*, PNWD-3001, Battelle—Pacific Northwest Division, Richland, WA.

Kurath DE, DL Blanchard, and JR Bontha. 2000b. *Small Column Ion Exchange Testing of Superlig 644 for Removal of ^{137}Cs from Hanford Tank Waste Envelope C (Tank 241-AN-107)*, PNWD-3039, Battelle—Pacific Northwest Division, Richland, WA.

McDowell AK. 2002. *Hanford Site Solid Waste Acceptance Criteria*, HNF-EP-0063, Fluor Hanford, Richland, Washington.

Distribution

**No. of
Copies**

**No. of
Copies**

OFFSITE

ONSITE

2   <u>Savannah River Technology Center</u>
Jim Marra
Building 773-43A
Aiken, South Carolina 29808

Harold Sturm
Building 773-A
Aiken, South Carolina 29808

7	<u>Battelle—Pacific Northwest Division</u>	
	S. T. Arm	P7-28
	D. L. Blanchard	P7-25
	D. E. Kurath	P7-28
	Project Office (2)	P7-28
	Information Release (2)	K1-06

3	<u>Bechtel National, Inc.</u>	
	J. F. Doyle	H4-02
	R. A. Peterson	H4-02
	M. R. Thorson	H4-02