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Aging Effects of Stored SuperLig®644 Ion Exchange Resin

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January 2004

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For W.L. Tamosaitis
ACCEPTED FOR
WTP PROJECT USE

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Test specification: 24590-PTF-TSP-RT-01-010, revision 0
Test plan: TP-RPP-WTP-166, revision 0
Test exceptions: 24590-WTP-TEF-03-034
R&T focus area: Pretreatment
Test Scoping Statement(s): B-53

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Completeness of Testing

This report describes the results of work and testing specified by test plan TP-RPP-WTP-166, Rev. 0 and test specification 24590-PTF-TSP-RT-01-010. 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

Gordon H. Beeman, Manager
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1/26/04
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-137 separation.

Objectives

This investigation was conducted according to the test plan prepared by Blanchard(a) in response to the test specification of Toth(b) and test scoping statement B-53 by Barnes et al.(c) The primary objective of this task was to determine the effect of storage conditions on resin performance. The test objective was satisfied, as described later in this summary.

Test Exceptions

Table S.1 describes the test exceptions initiated by Toth(d) for this test.

Table S.1. Test Exceptions

Test exception	Discussion
Do not perform any SuperLig®639 tests.	Based on review by the RPP-WTP project and the Office of River Protection, it has been determined that pretreatment technetium removal is not required in the WTP. Therefore, storage and aging testing of the SuperLig®639 is not required.
Change the storage temperatures from 20 ± 2^{o}C to 24 ± 2^{o}C.	The storage temperature in the test plan(a) is given as 20 ± 2^{o}C. However, the room temperature is between 22^{o}C and 25^{o}C. No adverse impact on satisfying the objective.
Increase the sample size used in the batch contacts to 0.2. Extend the batch contact times from 72 hours to 96 hours.	The test plan(a) indicates using 0.1g of resin and 10 mL of simulated LAW in the batch contact tests. The quantity of resin proposed may have been insufficient for sampling, due to the larger particle size of the resin (20/70 mesh).
Batch contact tests of resin after storage shall be performed in the stored form, without acid pretreatment prior to the batch contact.	Batch contact tests are performed on resins after storage. Pretreatment of the resin after storage and before batch contacts requires acid contact. Arm et al. (2003b) have shown that contacting the resins with acid prior to performing the batch contacts may reduce the capacity of the resin.

(a) Blanchard DL. 2002. *Measuring Physical and Chemical Properties of SuperLig®644 and SuperLig®639 Resins After Storage.* TP-RPP-WTP-166, Battelle—Pacific Northwest Division, Richland, WA.

(b) Toth JJ. 2002. *Measuring Physical and Chemical Properties of SuperLig®644 and SuperLig®639 Resins After Storage.* 24590-PTF-TSP-RT-01-010, RPP-WTP, Richland, WA.

(c) Barnes S, R Roosa, and R Peterson. 2001. *Research and Technology Plan.* 24590-WTP-PL-RT-01-002, Rev. 1, RPP-WTP project, Richland, WA.

(d) Toth JJ. 2003. Test exception 24590-WTP-TEF-RT-03-034, revision 0, RPP-WTP, Richland, WA.

Results and Performance Against Success Criteria

As described by Toth[(a)], the RPP-WTP project would consider this test successful when data are obtained to demonstrate the effect of storage temperature, storage medium, time in storage and the cation form of the resin on ion exchange performance. This success criterion was satisfied, as described later in this summary.

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.

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 has a contractual requirement to compare the results of such testing with those from similar tests using actual LAW. However, the conclusions from the tests described in this report are not expected to be dependent upon the waste composition since the objective is concerned with storage and not performance, except as a means of assessing the storage conditions. Therefore, tests with actual waste are not required.

Test Methodology

Small aliquots of SL-644 cesium ion exchange resin from Lot C-01-05-28-02-35-60 (the "25-gallon" batch) were stored under various conditions for up to 6 months. Storage time (up to 6 months), storage temperature (ambient and 40°C), storage medium (dry or submerged in DI water), storage cover gas (air or nitrogen) and resin form (as-received, sodium, or acid) were the conditions tested according to a partial factorial test design. Up to 40 mL of resin were stored in 40-mL vials loosely capped to minimize the evaporation of water while allowing the vial headspace to be open to the atmosphere. Resins stored wet were kept under DI water to a depth of approximately 10 mm above the resin-bed surface. No attempt

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(a) Toth JJ. 2002. *Measuring Physical and Chemical Properties of SuperLig®644 and SuperLig®639 Resins After Storage.* 24590-PTF-TSP-RT-01-010, RPP-WTP, Richland, WA.

(b) Blanchard DL. 2002. *Measuring Physical and Chemical Properties of SuperLig®644 and SuperLig®639 Resins After Storage.* TP-RPP-WTP-166, Battelle—Pacific Northwest Division, Richland, WA.

was made to de-aerate the DI water, which was assumed saturated with air. Resins stored in air at ambient temperature were kept in the open laboratory on a bench while a dry bath was used to store those in air at 40°C. A modified vacuum oven was used to store resins at 40°C under a nitrogen cover gas, and a pressurized paint tank was used to store resins at ambient temperature under nitrogen cover gas.

Batch-contact tests were performed to ascertain the impact of storage conditions on the equilibrium performance. The batch-contact tests were performed by contacting approximately 0.2 g of resin with 20 mL of simulated AW-101 low-activity waste (LAW) at cesium concentrations of nominally 5 mg/L, 150 mg/L, and 700 mg/L. The resin was contacted in the form that it was stored (i.e., either acid, sodium, or as-received).

Single-column tests were performed on the initial resin loaded in columns in the as-received, acid, and sodium forms and on the best performing resin stored dry in air for 6 months (the acid-form resin stored at ambient temperature). The apparatus consisted of an ion exchange column containing nominally 15 mL of SL-644 resin expanded in 0.25 M NaOH, a metering pump, a pressure relief valve, a pressure gage, and three 3-way valves. The as-received resin was first conditioned by rinsing it with DI water, 0.5 M nitric, again with DI water and then 0.25 M sodium hydroxide. The acid form and stored resins were rinsed with DI water and 0.25 M sodium hydroxide while the sodium-form resin was only rinsed with 0.25 M sodium hydroxide. All of the resins were then subjected to a load-elute cycle in which they processed a dummy simulated LAW and 0.1 M sodium hydroxide and DI water rinses before being converted to the acid form with 0.5 M nitric acid. A DI water rinse was followed by regeneration with 0.25 M sodium hydroxide to convert the resin back to the sodium form. The simulated AW-101 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 test finished with a rinse of DI water. Simulated LAW effluent and eluate samples were periodically collected to monitor cesium-exchange behavior. The bed height and effluent bottle mass were measured during sampling events. The samples and composite effluents were analyzed by GEA for their cesium-137 content. The concentrations of metals and anions were determined in the composite eluates.

Test Results

Resin equilibrium-distribution coefficients and column performance decreased with increasing storage time. However, the rate of reduction in the equilibrium-distribution coefficient decreased with increasing time. In general, the acid form of the resin provided the best performance throughout storage for the same time, temperature, medium, and cover gas, and significantly better performance was obtained when the resin was stored submerged in DI water. The form of the resin and its storage medium appeared to affect the deterioration in both the resin's selectivity and its capacity. Whether the resin was stored at ambient temperature or 40°C had no statistically significant impact on the resin performance over the 6-month storage period at a cesium concentration representative of that in Envelope A LAW. However, performance at lower cesium concentrations was significantly worse after storage at 40°C. Likewise, resin performance was not significantly impacted whether the resin was stored under air or nitrogen cover gas at a cesium concentration representative of that in Envelope A LAW. Like temperature, the cover gas appears to mainly affect the resin's selectivity since storage under nitrogen provided better performance at lower cesium concentrations. The poorer performance at low cesium concentrations is significant because the stored resin will be used first in the polishing-column position in the WTP where the LAW feed cesium concentration is very low.

Single-column tests were performed with the resin loaded into the columns in the acid, sodium, and as-received forms upon initiation of storage (reference resins) and with the best performing resin stored dry in air after 6 months. Column-distribution coefficients of ~220 were observed for the reference resins and ~100 for the stored resin. The equilibrium-distribution coefficient underestimated the column-distribution coefficients of the reference resins by ~50%. However, the stored-resin column-distribution coefficient was predicted to within 10% by the equilibrium behavior. There appeared to be no impact of storage on the elution performance of the resin. Poor performance of the 6-month air-stored resin in the column test makes its capability to satisfy baseline cesium-removal requirements under baseline operating conditions questionable. Storage of the resin under water is expected to result in significantly better performance, but quantification of this improvement was not possible within the scope of this study. Minimization of storage time for the SL-644 resin is highly recommended.

The resin is best stored in the acid form submerged in water. Maintaining a temperature of ~23^{o}C and a nitrogen atmosphere above the resin will further reduce its rate of deterioration, but these factors have a lesser effect than resin form or storage medium.

Discrepancies and Follow-on Tests

The negligible impact of resin storage in nitrogen gas on performance was surprising because previous work (e.g., by Arm et al. (2003a)) had indicated oxidation to be the major degradation mechanism. The test therefore appears to show that oxygen within the resin may be responsible for the observed degradation. Further tests to investigate degradation mechanisms are recommended to provide the fundamental understanding needed to optimize the storage conditions.

The poor performance of the 6-month air-stored resin in the column test makes its capability to satisfy baseline cesium-removal requirements under baseline operating conditions questionable. Storage of the resin under water is expected to result in significantly better performance, but quantification of this improvement in a column test was not possible within the scope of this study. Therefore, further column tests are recommended to quantify the column performance of resin stored submerged.

Contents

Figures

Tables

Acronyms, Abbreviations, and Definitions

ASTM	American Society for Testing and Materials
AV	apparatus volume
BNI	Bechtel National, Inc.
BV	bed volume
DI	de-ionized (water)
FMI	Fluid Metering, Inc.
GEA	gamma energy analysis
HLW	high-level waste
HP	hot persulfate method
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
RPL ASO	Radiochemical Processing Laboratory Analytical Service Operations
RPP-WTP	River Protection Project – Waste Treatment Plant
SL	SuperLig®
TC	total carbon
TIC	total inorganic carbon
TOC	total organic carbon
RPP-WTP	River Protection Project-Waste Treatment Plant
WTPSP	Waste Treatment Plant Support Project

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) ion exchange resin was selected by the project to perform the cesium-137 separation and is available from IBC Advanced Technologies, Inc., American Fork, Utah. Kurath et al. (2000), Fiskum at al. (2002a), Fiskum et al. (2003a) and Fiskum et al. (2003b), for example, have tested this resin with actual waste and shown that it satisfies the performance criteria delineated by the RPP-WTP project. Arm et al. (2003a) and Arm et al. (2003b) have tested the chemical and radiolytic stability, respectively, of this resin.

The deterioration in performance of an ion exchange resin during storage is an important characteristic to understand for design and operational purposes. The rate of deterioration under different conditions will determine the shelf life of the resin and provide information for an assessment of the best means of its storage.

1.2 Objectives

The primary objective of this task was to determine the effect of storage conditions on resin performance. The parameters evaluated included storage temperature, storage medium (dry or under water), storage environment (air or inert gas), storage time (up to 6 months), and resin form (as-received, acid, or sodium). This investigation was conducted according to the test plan prepared by Blanchard(a) in response to the test specification of Toth(b) and test-scoping statement B-53 by Barnes et al.(c)

1.3 Purpose

This report documents the testing, analysis, results, and interpretations associated with the SL-644 storage investigation. The purpose of the investigation was to provide information for an assessment of the best means of storing the SL-644 ion exchange resin. The report is intended to aid the RPP-WTP project in decisions regarding the design and operation of the cesium ion exchange and resin-storage systems in the WTP.

(a) Blanchard DL. 2002. *Measuring Physical and Chemical Properties of SuperLig®644 and SuperLig®639 Resins After Storage.* TP-RPP-WTP-166, Battelle—Pacific Northwest Division, Richland, WA.

(b) Toth JJ. 2002. *Measuring Physical and Chemical Properties of SuperLig®644 and SuperLig®639 Resins After Storage.* 24590-PTF-TSP-RT-01-010, RPP-WTP, Richland, WA.

(c) Barnes S, R Roosa, and R Peterson. 2001. *Research and Technology Plan.* 24590-WTP-PL-RT-01-002, Rev. 1, RPP-WTP project, Richland, WA.

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 PNWD's procedures for this work is given by Blanchard (2002). 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 (2002), 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 by Blanchard (2002). Blank spike and/or Lab Control Sample QC failures will result in re-analyzing the sample for the particular analyte for which the spike failed. Matrix spike and/or duplicate analysis QC failures will not result in reanalyzing the sample, but probable reasons for the failure will be discussed in the analytical report to be stored in the project files. A qualitative impact assessment of the failure on the results is 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 gamma energy analysis (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 (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 for each 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 that the reported work satisfies the test plan objectives. This review procedure is part of PNWD's *WTPSP Quality Assurance Requirements and Description Manual*.

2.0 Test Design and Operation

This section describes the process for preparing simulated AW-101 LAW, preparing reagents, and preparing the ion exchange resin. It also describes the resin-storage methods, batch-contact procedure, and the ion exchange column test set-up.

2.1 SL-644 Physical Properties and Conversion Methods

2.1.1 SL-644 Receipt and Sampling

Five gallons of SL-644 cesium ion exchange resin of Lot C-01-05-28-02-35-60 were received in mid-2002 from the Savannah River Technology Center. The SL-644 was manufactured by IBC in May, 2002, as part of a 25-gal batch. The resin was shipped and stored in an airtight container submerged in water. Samples of resin were collected in October 2002 from the container according to American Society for Testing and Materials (ASTM) Method D2687-95 but modified to account for the smaller sample and container envisioned for the method. The method used to extract 1.2 L of resin in this test follows:

1. The rim of the bucket was marked every 8.4 cm to provide 10 sample positions.
2. A ½-in. PVC tube was inserted into the resin a distance of 4.4 cm from the sample mark measured towards the bucket's center.
3. The end of the tube was covered and then extracted.
4. The contents of the tube were emptied into the sample bottle by uncovering the end.
5. Steps b through d were repeated for each sample position.
6. Steps b through e were repeated twice more to collect ~1.2 L of resin.

Working batches of resin were sampled using a plastic tube formed by cutting the bulb off from a 10-mL transfer pipette. The cut end of the pipette was inserted into the resin, and the sample was extracted by removing the pipette while covering the upper end. The desired sample size was formed by extracting resin from sufficient locations positioned equidistantly around the circumference of a circle of diameter approximately 2/3 that of the container.

2.1.2 Physical-Properties Determination

2.1.2.1 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. 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.

2.1.2.2 L and I Factors

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 dry-bed density of the wet as-received resin was first determined by drying in air 5mL of the resin and determining its weight and F-factor. The L-factor was then determined by contacting 10 mL of wet as-received resin (containing a known weight of resin, given the dry bed density) three times with 50 mL of 0.5 M nitric acid for 1 hour. The resin was then rinsed five times with 50 mL of DI water before it was dried in air. The dry acid-form resin was then weighed and its F-factor determined to complete the data required for the L-factor determination.

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 sodium-form resin. The I-factor was determined by contacting 5 mL of wet acid-form resin (containing a known weight of resin, given the dry-bed density determined during the L-factor determination) three times with 25 mL of 1 M sodium hydroxide for 1 hour. The resin was then rinsed six times with 25 mL of DI water before it was dried in air. The dry sodium-form resin was then weighed and its F-factor determined to complete the data required for the I-factor determination

2.2 Preparation of Resins for Storage and Storage Methods

2.2.1 Resin Preparation

Note that equal weights of resin were originally intended to be stored to minimize the number of test variables. However, the total volume of as-received resin slurry required for conversion to the acid and sodium forms was underestimated, and the weights stored are ~50% less than those of as-received resin. Section 3.8 discusses the potential variability introduced as a result.

2.2.1.1 As-Received Resin Preparation

The as-received resin was dried under a flowing stream of nitrogen gas for 8 weeks before samples of ~8.9 g (~7.3 g dried under vacuum at $50^{o}C$) were extracted and placed into the 40-mL storage vials. Sufficient DI water was then added to the vials containing resin for submerged storage to provide a head of fluid of height ~10 mm. Thus, ~11 mL of resin was stored dry, and ~22 mL was stored submerged in DI water.

2.2.1.2 Acid-Form Resin Preparation

Approximately 900 mL of wet as-received resin was washed three times with ~4.5 L of 0.5 M nitric acid. The slurry was allowed to stand for 1 hour before the supernatant acid was decanted and the wash repeated. The resin was then rinsed three times with ~4.5 L of DI water when the supernate pH became that of DI water. The slurry was allowed to stand for 10 minutes before the supernate was decanted and the wash repeated. Approximately 700 mL of the acid-form resin was then dried under a flowing stream of nitrogen gas for 8 weeks before samples of ~5.2 g (~5.0 g dried under vacuum at $50^{o}C$) were extracted and placed into the 40-mL storage vials. Sufficient DI water was again added to the vials containing resin for submerged storage to provide a head of fluid of height ~10 mm. Thus, ~8.3 mL of resin was stored dry and ~17 mL stored submerged in DI water.

2.2.1.3 Sodium-Form Resin Preparation

Approximately 230 mL of wet acid-form resin was washed three times with ~1.2 L of 1 M sodium hydroxide. The slurry was allowed to stand for 1 hour before the supernatant sodium hydroxide was decanted and the wash repeated. The resin was then rinsed 24 times with ~1.2 L of DI water when the supernate pH became that of DI water. The slurry was allowed to stand for 10 minutes before the supernate was decanted and the wash repeated. The sodium-form resin was then dried under a flowing stream of nitrogen gas for 8 weeks before samples of ~5.9 g (~4.9 g dried under vacuum at $50^{o}C$) were extracted and placed into the 40-mL storage vials. Sufficient DI water was again added to the vials containing resin for submerged storage to provide a head of fluid of height ~10 mm. Thus, ~9 mL of resin was stored dry and ~24 mL stored submerged in DI water.

2.2.2 Resin Storage Methods

Storage time (up to 6 months), storage temperature (ambient and $40^{o}C$), storage medium (dry or wet), storage cover gas (air or nitrogen), and resin form (as-received, sodium or acid) were the parameters considered for testing. A partial factorial test design was established to assess the relevance of each condition as well as the inter-relations of conditions as detailed in Table 2.1. Note that more tests were undertaken than initially required by Blanchard[1] to fulfill the statistical requirements of the partial factorial design. Table 2.1 includes the test identification from Blanchard(a) and the test identifications used throughout this report.

The 40-mL storage vials were loosely capped to minimize the evaporation of water while allowing the vial headspace to be open to the atmosphere. Resins stored wet were kept submerged under DI water to a depth of approximately 10 mm above the resin-bed surface. No attempt was made to de-aerate the DI water, which was assumed saturated with air. In addition, no attempt was made to aerate the DI water during the contact period with the resin. The water levels over the resins stored wet were checked weekly, and DI water was added where appropriate to maintain a depth of approximately 10 mm above the resin-bed surface. A head of water was always maintained above the resin surface.

Resins stored in air at ambient temperature were kept in the open laboratory on a bench while a dry bath was used to store those in air at $40^{o}C$. A modified vacuum oven was used to store dry and submerged resins at $40^{o}C$ under a nitrogen cover gas. Note that the humidity inside the oven was not measured, although it should probably be assumed saturated due to evaporation of water covering the stored resins. The oven was first evacuated and then back-filled with nitrogen of 99.9% purity and assumed dry, to a pressure of approximately 3 psi to prevent air in-leakage. A pressurized paint-tank was used to store resins at ambient temperature under nitrogen cover gas.

(a) Blanchard DL. 2002. *Measuring Physical and Chemical Properties of SuperLig®644 and SuperLig®639 Resins After Storage.* TP-RPP-WTP-166, Battelle—Pacific Northwest Division, Richland, WA.

Ambient temperature and humidity, dry bath and oven temperatures, and oven and paint-tank pressures were recorded weekly, and controlled parameters were adjusted appropriately. Some indicative temperature and humidity statistics derived from the data recorded over the 6-month storage period are provided in Table 2.2.

Table 2.1. Partial Factorial Test Design for SL-644 Storage

Test Identification (Blanchard (2002))	Test Identification	Resin Form	Storage Medium	Storage Cover Gas	Storage Temperature	Storage Time
644-1a	20DAH1	Acid	Dry	Air	ambient	1
644-1b	20DAH2	Acid	Dry	Air	ambient	2
644-1c	20DAH3	Acid	Dry	Air	ambient	3
644-1d	20DAH6	Acid	Dry	Air	ambient	6
644-2a	40DAH3	Acid	Dry	Air	40	3
644-2b	40DAH6	Acid	Dry	Air	40	6
644-9	20DNH6	Acid	Dry	Nitrogen	ambient	6
644-10	40DNH6	Acid	Dry	Nitrogen	40	6
644-7	20WAH6	Acid	Wet	Air	ambient	6
Not identified	40WAH1	Acid	Wet	Air	40	1
644-8	40WAH6	Acid	Wet	Air	40	6
Not identified	20WNH6	Acid	Wet	Nitrogen	ambient	6
Not identified	40WNH6	Acid	Wet	Nitrogen	40	6
644-3a	20DAN3	Sodium	Dry	Air	ambient	3
644-3b	20DAN6	Sodium	Dry	Air	ambient	6
644-4a	40DAN3	Sodium	Dry	Air	40	3
644-4b	40DAN6	Sodium	Dry	Air	40	6
644-13	20DNN6	Sodium	Dry	Nitrogen	ambient	6
Not identified	40DNN1	Sodium	Dry	Nitrogen	40	1
644-14	40DNN6	Sodium	Dry	Nitrogen	40	6
644-11	20WAN6	Sodium	Wet	Air	ambient	6
Not identified	20WAN1	Sodium	Wet	Air	ambient	1
644-12	40WAN6	Sodium	Wet	Air	40	6
Not identified	20WNN6	Sodium	Wet	Nitrogen	ambient	6
Not identified	40WNN1	Sodium	Wet	Nitrogen	40	1
Not identified	40WNN6	Sodium	Wet	Nitrogen	40	6
644-5a	20DAAR3	As-received	Dry	Air	ambient	3
644-5b	20DAAR6	As-received	Dry	Air	ambient	6
644-6a	40DAAR3	As-received	Dry	Air	40	3
644-6b	40DAAR6	As-received	Dry	Air	40	6
Not identified	20DNAR1	As-received	Dry	Nitrogen	ambient	1
Not identified	40WAAR6	As-received	Wet	Air	40	6
Not identified	20WNAR1	As-received	Wet	Nitrogen	ambient	1
Not identified	40WNAR1	As-received	Wet	Nitrogen	40	1

Table 2.2. Indicative Temperature and Humidity Statistics from 6-Month Storage Period

Parameter	Average Recorded Value	Minimum Recorded Value	Maximum Recorded Value
Ambient temperature	23.1°C	22.3°C	24.3°C
Ambient relative humidity	27%	20%	39%
Dry bath temperature	39.8°C	39.0°C	41.2°C
Oven temperature	40°C	42°C	39°C

2.3 Simulated AW-101 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-AW-101 (AW-101) 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. In addition, Fiskum et al. (2002a) have recently used simulated AW-101 LAW to extensively test a prior batch of SL-644.

Golcar et al. (2000) provides the recipe for preparing simulated AW-101 LAW. The composition is presented in Table 2.3. Note that cesium-133 is not presented in Table 2.3 but was added as cesium nitrate to represent all cesium isotopes present in actual LAW. Cesium concentrations higher than that of 8.5 mg/L provided by Golcar et al. (2000) were used for testing and resin-assessment purposes. Cesium-133 was added to simulated LAW batches at several concentrations (refer to Section 2.5 for more details) to assess equilibrium performance across a range of concentrations. The column tests processed simulated LAW containing cesium-133 at a concentration of ~15 mg/L, which is sufficient to provide significant breakthrough within a reasonable processing time (refer to Section 2.6 for more details). Cesium-137 was also added as a tracer to facilitate the evaluation of cesium ion exchange performance by gamma energy analysis (GEA). Solutions were filtered immediately before use.

Batches of simulated LAW were prepared as required and were analyzed by the following methods.

- Ion chromatography (IC)
- Inductively coupled plasma – atomic emission spectrometry (ICP-AES)
- Inductively coupled plasma – mass spectrometry (ICP-MS)
- Carbon oxidation using hot persulfate (HP) for total inorganic and organic carbon (TIC and TOC)
- Carbon oxidation using a furnace for total carbon (TC).

Table 2.3. Simulated AW-101 LAW Component List

Species	Final Target Concentration (M)	Formula Weight
Ethylenediaminetetraacetic acid	3.70E-03	292.24
Citric acid	3.70E-03	210.14
Sodium hydroxyethylethylenediaminetriacetate	3.70E-03	344.00
Sodium nitrilotriacetate	3.70E-03	257.10
Sodium gluconate	3.70E-03	218.00
Sodium iminodiacetate	3.70E-03	177.07
Iron nitrate	5.00E-05	404.02
Magnesium nitrate	1.50E-03	256.40
Manganese nitrate	6.63E-05	(1)
Molybdenum oxide	2.86E-04	143.95
Nickel nitrate	1.33E-04	290.80
Silicon oxide	2.93E-03	60.08
Barium nitrate	1.33E-04	261.38
Calcium nitrate	4.13E-04	236.16
Strontium nitrate	1.30E-05	211.65
Rubidium nitrate	1.00E-05	147.47
Lithium nitrate	5.51E-04	69.00
Potassium hydroxide	4.30E-01	56.11
Sodium hydroxide	3.89E+00	40.00
Aluminum nitrate	5.06E-01	375.15
Sodium carbonate	1.00E-01	105.99
Sodium sulfate	2.36E-03	142.05
Sodium phosphate	1.73E-03	268.07
Sodium chloride	6.93E-02	58.45
Sodium flouride	1.10E-02	41.99
Sodium nitrite	7.90E-01	69.00

1. Manganese nitrate added as a solution of concentration 4.3M.

The compositions of the batches of simulated LAW used throughout the reported tests are provided in Table 2.4 and show general agreement with the target composition. The concentration of iron was up to three times higher than targeted for reasons unknown at present, but this is not expected to have significantly affected the results. Also of note is the sulfate concentration in Batch 262 that was 1.7 times higher than targeted, but this again was not expected to impact the results. Of potentially more concern is the variability in the potassium concentration since this analyte is a major competitor to cesium for ion exchange. The variability of 13% for an average concentration of 14,300 mg/L introduces uncertainty when comparing results from tests processing different batches.

Table 2.5 shows for which test each batch of simulated LAW was used.

Table 2.4. Chemical Composition of Simulated AW-101 LAW Batches

Analyte	Analysis Method	Concentration(a,b) (mg/L)						
		Target	Batch 199	Batch 200	Batch 226	Batch 233	Batch 250	Batch 262
Aluminum	ICP-AES	13,700	12,600	12,600	12,700	13,600	13,600	14,600
Barium	ICP-AES	18.3	16.5	16.5	16.4	17.9	18.0	18.7
Calcium	ICP-AES	16.6	22.8	23.2	24.7	*33*	*30*	*31*
Chloride	IC	2,460	2,450	2,540	2,490	2,470	2,450	2,520
Cesium	ICP-MS	16(e)	15.4(g)	15.7	(f)	(f)	(f)	13.4
Fluoride(d)	IC	209	*499*	*513*	*493*	*500*	*200*	*200*
Iron	ICP-AES	2.79	7.16(c)	6.51(c)	5.91(c)	*7.2*	*5.8*	*5.3*
Potassium	ICP-AES	16,800	13,450	13,300	13,300	14,500	15,100	16,100
Lithium	ICP-AES	3.82	2.54	3.3	4.03	*5.0*	*4.7*	*4.9*
Manganese	ICP-AES	3.64	1.96	2.69	3.26	3.46	2.04	2.35
Molybdenum	ICP-AES	27.4	26.3	26.6	26.6	29.5	29.3	31.3
Sodium	ICP-AES	115,000	109,000	115,000	112,000	111,000	111,000	120,000
Nitrite	IC	36,300	35,100	36,000	36,200	36,400	34,700	37,900
Nitrate	IC	94,400	89,600	90,300	90,900	91,700	88,700	95,500
Nickel	ICP-AES	7.81	7.81	7.84	7.82	*7.3*	*7.8*	*8.1*
Phosphorus	ICP-AES	53.5	59.1	59.8	60.9	65.5	64.0	65.7
Phosphate	IC	164	*180*	*170*	*25*(h)	*170*	*170*	<25(h)
Rubidium	ICP-MS	0.855	2.00	2.01	2.35			
Sulfate	IC	227	190	200	190	<320	<250	*390*
Silicon	ICP-AES	82.3	73.5	71.7	69.5	*77*	*81*	<3.7
Strontium	ICP-AES	1.14	1.71	1.45	1.19	1.53	1.57	1.73
TIC (as carbonate)	HP	1,200	1,260	1,280	1,240	1,310	1,370	1,580
TOC	HP	1,860	1,680	1,670	1,700	1,570	1,580	1,660
TC	Furnace	3,060	5,040	2,860	2,970	Not measured		

(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 (QC) criteria unless otherwise noted.

(c) The relative percent difference for iron of 38% between duplicate samples did not satisfy the acceptance criterion of 20%. No significant impact on results interpretation expected.

(d) Results are upper-bound values due to interferences from co-eluting anions (e.g., acetate) during analysis.

(e) Target for column tests only.

(f) These batches were only used for batch contacts, and cesium was added to three sub-batches at different concentrations. Refer to Section 2.5 for cesium concentrations in fractions.

(g) This concentration refers to the column test only. Refer to Section 2.5 for cesium concentrations in batch-contact fractions.

(h) The reason for the anomalously low phosphate concentrations is not known. The phosphorus concentration determined by ICP-AES is considered the more reliable.

Table 2.5. Test and Simulated LAW Batch Correlation

Simulated LAW Batch	Test
199	Reference resin batch contacts and as-received and acid-form reference resin column tests.
200	Sodium-form reference resin column test.
226	Batch contacts on 1-month stored resins.
233	Batch contacts on 2-month and 3-month stored resins.
250	Batch contacts on 6-month stored resins.
262	6-month stored-resin-column test.

2.4 Reagent Preparation

All reagents were "reagent grade." Sodium hydroxide solutions were prepared by dissolving the required mass of sodium hydroxide pellets in de-ionized (DI) water. The solution of 0.5 M HNO_3 was prepared by diluting the 68- to 70-wt% HNO_3 commercial stock with DI water.

2.5 Batch-Contact Procedure

Batch-contact tests were performed to ascertain the equilibrium performance of the stored resins. The resin was contacted in the form that it was stored (i.e., either acid, sodium, or as-received). There was no significant impact on the simulated LAW composition as a result of the resin being in the acid form due to the large excess of solution. No attempt was made to remove degradation products that may have accumulated during storage, by, for example, rinsing the resin or cycling it through the sodium and acid forms.

The submerged resins were transferred from their storage vials to containers of larger volume and dried under a flowing nitrogen gas stream to a free-flowing state. The resins were well-mixed by shaking before triplicate samples of approximately 0.2 g, measured to an accuracy of 0.001 g, of resin were extracted and placed into the 40-mL contact vials. Duplicate samples of mass between 0.2 g and 0.3 g were also extracted with those required for the batch-contact tests for F-factor determination (refer to Section 2.1.2.1 for details).

The batch-contact tests were performed by contacting the resin samples with 20 mL of simulated AW-101 LAW at cesium concentrations of nominally 5 mg/L, 150 mg/L, and 700 mg/L. The simulated LAW was transferred to the 40-mL contact vials by pipette, and the actual volume was determined from the net mass and density. The contact vials containing the resin and simulated LAW were shaken in a horizontal shaker at a frequency of approximately 2 Hz for 96 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. Blanchard(1) did not require the temperature of the contacts to be controlled, but the temperatures measured at the end of the contact periods are recorded in Table 2.6 and show the temperature of the contacts to be $28.5 \pm 1.5^{o}C$.

Table 2.6. Batch-Contact Temperatures

Test	Temperature Upon Contact Termination (^{o}C)
Reference	28
1-month storage	27
2-month storage	27
3-month storage	26
6-month storage	29 (resins stored dry) and 30 (resins stored submerged)

After contacting with the resin, the simulated LAW was filtered, and the cesium-137 concentrations of the solutions were determined by GEA. The equilibrium-distribution coefficients (K_d) were determined from all but the reference batch contact test results by the relationship,

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(1) Blanchard DL. 2002. *Measuring Physical and Chemical Properties of SuperLig®644 and SuperLig®639 Resins After Storage.* TP-RPP-WTP-166, Battelle—Pacific Northwest Division, Richland, WA.

$$K_d = \frac{(C_0 - C_1)}{C_1} \frac{V}{MF} \tag{2.4}$$

where C_0 and C_1 = initial and final cesium-137 concentrations
V = volume of simulated LAW (mL)
M = mass of sodium-form ion exchange resin (g)
F = F-factor.

The reference batch-contact stock solutions were inadvertently not homogenized after adding cesium-133 and cesium-137. Therefore, the concentration of cesium-137 on the resin, as well as in solution, had to be determined. The resins were prepared by decanting the supernatant simulated LAW, rinsing them with water, and then allowing them to dry before adding 5 mL of 0.5 M nitric acid to redistribute the cesium from the resin into the proper 5-mL counting geometry. The vials were subsequently counted by GEA with the resin settled on the vial bottom (it was assumed that all of the cesium was eluted from the resin). The equilibrium-distribution coefficient was then derived by the ratio of the cesium-137 concentration on the resin and in the liquid portion. The equilibrium cesium-133 concentrations in the contact simulated LAW solutions were determined by analyzing these solutions by ICP-MS.

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 15 mL of SL-644 resin expanded in 0.25 M NaOH, a metering pump, pressure-relief valve, pressure gage (indicated by “P”), and three 3-way valves.

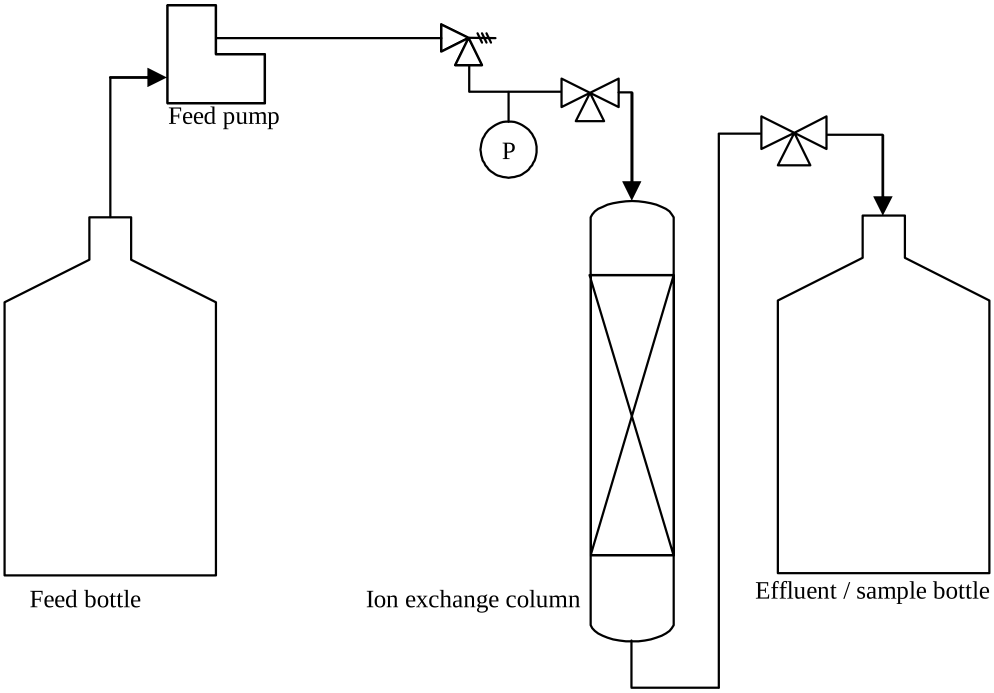

Figure 2.1. SL-644 Column Test Process Schematic

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. The internal diameter of the column was 2.5 cm to provide a bed height-to-diameter ratio of nominally 1.2, which is close to the WTP design basis of 1.1.

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 0.5 mL/h and 50 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. Valves placed between the pump outlet and the column were used to eliminate air from the system or isolate the column from the pump. The valve placed after the column exit was used to prevent the column from draining while the pump was stopped. The equipment and fittings were connected using $^1/_{16}$-in. internal-diameter polyethylene tubing. Section 4.0 provides details regarding the flow rates and reagent volumes processed during the column tests.

2.7 Cesium-137 Analysis

The cesium-137 tracer that was used in the batch contacts and column tests was counted using a GEA system consisting of a multi-channel analyzer and a high-purity germanium detector. Absolute counting efficiency and energy calibration were not required since the analysis was always comparative to that of feed samples. 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 each day the system was used. Sample count times were either 1 hour or sufficient to count 10,000 counts, whichever was shorter. Errors were, therefore, typically ±<1% for more than 10,000 counts but ~±3% for the ~1,000 counts measured for initial breakthrough and elution tail samples.

3.0 Batch-Equilibrium Test Results

This section describes results from the batch-equilibrium testing of the stored and reference resins. Results from batch contacts performed after 1 and 3 months are not described (to simplify the discussion), except for the resin stored dry at ambient temperature in air in the acid form. However, these results were used in the statistical analysis to derive the temporal effect on equilibrium performance for the different forms. Results should be viewed in terms of the resin history. The resin was produced in May, 2002 and stored submerged in water before samples were extracted and dried in October, 2002. Storage under the test conditions commenced when the resin was dry in December 2002 and finished in June, 2003.

The equilibrium-distribution coefficients are presented on a linear scale as a function of the equilibrium sodium-to-cesium molar ratio on a logarithmic scale. An error propagation analysis indicated that the error, given by the first standard deviation, associated with the equilibrium distribution coefficient is between 10% and 15%. For all results except those from the reference resins, separate straight lines were fitted to the data between the lowest and mid cesium concentrations and then between the mid and highest concentrations for all but the reference-resin results. Each end of such lines was determined by taking the average equilibrium-distribution coefficient and the average equilibrium sodium-to-cesium molar ratio. Linear regression was used to fit lines to the results from the reference resins. Table 3.1 provides interpolated equilibrium coefficients for the equilibrium sodium-to-cesium molar ratio of 7.47×10^4 (the ratio in actual AW-101 LAW measured by Kurath et al. [2000] providing a cesium concentration of 8.2 mg/L for a sodium concentration of 4.59M) that were used in the statistical analysis. Appendix A provides all of the batch-contact results in tabular form.

The equilibrium-distribution coefficients are presented on a sodium-form resin mass basis. Weights of resins in the acid form were converted to the equivalent sodium-form weights by multiplying the former by the I-factor, 1.10. Likewise, those weights of resins in the as-received form were converted to the equivalent sodium-form weights by multiplying the former by the L-factor, 0.75, and then the I-factor, 1.10.

As-received and sodium-form resins were initially black while the acid form was deep red. However, all of the resins were black when removed from storage, and no significant mass loss was observed during storage.

Table 3.1. Interpolated Equilibrium Performance Data for Equilibrium Sodium-to-Cesium Molar Ratio of 7.47×10^4 Derived from Each Batch-Contact Test

Test Identification	Cesium Capacity (mmol/g sodium-form resin)	Cesium Capacity as Percentage of Reference Capacity (%)	Equilibrium Distribution Coefficient (mL/g sodium-form resin)
Reference-H	0.094	100	1490
20DAH1	0.086	91	1310
20DAH2	0.038	40	590
20DAH3	0.040	43	610
20DAH6	0.031	33	480
40DAH3	0.025	27	380
40DAH6	0.020	21	300
20DNH6	0.041	44	630
40DNH6	0.027	29	420
20WAH6	0.054	57	830
40WAH1	0.095	101	1460
40WAH6	0.052	55	810
20WNH6	0.060	64	930
40WNH6	0.054	57	830
Reference-N	0.033	100	520
20DAN3	0.021	64	330
20DAN6	0.019	58	300
40DAN3	0.022	67	340
40DAN6	0.022	67	330
20DNN6	0.014	42	210
40DNN1	0.038	115	590
40DNN6	0.014	42	220
20WAN6	0.028	85	430
20WAN1	0.031	94	470
40WAN6	0.027	82	420
20WNN6	0.029	88	450
40WNN1	0.036	109	550
40WNN6	0.028	85	440
Reference-AR	0.048	100	760
20DAAR3	0.026	54	400
20DAAR6	0.025	52	380
40DAAR3	0.032	67	490
40DAAR6	0.028	58	430
20DNAR1	0.068	142	1040(a)
40WAAR6	0.038	79	590
20WNAR1	0.032	67	490
40WNAR1	0.036	75	560

(a) This result is significantly above the value of 760 mL/g for the reference resin and compares with a value of 490 mL/g for the resin stored under the same conditions except submerged. The value is probably artificially high as a result of interpolating it from a region of the equilibrium profile inadequately defined by experimental data.

3.1 Performance of Reference Resins

Figure 3.1 illustrates the equilibrium performance of the reference resins. There is more variability in the results from the reference resins than in those from the stored resins, particularly for the acid form, which probably results from the alternative test method that was required, as described in section 2.5. The equilibrium-distribution coefficients were correlated by linear regression to obtain the values for the equilibrium sodium to cesium molar ratio of 7.47×10^4. Many of the equilibrium profiles generated from the reference and stored resins exhibited a kink at equilibrium sodium to cesium molar ratios of ~10^5. Correlating the acid-form equilibrium-distribution coefficients for equilibrium sodium-to-cesium molar ratios below 10^5 was considered unreasonable given the scarcity of data and the possibility of a kink in the profile . At equilibrium sodium-to-cesium molar ratios above 10^5, the equilibrium-distribution coefficient, K_d, was fitted by the equation,

$$K_d = 207 \times \mathrm{Ln}\left(\frac{[\mathrm{Na}]}{[\mathrm{Cs}]}\right) - 835 \tag{3.1}$$

This correlation provided an equilibrium distribution coefficient of 1490 mL/g for the equilibrium sodium to cesium molar ratio of 7.47×10^4. Correlating all of the acid form resin equilibrium distribution data provided an apparently better fitting correlation and an equilibrium distribution coefficient of 1280 mL/g for the equilibrium sodium to cesium molar ratio of 7.47×10^4. The difference between these equilibrium distribution coefficients is consistent with the 95% confidence interval generated by the statistical analysis in section 3.8. Therefore, the former value was used in subsequent analyses with only the correlation for data at equilibrium sodium-to-cesium molar ratios above 10^5.

For equilibrium sodium-to-cesium molar ratios above 10^4, the as-received form equilibrium-distribution coefficient was fitted by the equation,

$$K_d = 220 \times \mathrm{Ln}\left(\frac{[\mathrm{Na}]}{[\mathrm{Cs}]}\right) - 1705 \tag{3.2}$$

The sodium-form equilibrium-distribution coefficients were correlated by a single equation across the range of cesium concentrations,

$$K_d = 100 \times \mathrm{Ln}\left(\frac{[\mathrm{Na}]}{[\mathrm{Cs}]}\right) - 596 \tag{3.3}$$

Figure 3.1 shows the superior performance, as indicated by the high equilibrium-distribution coefficient, of the acid-form resin in the batch-equilibrium tests. For example, the derived equilibrium-distribution coefficients were 1490 mL/g, 760 mL/g, and 520 mL/g for the acid, as-received, and sodium forms, respectively, at the equilibrium sodium-to-cesium molar ratio of 7.47×10^4. The value for the acid-form resin was derived by extrapolation using the correlation fitted for data at sodium cesium molar ratios above 10^5 considering the value 7.47×10^4 to be sufficiently close. The statistical analysis described in section 3.8 shows this approach to introduce little variability when considering results from both reference and stored resins. The difference between the acid forms is more apparent at low cesium concentrations; coefficients of 2030 mL/g, 1330 mL/g, and 780 mL/g were derived for the acid, as-received, and sodium forms, respectively, at the equilibrium sodium-to-cesium molar ratio of 10^6. At high cesium concentrations (equilibrium sodium-to-cesium molar ratios below ~10^4), the difference between the resin forms appears insignificant, although the performance of the acid-form may be somewhat superior.

The reference as-received resin performance shows excellent consistency with a previous batch of SL-644 resin, 010319SMC-IV-73 (IV-73), tested by Fiskum et al. (2002b) in the as-received and acid forms. However, equilibrium performance of the IV-73 batch did not improve upon conversion to the acid form as displayed by the reference resin tested here.

Therefore, conversion of the resin to the acid form appears to improve the batch-equilibrium performance over that of the as-received and sodium forms. Arm et al. (2003a) have observed the greater susceptibility of the expanded resin forms to oxidation, and the inferior performance of the as-received and sodium forms perhaps represents the greater oxidation sustained while dry. The improvement in performance of the acid form over the as-received form may also have been caused by the resin being washed of deleterious constituents residual from its manufacture. The poor performance of the sodium-form resin, relative to the as-received form, at low cesium concentrations may be caused by oxidation sustained during the extensive washing during conversion.

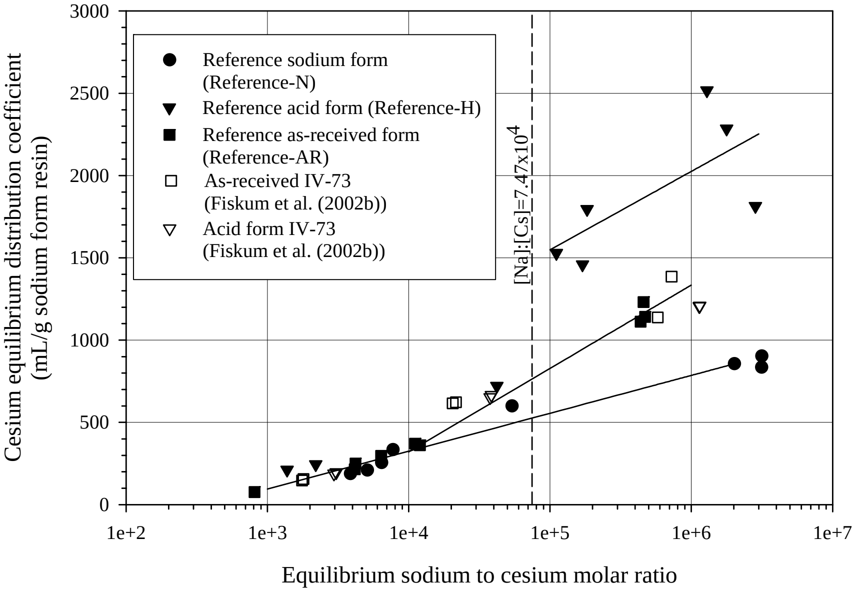

Figure 3.1. Equilibrium Performance of Reference Resins

3.2 Performance of Resins Stored Dry for 6 Months

Figure 3.2 also shows the effect on the batch-equilibrium performance of storing each form of resin dry in air at ambient temperature for 6 months. Significant reductions in the equilibrium distribution coefficients are evident across the range of cesium concentrations. For the equilibrium sodium-to-cesium molar ratio of 7.47×10^4, the equilibrium distribution coefficients were reduced by 68%, 42%, and 50% for the acid, sodium, and as-received forms, respectively. The smaller reduction for the sodium form compared to the acid form may be because the former had already sustained significant oxidation during conversion, as noted above, and that the rate of degradation decreases with increasing oxygen exposure as described in Section 3.3. The equilibrium distribution coefficient of the as-received resin was reduced by an order-of-magnitude between that of the as-received and sodium forms, and this may be an indication that residual manufacturing contaminants were shielding the active sites from oxygen exposure.

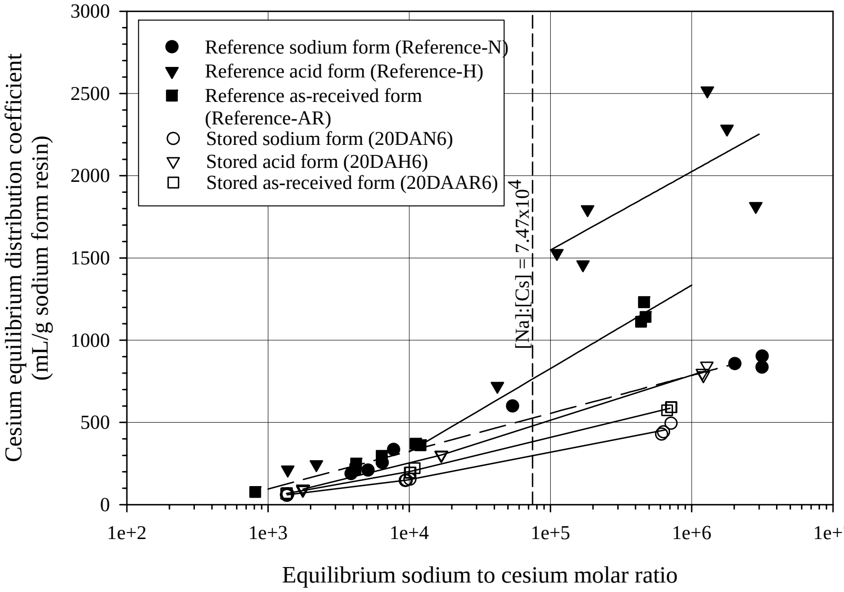

Figure 3.2. Effect of Stored Resin Form on Batch-Equilibrium Performance for Dry Storage in Air at Ambient Temperature for 6 Months

3.3 Impact of Dry-Storage Time on Equilibrium Performance

Four batches of acid-form resin were stored dry in air at ambient temperature for up to 6 months. Batch contacts were performed on these batches to ascertain the temporal effect on equilibrium performance. The results are presented in Figure 3.3. Equilibrium performance appeared not to be impacted for equilibrium sodium-to-cesium molar ratios below ~10^5 for storage up to 1 month. However, resin performance significantly deteriorated at higher sodium-to-cesium molar ratios such that the equilibrium-distribution coefficient had reduced from ~2030 mL/g to 1400 mL/g at the ratio of ~10^6. Deterioration in performance at all cesium concentrations was evident after 2 months, and the equilibrium-distribution coefficient was more than halved from 1490 mL/g to 600 mL/g at the equilibrium sodium-to-cesium molar ratio of 7.47×10^4. However, there was little further deterioration in performance at the higher equilibrium sodium-to-cesium ratios. The rate of deterioration slowed significantly after this time, and there was little difference between the results at 2 and 3 months. Finally, the equilibrium-distribution coefficients had reduced from 1490 mL/g to 480 mL/g and from 2030 mL/g to 750 mL/g at equilibrium sodium-to-cesium molar ratios of 7.47×10^4 and 10^6, respectively, after 6 months.

These results show significant deterioration in the equilibrium performance, first at low cesium concentrations, implying that the resin loses selectivity rather than capacity during the first month of storage. The resin loses both capacity and selectivity after 1 month, which is manifested in the deterioration in equilibrium performance across the range of cesium concentrations. The rate of degradation decreases with increasing storage time and, therefore, oxygen exposure.
Storing the resin submerged in DI water (wet) always provided better equilibrium performance, reducing the magnitude of reduction in the equilibrium-distribution coefficient by between 36% and 59% at the equilibrium sodium-to-cesium ratio of 7.47×10^4.

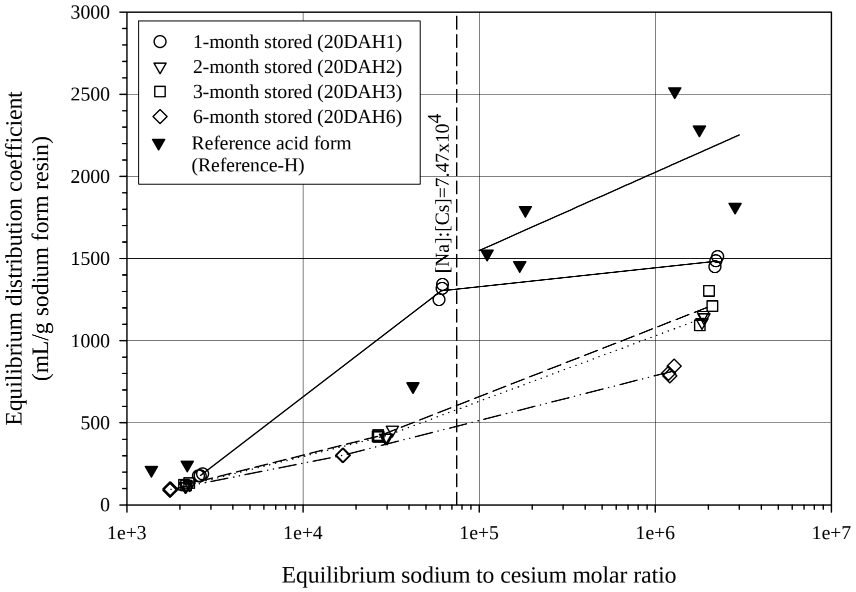

Figure 3.3. Effect of Time on the Batch-Equilibrium Performance of SL-644 Stored Dry in Air at Ambient Temperature in the Acid Form

3.4 Impact of Storage Media and Temperature on Equilibrium Performance

Figure 3.4, Figure 3.5, and Figure 3.6 present the impact of storage media and temperature on the performance of acid, sodium, and as-received resin forms, respectively, stored for 6 months in air. For the acid-form resin stored dry, there is a clear deterioration in equilibrium performance at the higher temperature with the equilibrium-distribution coefficient reducing by 80% at 40°C compared to 68% at ambient temperature at the equilibrium sodium-to-cesium molar ratio of 7.47×10^4. In contrast, for the sodium-form resin stored dry, there appears to be an improvement in equilibrium performance at the higher temperature, although the difference of ~5% at the equilibrium sodium-to-cesium molar ratio of 7.47×10^4 may not be significant. No tests were performed to store the as-received resin submerged at ambient temperature in air but there is clearly little effect of temperature for the resin stored dry. Storing the resin wet appears to negate any impact of temperature (within the tested range) for both resin forms.

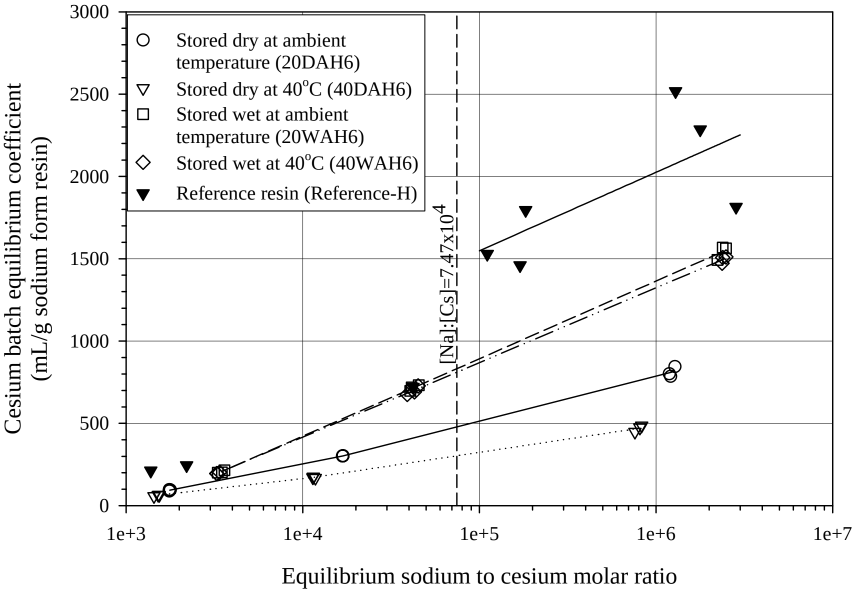

Figure 3.4. Effect of Storage Media and Temperature on Acid-Form Resin Stored in Air for 6 Months

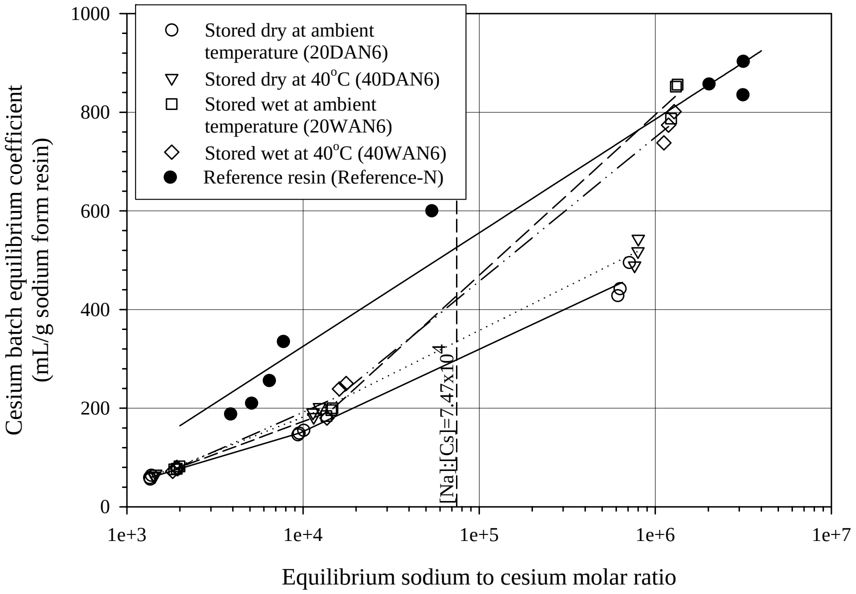

Figure 3.5. Effect of Storage Media and Temperature on Sodium-Form Resin Stored in Air for 6 Months

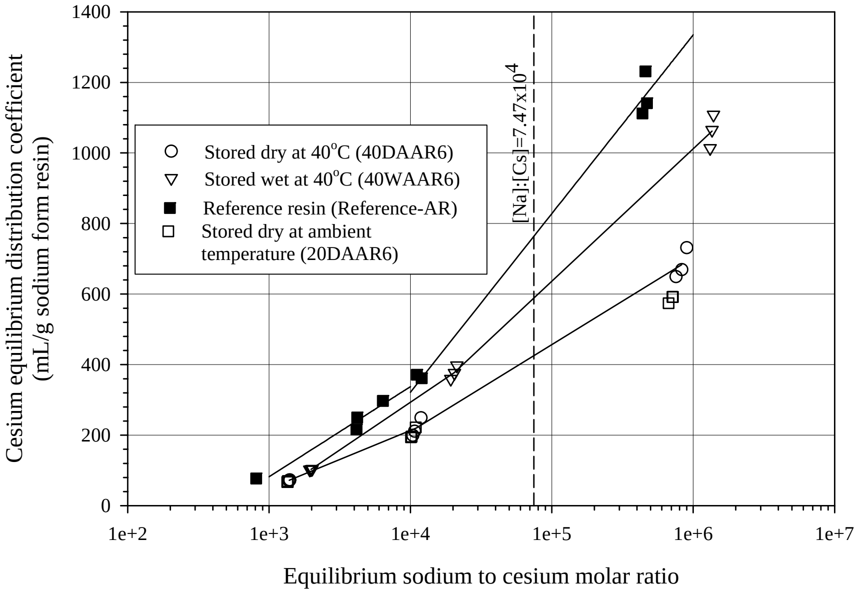

Figure 3.6. Effect of Storage Media on As-Received Resin Stored in Air at 40°C for 6 Months

3.5 Impact of Storage Cover Gas and Temperature on Equilibrium Performance of Resins Stored Dry

The impact of storage cover gas (air or nitrogen) and temperature on the equilibrium performance of resins stored dry in the acid and sodium forms is illustrated in Figure 3.7 and Figure 3.8, respectively. Storage of the acid-form resin in nitrogen appears to better preserve its equilibrium performance, particularly at low cesium concentrations, and the reduction in the equilibrium-distribution coefficients is improved by ~15% at the equilibrium sodium-to-cesium molar ratio of 7.47×10^4. In contrast, storage of the sodium form in nitrogen appears to degrade the resin further than when it was stored in air. This was surprising because resin oxidation is known to be the main degradation mechanism, and no explanation for this phenomenon can be offered at this time. Equilibrium performance, particularly at the lowest cesium concentration, is better preserved at the lower temperature when the acid form is stored in either air or nitrogen. There is no impact of temperature on equilibrium performance when the resin is stored in the sodium form.

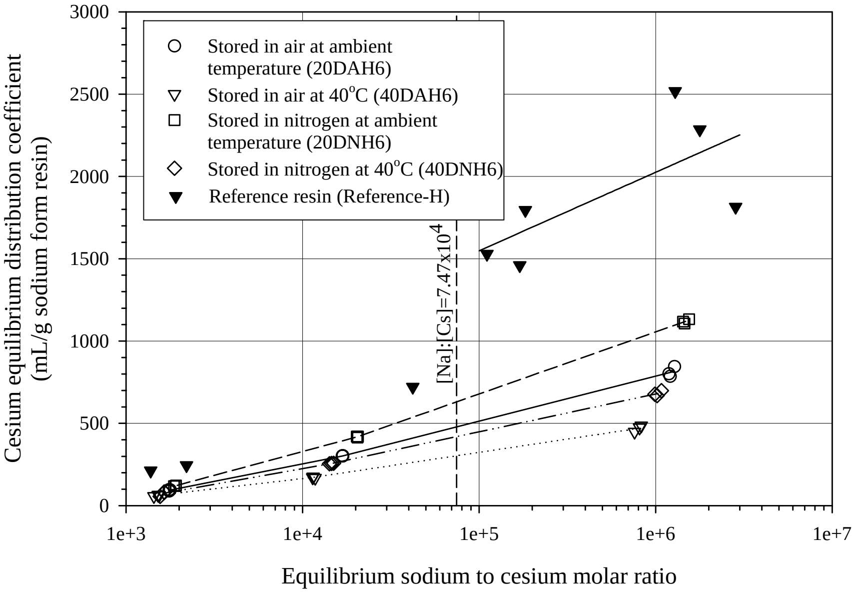

Figure 3.7. Effect of Storage Cover Gas and Temperature on Acid-Form Resin Stored Dry for 6 Months

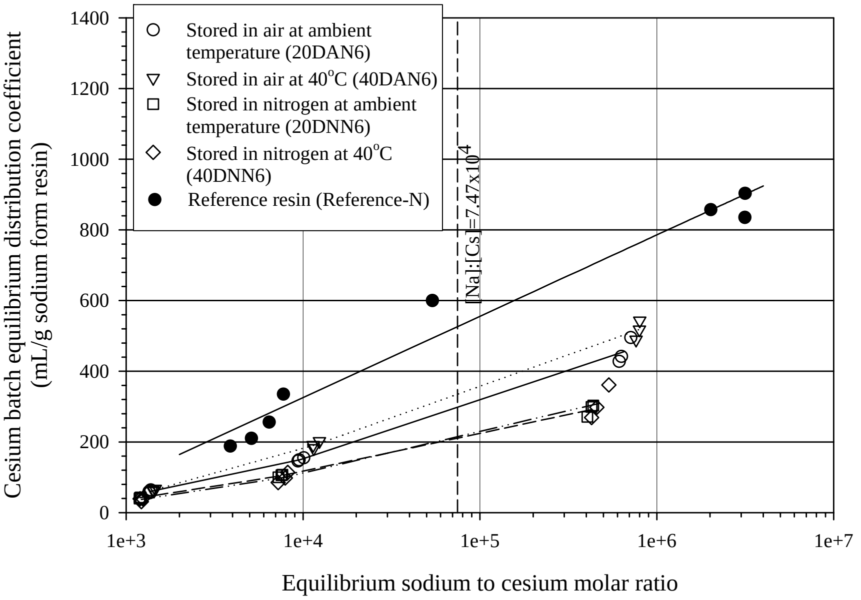

Figure 3.8. Effect of Storage Cover gas and Temperature on Sodium-Form Resin Stored Dry for 6 Months

3.6 Impact of Storage Cover Gas on Equilibrium Performance of Resins Stored Wet

Figure 3.9 shows that storing in nitrogen and submerging in DI water better preserves the equilibrium performance of the acid-form resin than if it were stored dry in air; the deterioration in the equilibrium-distribution coefficient is reduced by 46% when stored submerged in DI water in nitrogen. Storage of the acid-form resin submerged in water and with air cover gas is better than storage dry in nitrogen. As before, the impact of storage under nitrogen is more pronounced at the lowest cesium concentration.

Figure 3.10 shows that there is no impact of storage cover gas on the equilibrium performance of the sodium-form resin when it is stored submerged in DI water. There is a reduction of 70% in the deterioration of the equilibrium-distribution coefficient when the resin is stored submerged in DI water in nitrogen compared to dry storage in air.

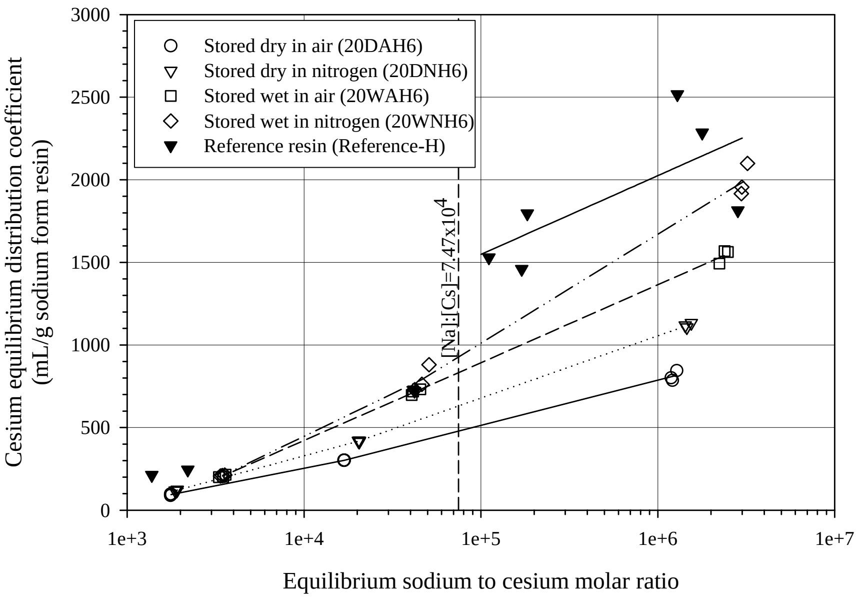

Figure 3.9. Effect of Storage Cover Gas on Acid-Form Resins Stored Wet and Dry at Ambient Temperature for 6 Months

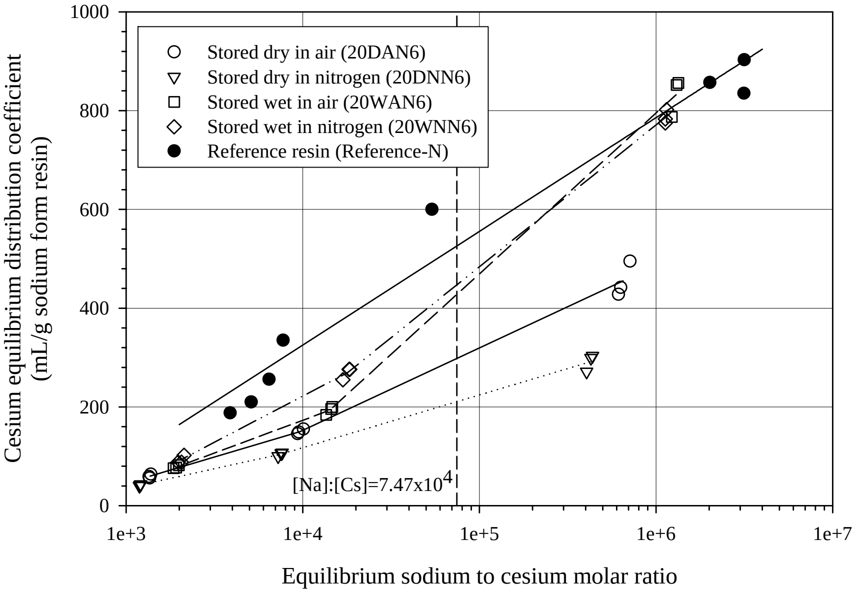

Figure 3.10. Effect of Storage Cover Gas on Sodium-Form Resins Stored Wet and Dry at Ambient Temperature for 6 Months

3.7 Impact of Storage Cover Gas and Temperature on Equilibrium Performance of Resins Stored Wet

The effects of temperature and submergence when the resin is stored in air are repeated for storage in nitrogen. For example, Figure 3.7 shows that storage at 40°C compared to ambient temperature has the similar deleterious impact on equilibrium performance when the resin is stored in the dry-acid form in nitrogen as in air. There is again little impact of temperature on the equilibrium performance when the resin is stored in the dry-sodium form in nitrogen as in air as shown in Figure 3.8. Figure 3.8 also shows that storing resin in the dry-sodium form in nitrogen yields worse equilibrium-distribution coefficients at both ambient temperature and 40°C than if it were stored in air.

The trends observed above for resin stored dry in the acid form are repeated for acid-form resin stored submerged in DI water, as illustrated in Figure 3.11. Increasing the temperature appears to have a greater deleterious impact when the acid-form resin is stored wet in nitrogen than in air, though storage in nitrogen is always better than in air, particularly at the lowest cesium concentrations. The difference between the best and worse equilibrium-distribution coefficients at the equilibrium sodium-to-cesium molar ratio of 7.47×10^4 is only ~7%. Figure 3.12 shows that there is no impact of temperature or cover gas on the storage of wet-sodium-form resin.

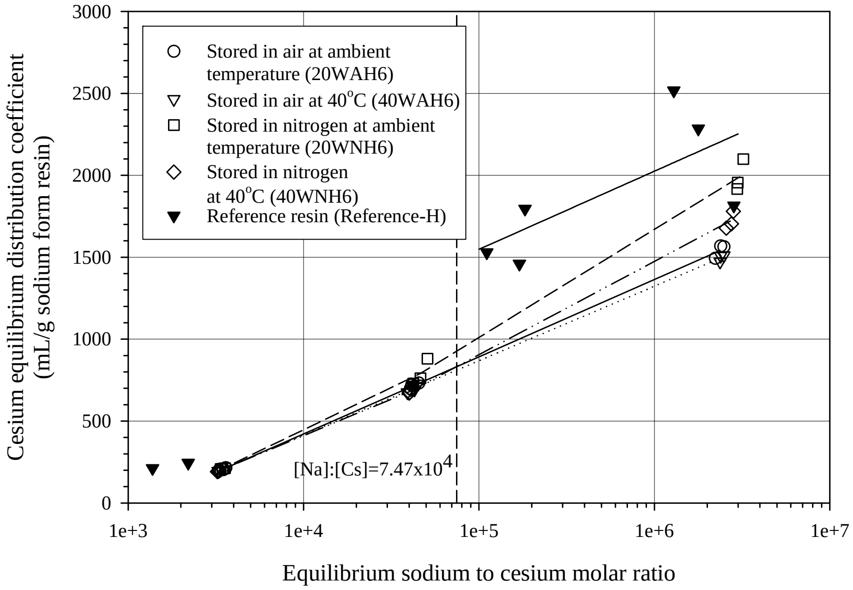

Figure 3.11. Effect of Storage Cover Gas and Temperature on Acid-Form Resins Stored Wet for 6 Months

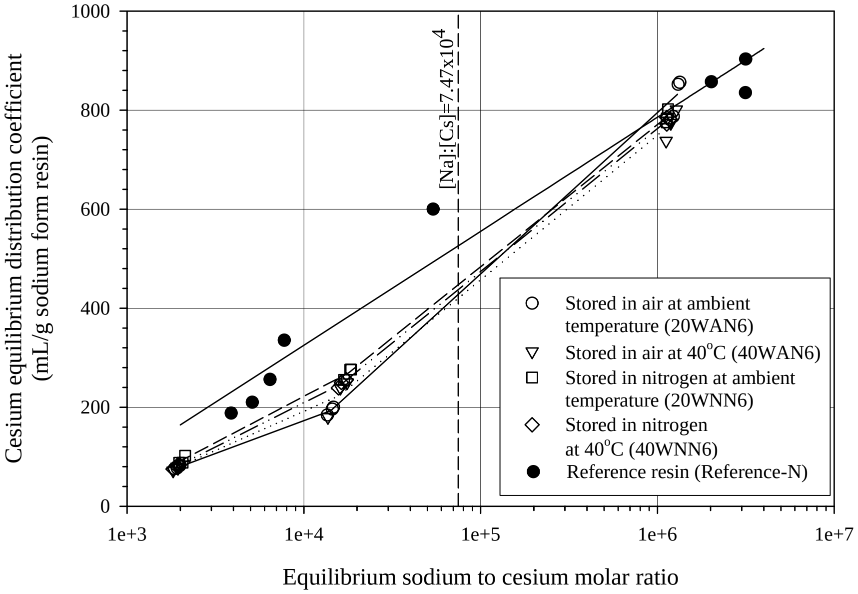

Figure 3.12. Effect of Storage Cover Gas and Temperature on Sodium-Form Resins Stored Wet for 6 Months

3.8 Statistical Analysis of Batch-Contact Results

A statistical analysis of the results was performed to determine the significance of the parameters studied on resin performance and to derive a mathematical correlation. The analysis used the cesium equilibrium-distribution coefficients interpolated for the equilibrium sodium-to-cesium molar ratio of 7.47×10^4 (corresponding to a cesium concentration of 6.2 mg/L at a sodium concentration of 4.59M), as provided in Table 3.1. The details of the analysis are provided in Appendix B, and a summary of the best model is provided here.

The statistical analyses showed only the resin form, its storage medium (submerged or dry), and time to be statistically important to resin performance at the equilibrium sodium-to-cesium molar ratio of 7.47×10^4. Whether the resin was stored under nitrogen or air at ambient temperature or 40^{o}C appeared to be statistically unimportant. The equilibrium distribution coefficients were fitted to a correlation of the form:

$$\begin{aligned} K_d = 1150 - 305\{\mathrm{TIME}\} + 32.8\{\mathrm{TIME}\}^2 + A\{\mathrm{FORM}\} + B\{\mathrm{MEDIUM}\} + C\{\mathrm{FORM} \bullet \mathrm{MEDIUM}\} + \\ D\{\mathrm{FORM}\}\times\{\mathrm{TIME}\} + E\{\mathrm{FORM}\}\times\{\mathrm{TIME}\}^2 \\ + F\{\mathrm{MEDIUM}\}\times\{\mathrm{TIME}\} + G\{\mathrm{MEDIUM}\}\times\{\mathrm{TIME}\}^2 \end{aligned} \quad (3.4)$$

Here {TIME} is the time in months, and a quadratic term is included as a first approximation to account for the decreasing reduction in performance with increasing storage time. Application of the correlation beyond the experimental range of 6 months should be undertaken with caution because performance will appear to improve for greater {TIME} values.

The parameter {FORM} can be either as-received, acid, or sodium and upon which depends the value of A, D, and E as provided in Table 3.2.

Table 3.2. Values of the Coefficients A, D and E

Resin Form	Value of the Coefficient “A”	Value of the Coefficient “D”	Value of the Coefficient “E”
As-received	-77.0	-16.1	4.21
Acid	530	-167	17.6
Sodium	-453	183	-21.8

The parameter {MEDIUM} can be either submerged or dry, and the values of the coefficients B, F, and G are provided in Table 3.3.

Table 3.3. Values of the Coefficient B, F, and G

Medium	Value of the Coefficient “B”	Value of the Coefficient “F”	Value of the Coefficient “G”
Submerged	-222	174	-19.9
Dry	222	-174	19.9

The values of the coefficient C for the cross term between resin form and storage medium are provided in Table 3.4.

Table 3.4. Values of the Coefficient C

Resin Form	Medium	
	Dry	Submerged
As-received	105	-105
Acid	-110	110
Sodium	4.71	-4.71

The standard deviation on predicted values provided by the correlation is 108 so that the uncertainty associated with a 95% confidence interval is approximately 216. Of the equilibrium-distribution-coefficient variability, 92% is accounted for by considering time, resin form, and storage medium. The variability is considered good and shows the derived reference resin results to be consistent despite the variability described in section 3.1. A significant portion of the remaining 8% is considered to be caused by approximating the equilibrium-distribution-coefficient curve as linear in deriving the values for the equilibrium sodium-to-cesium molar ratio of 7.47×10^4 (i.e., limitations in the input data). Other factors contributing to the outstanding variability include

- variability in the potassium concentration between simulated LAW batches
- the scatter associated with the reference resin results
- the different volumes of stored resin.

Table 3.5 presents the equilibrium distribution coefficients predicted for each form stored either submerged or dry for 6 months, applicable to either ambient temperature or 40°C or either cover gas since they are not included in the correlation. In the dry state, the correlation predicts the as-received form to be marginally better than the acid form and no effect of submergence. However, these apparent phenomena are probably more due to uncertainty in the correlation since there were significantly fewer tests performed with the as-received resin than either the acid or sodium-form resins. Indeed, the measured values show that the acid form is superior when stored dry as well as wet and that submergence improves the equilibrium performance of the as-received resin.

The statistical analysis therefore confirms that the submerged-acid form of the resin is the best for storage and that neither temperature (at ambient or 40°C) nor cover gas (air or nitrogen) have a significant impact. However, note that these conclusions apply only for the equilibrium sodium-to-cesium molar ratio of 7.47×10^4. As noted in previous sections, temperature and cover gas are more important to performance at low cesium concentrations.

Table 3.5. Predicted Resin Performance at Equilibrium Sodium to Cesium Molar Ratio of 7.47×10^4 After 6 Months Storage

Resin form	Equilibrium-Distribution Coefficient After 6 Months Storage (mL/g sodium-form resin)			
	Dry		Submerged	
	Predicted	Measured(a)	Predicted	Measured(a)
Acid	440	460	870	860
As-received	470	410(b)	470	590(c)
Sodium	250	270	450	440

(a) Average of four values (unless otherwise stated) recorded for resins stored in air, nitrogen at ambient temperature, and 40°C.
(b) Only two values measured, both in air at ambient temperature and 40°C.
(c) Only one value measured in air at 40°C.

A measure of the deterioration in equilibrium performance of the resin during the 7-month period from when the resin was produced to when it was tested in the reference condition can be determined by extrapolating Equation 3.5 to negative four months for submerged as-received resin. The correlation predicts the equilibrium-distribution coefficient at the equilibrium sodium-to-cesium molar ratio of 7.47×10^4 to be 2610 mL/g upon resin production, compared to a reference value of 750 mL/g. Thus, the resin could have degraded by ~70% from when it was produced to when it was tested in the reference condition. The major uncertainty associated with this conclusion is the applicability of the time correlation since the suitability of an inverse exponential rather than quadratic form probably becomes more important outside the tested time period.

The observation that aging leads to a greater reduction in the equilibrium-distribution coefficient at low cesium concentrations (high sodium to cesium molar ratios) is significant. The cesium concentrations in the LAW feed to the polishing column in the WTP are expected to be very low under normal operating conditions. If resin charges with different storage histories are used in the different columns, it is possible that the length of the load cycle (i.e., volume of LAW feed processed) could switch from being limited by loading of the lead column (due to safety limitations or a standard cesium breakthrough) to the polishing-column cesium breakthrough. Rinsing the aged resin or cycling it through the sodium and acid forms may improve the cesium capacity at all cesium concentrations by removing degradation products, as observed by Arm et al. (2003a).

4.0 Column Test Results

This section presents the results from the column tests performed on the reference resins loaded into the column in the as-received, acid, and sodium forms. In addition, the best performing resin stored dry in air for 6 months was tested as required by Blanchard.(a) The acid-form resin stored at ambient temperature provided the best batch-distribution coefficients among the resins stored dry in air and was therefore selected for column testing. Results should be viewed in terms of the resin history. The resin was produced in May, 2002 and stored submerged in water before samples were extracted and dried in October, 2002. Storage under the test conditions commenced when the resin was dry in December 2002 and finished in June, 2003. Column tests on the as-received, acid and sodium form reference resins commenced 3, 4 and 5 weeks, respectively, after initiation of the test storage. The column test on the stored resin commenced four weeks after completing the 6-month storage period. Resins were stored submerged in DI water until tested.

4.1 Bed-Volume Definition

Solution volumes and flow rates are reported relative to the bed volume (BV) of sodium-form resin measured in 0.25 M sodium hydroxide in the regeneration operation immediately before processing simulated LAW.

4.2 Resin Conditioning

The reference resins were converted to the sodium and acid forms according to the procedures described in Section 2.2 and loaded into the column. The stored resin was loaded into the column in the acid form in which it was stored. Resins were not weighed before addition to the column because all but the sodium-form resin needed conditioning for conversion to the sodium form in which the target resin bed volume was specified. The manipulations involved in adding or extracting material to achieve the target sodium-form resin bed volume after conditioning were considered to potentially introduce unreasonable uncertainty in the resin mass. Instead, the resin mass upon test completion was measured. Arm et al. (2003a) found that SL-644 lost an average of approximately 1.4% of its mass every cycle over 25 cycles, and the expected loss in this test is ~3% from conditioning and a single cycle. The uncertainty associated with considering resin mass loss was considered small compared to that associated with measuring the initial mass and correcting for manipulations.

Once loaded, the resins were conditioned with various washes depending on the form of the resin in preparation for processing dummy LAW (defined later). The as-received resin was washed successively with 3 BVs of DI water, 3 BVs of 0.5 M nitric acid to wash out any potassium salts residual from its manufacture, and then 4 BVs of DI water before converting it to the sodium form with 5 BVs of 0.25 M sodium hydroxide. The acid-form resins were only rinsed with 4 BVs of DI water and then converted to the sodium form with 9 BVs of 0.25 M sodium hydroxide. Note that the initial flow rate was set for 3 BV/h for 1 hour to displace the DI water from the column and thereby ensure full conversion of the resin to the sodium form in which the target resin bed volume was to be measured (the as-received and sodium-form resin bed volumes were considered sufficiently close to their targets when initially loaded). The sodium-form resin was simply washed with 3 BVs of 0.25 M sodium hydroxide so that the column

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(a) Blanchard DL. 2002. *Measuring Physical and Chemical Properties of SuperLig®644 and SuperLig®639 Resins After Storage.* TP-RPP-WTP-166, Battelle—Pacific Northwest Division, Richland, WA.

was in a caustic environment suitable to process the dummy LAW. The initial conditioning details specific to each resin are detailed in Table 4.1.

Table 4.1. Initial Resin Conditioning-Process Details

Operation	Parameter	Resin			
		As-Received	**Acid**	**Sodium**	**Stored**
DI Water Rinse	Volume (mL)	48	Not performed	Not performed	Not performed
	Volume (BVs)	3			
	Flow rate (mL/h)	48			
	Flow rate (BV/h)	3			
	Resin bed volume (mL)	14			
Nitric Acid Rinse	Volume (mL)	46	Not performed	Not performed	Not performed
	Volume (BVs)	3			
	Flow rate (mL/h)	46			
	Flow rate (BV/h)	3			
	Resin bed volume (mL)	12			
DI Water Rinse	Volume (mL)	63	60	Not performed	47
	Volume (BVs)	4	4		3.5
	Flow rate (mL/h)	46	60		47
	Flow rate (BV/h)	3	4		3.5
	Resin bed volume (mL)	11	10		7
Regeneration (0.25 M Sodium Hydroxide)	Volume (mL)	71	151	45	110
	Volume (BVs)	5	9	3	8
	Flow rate (mL/h)	12	15/45(a)	45	18
	Flow rate (BV/h)	0.8	0.9/3(a)	3	1
	Resin bed volume (mL)	14	15	15	13

(a) Flow rate was 45 mL/h or 3 BV/h for an hour and then 15 mL/h or 0.9 BV/h for 6 hours.

Arm et al. (2003a) found that SL-644 performed significantly worse in the first cycle of processing simulated LAW than in the second and presumed this was due to the bed requiring a full cycle to achieve a physically equilibrated state. Therefore, a dummy LAW consisting of 2 M sodium hydroxide, 1.5 M sodium nitrate, and 1.5 M sodium nitrite was first processed in this test to ensure optimal performance when processing simulated LAW. Each resin processed nominally 24 BVs of the dummy LAW at 3 BV/h. Dummy LAW was then displaced from the test apparatus with the equivalent of two apparatus volumes (AVs) of 0.1 M sodium hydroxide at 3 BV/h. A rinse with 2 AVs of DI water at 3 BV/h subsequently displaced the 0.1 M sodium hydroxide from the apparatus. The resins were then converted to the acid form with up to 27 BVs of 0.5 M nitric acid at 1 BV/h and subsequently rinsed with 2 AVs of DI water at 3 BV/h. The resins were converted to the sodium form ready to process simulated AW-101 LAW with up to 10 BVs of 0.25 M sodium hydroxide at 1 BV/h. The details for resin-bed conditioning specific to each test are given in Table 4.2.

4.3 Simulated AW-101 LAW Processing

Approximately 180 BVs of simulated AW-101 LAW was processed through the column at nominally 3 BV/h. Column tests with the reference as-received and acid-form resins processed simulated LAW containing 15.4 mg/L of cesium from Batch 199, which is shown in Table 2.4. Batch 200 simulated LAW, containing 15.7 mg/L of cesium, was processed in the test with the reference sodium-form resin.

The stored resin processed simulated LAW from Batch 262 containing 16.5 mg/L of cesium. No process problems were encountered except for the reference sodium form resin, for which a white precipitate was observed on the bed surface. In addition, the resin bed had to be fluidized early in the operation to alleviate a high pressure drop across it, assumed caused by a line blockage. Table 4.3 provides the simulated LAW processing details and shows that the resin bed volumes reduced by ~5% (or ~1 mL) from the values attained during regeneration, except for the reference sodium-form resin, which remained at the same value. In addition, the table also shows that the reference sodium-form resin separated less cesium than the as-received or acid-form reference resins while the stored resin performed significantly worse. The resin-performance characteristics are further revealed with reference to Figure 4.1 that plots the breakthrough data presented in Appendix C

Table 4.2. Final Conditioning-Process Details

Operation	Parameter	Resin			
		As-Received	**Acid**	**Sodium**	**Stored**
Dummy LAW Processing	Volume (mL)	360	360	350	310
	Volume (BVs)	24	22	24	23
	Flow rate (mL/h)	45	45	44	39
	Flow rate (BV/h)	3	3	3	3
	Resin bed volume (mL)	15	17	15	Not measured
Feed Displacement	Volume (mL)	110	99	97	87
	Volume (BVs)	7	6	6	7
	Flow rate (mL/h)	49	50	49	44
	Flow rate (BV/h)	3.1	3	3	3.5
	Resin bed volume (mL)	15	17	16	Not measured
Pre-Elution Rinse (DI water)	Volume (mL)	92	92	90	81
	Volume (BVs)	6	6	6	6
	Flow rate (mL/h)	46	46	45	40
	Flow rate (BV/h)	3	3	3	3
	Resin bed volume (mL)	15	15	16	Not measured
Elution (0.5 M nitric acid)	Volume (mL)	230	230	300	350
	Volume (BVs)	16	15	20	27
	Flow rate (mL/h)	15	15	38	23
	Flow rate (BV/h)	1	1	2.5	2
	Resin bed volume (mL)	11	12	12	Not measured
Post-Elution Rinse (DI water)	Volume (mL)	80	92	91	90
	Volume (BVs)	5	6	6	7
	Flow rate (mL/h)	46	46	46	45
	Flow rate (BV/h)	2.9	3	3	3.5
	Resin bed volume (mL)	11	11	12	Not measured
Regeneration (0.25 M sodium hydroxide)	Volume (mL)	145	140	83	72(b)
	Volume (BVs)	10	9	6	5
	Flow rate (mL/h)	45/15(a)	45/15(a)	45/15(a)	12
	Flow rate (BV/h)	3/1(a)	3/1(a)	3/1(a)	0.8(b)
	Resin bed volume (mL)	15	16	15	13

(a) Flow rate was 45 mL/h or 3 BV/h for an hour and then 15 mL/h or 1 BV/h for 6 hours.

(b) The flow rate set point on the controller was underestimated and so the volume processed was lower than previously used. The resin bed volume of 13 mL compares well with the final resin bed volume of 12 mL after processing simulated LAW, which indicates the resin had fully converted to the sodium form.

Figure 4.1 shows that initial breakthrough of 0.1% occurred after the reference as-received and acid-form resins had processed ~90 BVs of simulated LAW but after ~20 BVs for the reference sodium-form resin. The 6-month stored resin exhibited nearly immediate breakthrough. The low initial breakthrough exhibited by the stored and reference sodium-form resins and the delayed breakthrough experienced with the acid and as-received reference resins indicates that there was no significant channeling through the bed.

Table 4.3. Simulated LAW Processing Details

Parameter	Resin			
	As-Received	**Acid**	**Sodium**	**Stored**
Volume (mL)	2750	2720	2730	2440
Volume (BVs)	181	170	190	180
Flow rate (mL/h)	46	46	46	41
Flow rate (BV/h)	3	3	3	3
Resin bed volume (mL)	14	14	15	12
Percentage of feed cesium in composite effluent	2.1	2.2	8.3	34

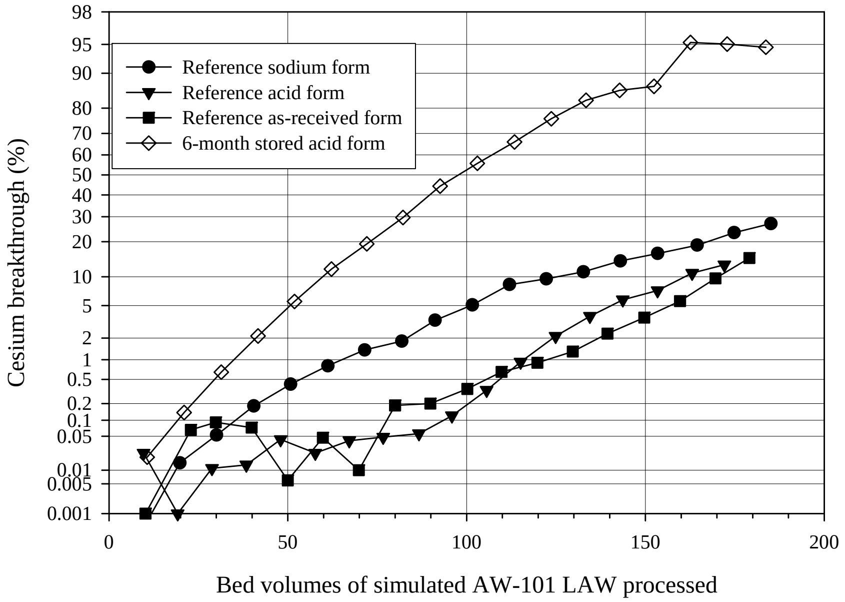

Figure 4.1. Breakthrough Profiles from Reference and 6-Month Stored Resins

The column-distribution coefficient is the number of BVs processed at 50% breakthrough and provides a measure of resin capacity. The breakthrough profiles were visually extrapolated to 50% breakthrough to provide column-distribution coefficients of 230, 220, and 210 for the reference as-received, acid, and sodium resins, respectively. A column-distribution coefficient of 100 was exhibited by the 6-month stored resin. Therefore, there appears to be no significant impact of resin form on column capacity, but that of the stored resin appears to have reduced by ~50%. Although there is no significant difference between the reference column-distribution coefficients, earlier breakthrough exhibited by the sodium-form resin may have been caused by a number of reasons:

- Chemical degradation caused by the extensive water rinsing conducted in the conversion process
- Slower mass transfer associated with precipitated material than was observed on the bed surface but that could have extended into the bed
- Fluidization of the bed.

The breakthrough profiles of the reference resins are approximately linear on the probability-linear plot of Figure 4.1 while there is a bow to that of the stored resin. Comparison of the breakthrough-profile shapes indicates that the ion exchange kinetics is impacted by storage though not by form.

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 feed were 40,860 for the as-received and acid-form resin tests and 42,540 for the sodium-form resin test. Column tests on the reference resins commenced within 5 weeks of completing the batch contacts and section 3.3 indicates that the equilibrium performance would not have significantly deteriorated over this time at the tested sodium to cesium molar ratios. Therefore, the expected column-distribution coefficients are 160, 360, and 130 for the as-received, acid, and sodium forms based on Equations 3.2, 3.1, and 3.3, and the average dry-bed density of 0.26 g/mL. These dry-bed densities were derived from the final resin masses in Section 4.6 and the resin bed volumes in 0.25 M sodium hydroxide given in Table 4.2. The value for the acid form is suspected biased high because the feed sodium-to-cesium molar ratio is outside of the range for which the correlation was derived. The batch-distribution coefficient underestimated the column-distribution coefficient for the as-received and sodium forms though they predict similar performance as observed. The reason for the under-estimation is unknown at present. The column-distribution coefficient of 110 predicted for the stored resin, which is based on the batch-contact results for acid-form resin stored dry in air under ambient conditions, agrees well with the observed value of 100. However, the predicted value is likely biased high since the column test was performed four weeks after the batch contact tests, though the statistical analysis in section 3.8 indicates little further degradation would have occurred over that period.

The significant reduction in performance of the air-stored resin, even after cycling once with the dummy LAW as described, highlights the vulnerability of SL-644 to degradation by oxidation. Extrapolation to a three-column system is difficult without the use of a modeling program, but based on the results shown here and on previous testing with multiple column systems, it is not clear that SL-644 resin stored in air for 6 months would satisfy the cesium-removal requirements using planned baseline operating conditions. The equilibrium batch-contact results suggest that the acid-form SL-644 stored under DI water will perform significantly better. However, the observed difficulty in predicting column performance from equilibrium batch-contact results, especially in the early loading region where kinetic performance is important, makes it impossible to quantify the improvement. Minimization of storage time for the SL-644 resin is highly recommended.

4.4 Column Preparation for Elution

The columns were rinsed with nominally 2 AVs 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 4.4. Feed Displacement and Pre-Elution Rinse Process Details
The BVs essentially increased to return to their values in 0.25 M sodium hydroxide during feed displacement and remained constant during the pre-elution rinse.

Table 4.4. Feed Displacement and Pre-Elution Rinse Process Details

Operation	Parameter	Resin			
		As-Received	Acid	Sodium	Stored
Feed Displacement (0.1 M Sodium Hydroxide)	Volume (mL)	87	92	92	90
	Volume (BVs)	6	6	6	7
	Flow Rate (mL/h)	44	46	46	45
	Flow Rate (BV/h)	3	3	3	3
	Resin bed volume (mL)	15	16	16	15
	Percentage of feed cesium in composite effluent	0.3	0.2	0.4	1.6
Pre-Elution Rinse (DI Water)	Volume (mL)	91	99	92	109
	Volume (BVs)	6	6	6	8
	Flow Rate (mL/h)	45	46	46	55
	Flow Rate (BV/h)	3	3	3	4
	Resin bed volume (mL)	15	16	15	14
	Percentage of feed cesium in composite effluent	0.01	0.01	0.02	0.1

4.5 Elution

The resins were eluted with nominally 15 BVs of 0.5 M nitric acid at a nominal flow rate of 1 BV/h. Eluate was collected in fractions of volume equivalent to 1 BV each to obtain elution profiles expressed in terms of the eluate to simulated LAW-feed cesium-concentration ratios. Table 4.5 provides the process details specific to each resin. Note that the 6-month stored acid form resin was initially eluted with 150 mL or 11 BVs of 0.5 M nitric acid and then rinsed with ~100 mL of DI water. A further 110 mL or 8 BVs of 0.5 M nitric acid was then processed to extend the elution profile to an eluate cesium concentration consistent with that obtained with the reference resins; the volume quoted includes ~100 mL of post-elution rinse effluent.

Table 4.5. Elution Process Details

Parameter	Resin			
	As-Received	Acid	Sodium	Stored
Volume (mL)	230	230	230	350$^{(a)}$
Volume (BVs)	15	15	15	26$^{(a)}$
Flow Rate (mL/h)	15	15	15	10
Flow Rate (BV/h)	1	1	1	0.7
Final resin bed volume (mL)	11	11	11	9
Recovered Percentage of Feed Cesium	97.9	97.2	95.3	61.3

(a) See text above.

Figure 4.2 through Figure 4.6 provide the elution and resin bed volume profiles of the reference and stored resins while Figure 4.7 provides a comparison of the elution profiles from the four resins. Appendix C provides the elution data in tabular form. The figures show the resin bed shrinking as the resin is converted from the sodium to the acid forms. The cesium-concentration ratios for eluate to simulated LAW feed peaked at ~100 when ~4 BVs of eluate were generated. However, the resins exhibited different peak spans. Defining the peak span as the number of BVs that the ratio of the eluate to the simulated LAW-feed cesium concentration remains above unity provides values of 6.5, 4.5, 6.0, and 4.0 for the reference as-received, acid, and sodium resins and stored resin, respectively. The peak in the ratio of the eluate to the simulated LAW-feed cesium concentration approximately coincides with the resin attaining a constant resin bed volume after reducing to 11 mL from typically 15 mL (27 volume% reduction) for the reference resins and to 9 mL from 14 mL (36 volume% reduction) for the stored resin.

All of the elution profiles exhibit tailing. Final ratios of the eluate to the simulated LAW-feed cesium concentration for the reference resins were 0.014, 0.023, and 0.018 for the as-received, acid, and sodium forms, respectively, after generating ~15 BVs of eluate. The tail of the elution profile from the stored resin appears longer than that from the reference resins, although comparison is difficult. The ratio of the eluate to the simulated LAW-feed cesium concentration with the stored resin was 0.21 when ~11 BVs of eluate were generated. That ratio compares to values of ~0.1 with the reference resins after generating the same volume of eluate. However, the ratio of the eluate to the simulated LAW-feed cesium concentration had reduced to 0.002 after a DI water rinse and after generating a further 8 BVs of eluate. Figure 4.6 shows a significant increase in the rate of reduction of eluate cesium concentration between the initial and resumed elutions that cannot be explained by any operational cause.

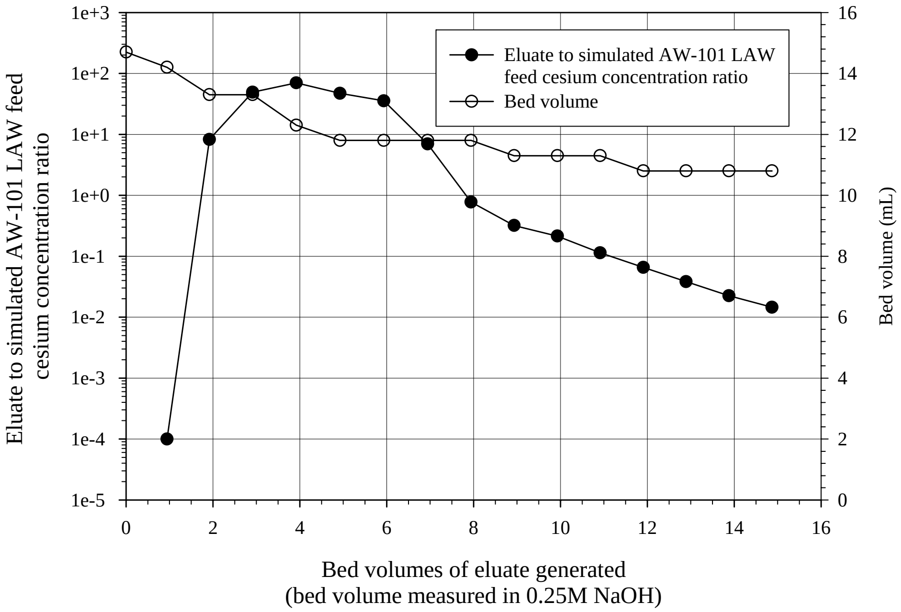

Figure 4.2. Elution and Bed-Volume Profile of Resin Loaded into the Column in the Reference As-Received Form

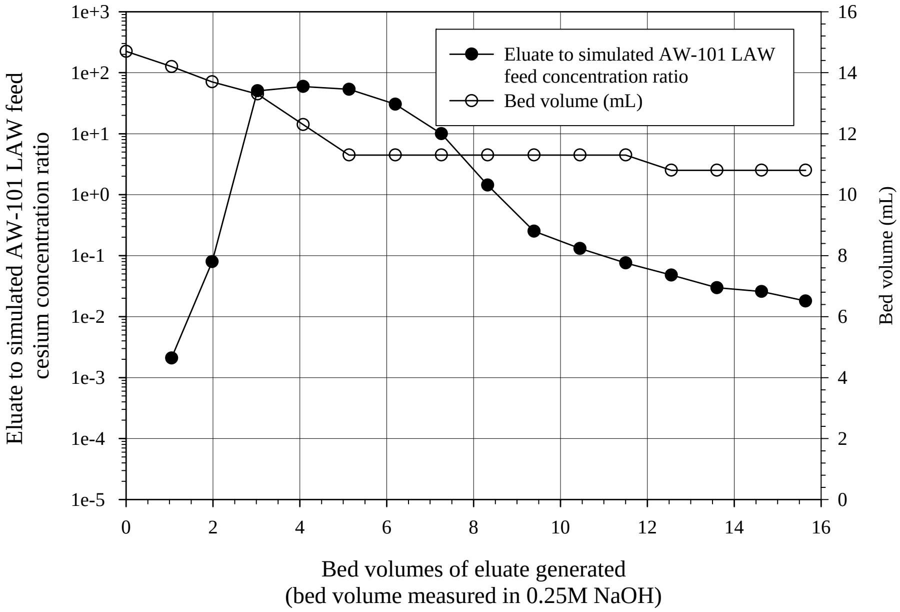

Figure 4.3. Elution and Bed-Volume Profile of Resin Loaded into the Column in the Reference Sodium Form

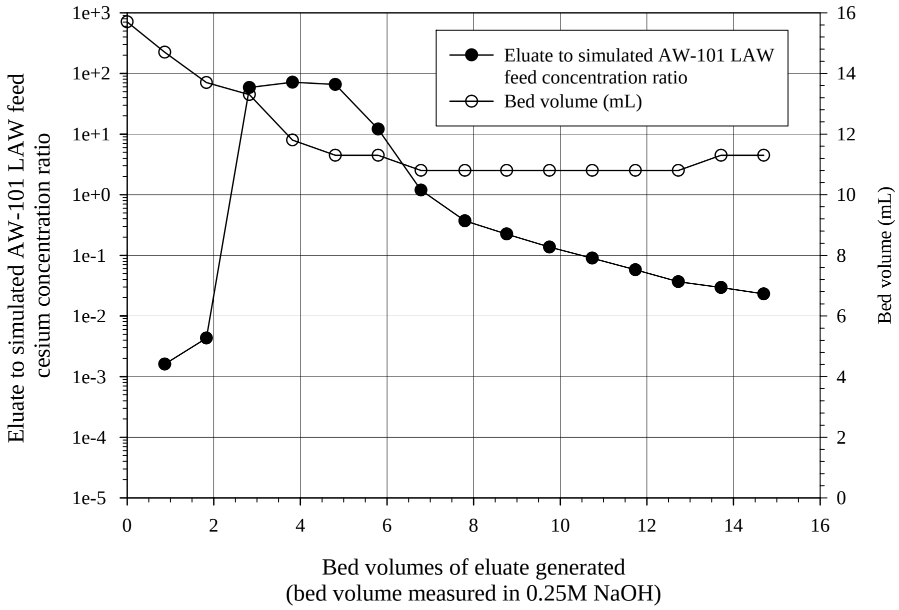

Figure 4.4. Elution and Bed-Volume Profile of Resin Loaded into the Column in the Reference Acid Form

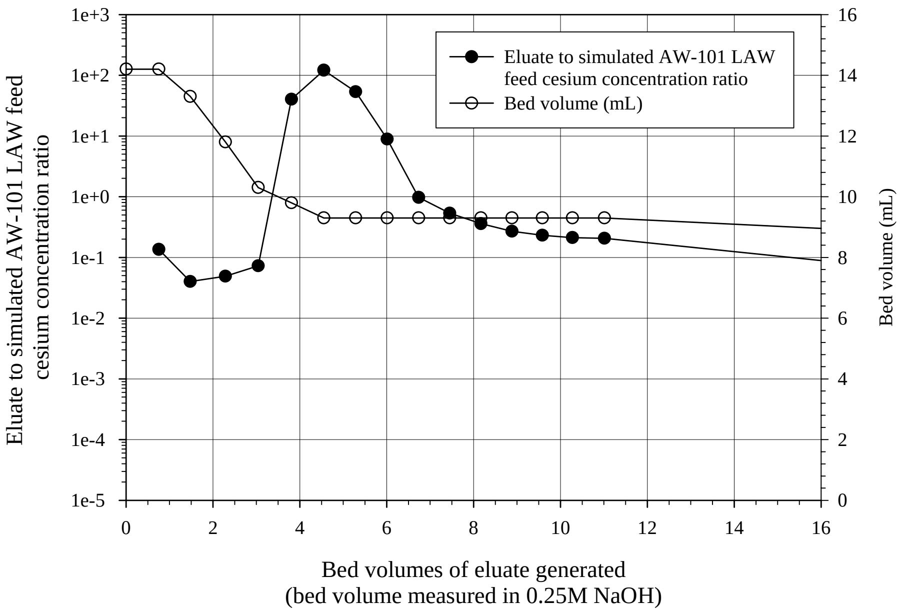

Figure 4.5. Elution and Bed-Volume Profile of Resin Loaded into the Column in the Stored Acid Form

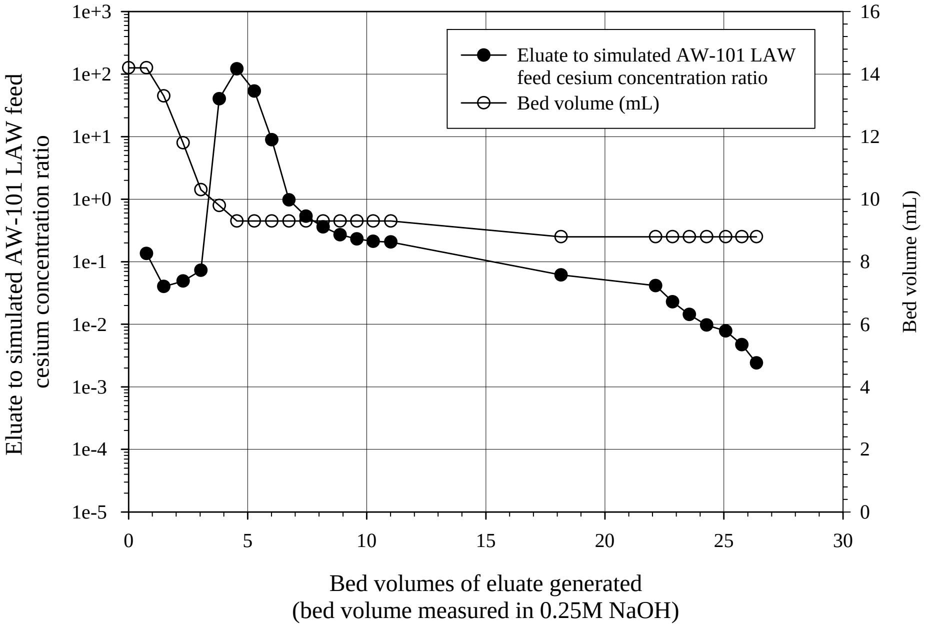

Figure 4.6. Complete Elution and Bed-Volume Profile of Resin Loaded into the Column in the Stored Acid Form

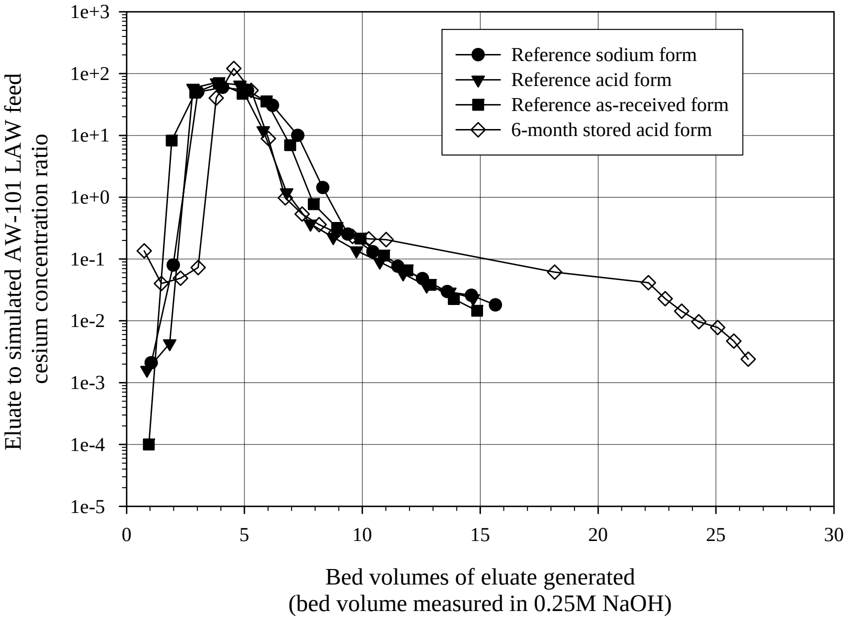

Figure 4.7. Comparison of Elution Profiles from Reference and 6-month Stored Resin Column Tests

Table 4.6 presents the composite eluate compositions and the derived separation factor. The separation factor is the ratio of the molar ratio of the analyte to that of sodium in the eluate to that in the feed LAW and so quantifies the resin selectivity. A separation factor greater than one indicates the concentration of the analyte in the eluate relative to sodium. As expected, the cesium selectivity is lowest for the stored resin, and the cesium selectivities for the reference resins are comparable. There appear to be no discernible trends in the separation factors of other analytes.

Table 4.6. Eluate Compositions and Separation Factors

Analyte	Concentration[a,b] (mg/L)				Separation factor[d]			
	As-Received	Acid	Sodium	Stored	As-Received	Acid	Sodium	Stored
Al	24.9	22.8	35.8	46.2	0.18	0.16	0.26	0.33
Ba	0.458	0.427	0.514	1.08	2.5	2.3	2.8	5.9
Ca	*2.4*	*1.4*	*1.8*	1.91	9.6	5.5	7.0	6.3
Cl	*12*	*13*	*9.5*	15	0.45	0.47	0.34	0.61
Cs	179	175	157	90.4[f]	1060	1020	900	600
F[c]	*5.8*	<1.3	*6.0*	*2.9*	1.1	<0.23	1.1	1.5
Fe	4.49	3.93	4.58	7.78	57	49	63	150
K	289	294	288	138	2.0	2.0	2.0	0.88
Li	<0.148	<0.144	*0.23*	0.086	<5.3	<5.1	6.3	1.8
Mn	0.649	0.523	1.12	0.203	30	24	37	8.9
Mo	<0.145	<0.141	<0.146	*0.045*	<0.51	<0.48	<0.49	0.15
Na	1,190	1,220	1,280	1,170	1.0	1.0	1.0	1.0
NO$_2$	*5.9*	*5.4*	*5.1*	*2.5*	0.015	0.014	0.013	0.007
NO$_3$	24,800	26,300	24,400	22,100	(e)	(e)	(e)	(e)
Ni	*0.53*	*0.72*	*0.74*	0.362	6.2	8.2	8.5	4.6
P	*0.75*	*0.87*	*0.85*	*0.13*	1.2	1.3	1.3	0.20
PO$_4$	*4.3*	<2.5	<2.5	<2.5	2.2	<1.2	<1.3	<10
Rb	0.623	0.63	0.592	(g)	28.5	28.5	26.5	(g)
SO$_4$	<2.5	<2.5	<2.5	*9.3*	<1.2	<1.2	<1.1	2.5
Si	*4.2*	*3.3*	*4.9*	9.05[i]	5.2	4.0	6.1	250[i]
Sr	*0.039*	<0.037	*0.044*	0.039	2.1	<1.9	2.7	2.3
TIC	<3	<3	<3	3	(h)	(h)	(h)	(h)
TOC (HP)	17	16	22	<4	0.93	0.86	1.2	<0.25

(a) Results in normal type have errors likely <15%, but those in italics are within 10 times their detection limit with errors likely exceeding 15%.
(b) Reported results satisfy the WTP project QC 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) The separation factor is the ratio of the molar ratio of the analyte to that of sodium in the eluate to that in the feed LAW.
(e) Not applicable since the eluant is nominally 0.5 M nitric acid (31,000 mg/L).
(f) Derived from the cesium-133 concentration in the LAW feed and the fraction of feed cesium-137 recovered in the eluate.
(g) Not measured.
(h) Not applicable since carbonate would have been destroyed in the 0.5 M nitric acid.
(i) The high value for silicon in these samples may be the result of leaching from the glass vials during storage.

4.6 Post-Elution Rinse and Resin Removal

The columns were rinsed with nominally 2 AVs 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 4.7 and show that the resin bed volume did not change from its final value attained during elution.

The resins were removed from the columns and dried at ambient pressure and 50°C to obtain the resin weights in Table 4.8 of between 3 g and 3.8 g.

Table 4.7. Post-Elution-Rinse Process Details

Parameter	Resin			
	As-Received	Acid	Sodium	Stored
Volume (mL)	91	92	90	96
Volume (BVs)	6	6	6	7
Flow rate (mL/h)	46	46	45	41
Flow rate (BV/h)	3	3	3	3
Resin bed volume (mL)	11	11	11	9
Recovered percentage of feed cesium	0.01	0.02	0.02	0.3

Table 4.8. Final-Acid-Form Resin Weights

Resin	Acid-Form Weight (g)	Equivalent Sodium-Form Weight (g)
As-received	3.440	3.784
Acid	3.615	3.977
Sodium	3.556	3.912
Stored	2.848	3.133

5.0 Conclusions

- Small batches of SL-644 cesium ion exchange resin from Lot C-01-05-28-02-35-60 (the “25-gallon” batch) were stored under various conditions for up to 6 months. The as-received resin was stored submerged in DI water for the 7 months between resin production and commencing test storage. Batch contacts were performed throughout the storage period to determine the impact of the storage conditions on the resin performance, as measured by the cesium equilibrium-distribution coefficient in simulated AW-101 LAW. Conclusions regarding the impact of the storage variables of time (0 to 6 months), resin form (as-received, acid, or sodium), medium (dry or submerged in DI water), cover gas (air or nitrogen) and temperature (ambient or 40°C) are provided below:
    - Resin performance decreased with increasing storage time. However, the rate of reduction in the equilibrium-distribution coefficient decreased with increasing time.
    - In general, the acid form of the resin provided the best performance throughout storage for the same time, temperature, medium, and cover gas. The stored form of the resin therefore appears to affect both its selectivity and capacity.
    - Significantly better performance was obtained when the resin was stored submerged in DI water so that both selectivity and capacity are affected.
    - Whether the resin was stored at ambient temperature or 40°C had no statistically significant impact on the resin performance over the 6-month storage period at a cesium concentration representative of that in Envelope A LAW. However, performance at lower cesium concentrations was significantly worse after storage at 40°C. Temperature, therefore, appears to mainly affect the resin’s selectivity.
    - Resin performance was not significantly impacted whether the resin was stored under air or nitrogen cover gas at a cesium concentration representative of that in Envelope A LAW. The cover gas appears to mainly affect the resin’s selectivity since storage under nitrogen provided better performance at lower cesium concentrations.

- Single-column tests were performed with resins loaded into the column in the acid, sodium, and as-received forms upon initiation of storage (reference resins) and with the best performing resin stored dry in air after 6 months. Column-distribution coefficients of ~220 were observed for the reference resins and ~100 for the stored resin. The equilibrium-distribution coefficient underestimated the column-distribution coefficients of the reference resins by ~50%. However, the stored-resin column-distribution coefficient was predicted to within 10% by the equilibrium behavior. There appeared to be no impact of storage or resin form on the elution performance of the resin.

- Only resin selectivity appears to initially deteriorate, as manifested in the poorer equilibrium performance at low cesium concentrations, but it maintained performance at higher concentrations. Both capacity and selectivity then deteriorate, and this manifests itself in lower column-distribution coefficients.

- The acid form provided consistently better performance over the as-received or sodium forms for the same storage conditions and its submergence in DI water is recommended as best for storage. Maintaining an ambient temperature of ~23°C and a nitrogen atmosphere above the resin will further reduce its rate of deterioration, but these factors have a lesser effect than resin form or storage medium.

- Poor performance of the 6-month air-stored resin in the column test makes its capability to satisfy baseline cesium-removal requirements under baseline operating conditions questionable. Storage of the resin under water is expected to result in significantly better performance, but quantification of this improvement was not possible within the scope of this study. Minimization of storage time for the SL-644 resin is highly recommended.

6.0 References

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Appendix A

Batch-Contact Results

Appendix A: Batch-Contact Results

Reference Resins

Table A1. Acid Form (Reference-H)

Equilibrium Sodium-to-Cesium Molar Ratio	Equilibrium-Distribution Coefficient (mL/g sodium-form resin)
1.29E+06	2517
1.78E+06	2285
2.84E+06	1814
1.11E+05	1529
1.83E+05	1795
1.70E+05	1459
1.38E+03	212
4.21E+04	721
2.20E+03	245

Table A2. Sodium Form (Reference-N)

Equilibrium Sodium-to-Cesium Molar Ratio	Equilibrium-Distribution Coefficient (mL/g sodium-form resin)
3.16E+06	903
3.15E+06	835
2.02E+06	857
5.39E+04	600
5.11E+03	210
6.44E+03	256
3.88E+03	188
7.75E+03	335

Table A3. As-Received Form (Reference-AR)

Equilibrium Sodium-to-Cesium Molar Ratio	Equilibrium-Distribution Coefficient (mL/g sodium-form resin)
4.60E+05	1231
4.38E+05	1112
4.72E+05	1141
1.20E+04	361
6.39E+03	297
1.11E+04	371
4.20E+03	250
4.15E+03	216
8.11E+02	77

1-Month Stored Resins

Table A4. Sodium Form Submerged in Air at Ambient Temperature (20WAN1)

Equilibrium Sodium-to-Cesium Molar Ratio	Equilibrium Distribution Coefficient (mL/g sodium-form resin)
5.68E+05	535
5.52E+05	523
5.72E+05	538
1.48E+04	426
1.45E+04	421
1.43E+04	403
1.22E+03	56
1.21E+03	53
1.20E+03	51

Table A5. As-Received Form Dry in Nitrogen at Ambient Temperature (20DNAR1)

Equilibrium Sodium-to-Cesium Molar Ratio	Equilibrium Distribution Coefficient (mL/g sodium-form resin)
1.24E+06	1155
1.33E+06	1225
1.25E+06	1167
3.41E+04	993
3.43E+04	1017
3.38E+04	990
1.74E+03	130
1.63E+03	111
1.70E+03	123

Table A6. Sodium Form Submerged in Nitrogen at 40^{o}C (40WNN1)

Equilibrium Sodium-to-Cesium Molar Ratio	Equilibrium Distribution Coefficient (mL/g sodium-form resin)
7.49E+05	586
7.82E+05	632
8.12E+05	657
2.04E+04	521
1.94E+04	478
2.06E+04	516
1.42E+03	73
1.30E+03	57
1.37E+03	66

Table A7. Acid Form Submerged in Air at 40^{o}C (40WAH1)

Equilibrium Sodium-to-Cesium Molar Ratio	Equilibrium Distribution Coefficient (mL/g sodium-form resin)
2.34E+06	1774
2.22E+06	1653
2.22E+06	1661
5.96E+04	1479
5.54E+04	1354
6.17E+04	1491
2.54E+03	199
2.41E+03	180
2.27E+03	165

Table A8. As-Received Form Submerged in Nitrogen at Ambient Temperature (20WNAR1)

Equilibrium Sodium-to-Cesium Molar Ratio	Equilibrium Distribution Coefficient (mL/g sodium-form resin)
4.42E+05	512
4.56E+05	544
4.65E+05	562
1.22E+04	436
1.28E+04	466
1.22E+04	439
1.16E+03	60
1.18E+03	64
1.16E+03	62

Table A9. Sodium Form Dry in Nitrogen at 40^{o}C (40DNN1)

Equilibrium Sodium-to-Cesium Molar Ratio	Equilibrium Distribution Coefficient (mL/g sodium-form resin)
9.90E+05	723
9.02E+05	654
8.85E+05	621
2.38E+04	533
2.53E+04	567
2.42E+04	558
1.51E+03	76
1.54E+03	77
1.47E+03	69

Table A10. Acid Form Dry in Air at Ambient Temperature (20DAH1)

Equilibrium Sodium-to-Cesium Molar Ratio	Equilibrium Distribution Coefficient (mL/g sodium-form resin)
2.18E+06	1450
2.26E+06	1511
2.21E+06	1486
6.17E+04	1317
6.20E+04	1342
5.92E+04	1249
2.61E+03	177
2.69E+03	188
2.55E+03	176

Table A11. As-Received Form Submerged in Nitrogen at 40°C (40WNAR1)

Equilibrium Sodium-to-Cesium Molar Ratio	Equilibrium Distribution Coefficient (mL/g sodium-form resin)
4.96E+05	647
4.94E+05	641
5.20E+05	697
1.20E+04	462
1.17E+04	445
1.21E+04	469
1.14E+03	60
1.18E+03	71
1.10E+03	47

2-Month Stored Resins

Table A12. Acid Form Dry in Air at Ambient Temperature (20DAH2)

Equilibrium Sodium-to-Cesium Molar Ratio	Equilibrium Distribution Coefficient (mL/g sodium-form resin)
1.81E+06	1157
1.82E+06	1142
1.78E+06	1112
2.84E+04	409
3.11E+04	457
2.89E+04	409
2.09E+03	115
2.19E+03	124
2.08E+03	113

3-Month Stored Resins

Table A13. Acid Form Dry in Air at Ambient Temperature (20DAH3)

Equilibrium Sodium-to-Cesium Molar Ratio	Equilibrium Distribution Coefficient (mL/g sodium-form resin)
1.73E+06	1093
1.96E+06	1303
2.04E+06	1211
2.56E+04	416
2.58E+04	426
2.60E+04	414
2.19E+03	133
2.03E+03	122
2.10E+03	119

Table A14. Acid Form Dry in Air at 40^{o}C (40DAH3)

Equilibrium Sodium-to-Cesium Molar Ratio	Equilibrium Distribution Coefficient (mL/g sodium-form resin)
9.18E+05	621
9.05E+05	624
9.37E+05	643
1.70E+04	240
1.59E+04	223
1.67E+04	234
1.72E+03	78
1.78E+03	85
1.75E+03	82

Table A15. Sodium Form Dry in Air at Ambient Temperature (20DAN3)

Equilibrium Sodium-to-Cesium Molar Ratio	Equilibrium Distribution Coefficient (mL/g sodium-form resin)
8.60E+05	533
9.26E+05	541
8.43E+05	558
1.22E+04	171
1.21E+04	162
1.23E+04	175
1.41E+03	58
1.47E+03	64
1.43E+03	62

Table A16. Sodium Form Dry in Air at 40^{o}C (40DAN3)

Equilibrium Sodium-to-Cesium Molar Ratio	Equilibrium Distribution Coefficient (mL/g sodium-form resin)
8.98E+05	529
9.06E+05	593
8.89E+05	569
1.39E+04	181
1.47E+04	196
1.42E+04	195
1.55E+03	63
1.55E+03	67
1.54E+03	67

Table A17. As-Received Form Dry in Air at Ambient Temperature (20DAAR3)

Equilibrium Sodium-to-Cesium Molar Ratio	Equilibrium Distribution Coefficient (mL/g sodium-form resin)
7.17E+05	623
7.90E+05	694
7.57E+05	636
1.22E+04	203
1.20E+04	191
1.25E+04	213
1.39E+03	66
1.38E+03	69
1.43E+03	70

Table A18. As-Received Form Dry in Air at 40^{o}C (40DAAR3)

Equilibrium Sodium-to-Cesium Molar Ratio	Equilibrium Distribution Coefficient (mL/g sodium-form resin)
1.11E+06	872
1.04E+06	861
1.05E+06	819
1.70E+04	305
1.67E+04	301
1.49E+04	267
1.59E+03	92
1.59E+03	89
1.58E+03	86

6-Month Stored Resins

Table A19. Acid Form Dry in Air at Ambient Temperature (20DAH6)

Equilibrium Sodium-to-Cesium Molar Ratio	Equilibrium Distribution Coefficient (mL/g sodium-form resin)
1.28E+06	845
1.19E+06	801
1.21E+06	786
1.69E+04	303
1.69E+04	301
1.68E+04	301
1.76E+03	89
1.78E+03	95
1.76E+03	97

Table A20. Acid Form Dry in Air at 40^{o}C (40DAH6)

Equilibrium Sodium-to-Cesium Molar Ratio	Equilibrium Distribution Coefficient (mL/g sodium-form resin)
8.29E+05	486
8.12E+05	474
7.61E+05	448
1.18E+04	168
1.15E+04	175
1.14E+04	171
1.54E+03	64
1.44E+03	57
1.52E+03	65

Table A21. Sodium Form Dry in Air at Ambient Temperature (20DAN6)

Equilibrium Sodium-to-Cesium Molar Ratio	Equilibrium Distribution Coefficient (mL/g sodium-form resin)
6.31E+05	442
6.13E+05	428
7.13E+05	495
9.51E+03	149
9.37E+03	146
1.01E+04	155
1.36E+03	56
1.38E+03	64
1.35E+03	59

Table A22. Sodium Form Dry in Air at 40°C (40DAN6)

Equilibrium Sodium-to-Cesium Molar Ratio	Equilibrium Distribution Coefficient (mL/g sodium-form resin)
8.01E+05	543
7.98E+05	518
7.64E+05	489
1.24E+04	202
1.14E+04	191
1.15E+04	182
1.44E+03	62
1.42E+03	63
1.46E+03	67

Table A23. As-Received Form Dry in Air at Ambient Temperature (20DAAR6)

Equilibrium Sodium-to-Cesium Molar Ratio	Equilibrium Distribution Coefficient (mL/g sodium-form resin)
7.19E+05	592
6.71E+05	574
7.14E+05	592
1.09E+04	222
1.02E+04	196
1.01E+04	194
1.35E+03	67
1.35E+03	67
1.36E+03	70

Table A24. As-Received Form Dry in Air at 40°C (40DAAR6)

Equilibrium Sodium-to-Cesium Molar Ratio	Equilibrium Distribution Coefficient (mL/g sodium-form resin)
9.01E+05	731
8.30E+05	669
7.56E+05	649
1.19E+04	249
1.07E+04	211
1.04E+04	199
1.38E+03	71
1.40E+03	72
1.40E+03	73

Table A25. Acid Form Dry in Nitrogen at Ambient Temperature (20DNH6)

Equilibrium Sodium-to-Cesium Molar Ratio	Equilibrium Distribution Coefficient (mL/g sodium-form resin)
1.43E+06	1118
1.46E+06	1106
1.55E+06	1133
2.06E+04	420
2.05E+04	414
2.03E+04	420
1.91E+03	119
1.92E+03	123
1.87E+03	119

Table A26. Sodium Form Dry in Nitrogen at 40^{o}C (40DNN6)

Equilibrium Sodium-to-Cesium Molar Ratio	Equilibrium Distribution Coefficient (mL/g sodium-form resin)
5.36E+05	361
4.58E+05	298
4.28E+05	269
7.24E+03	85
7.93E+03	98
8.21E+03	114
1.20E+03	39
1.22E+03	31
1.24E+03	40

Table A27. Sodium Form Dry in Nitrogen at Ambient Temperature (20DNN6)

Equilibrium Sodium-to-Cesium Molar Ratio	Equilibrium Distribution Coefficient (mL/g sodium-form resin)
4.05E+05	271
4.28E+05	299
4.38E+05	303
7.27E+03	100
7.65E+03	107
7.55E+03	106
1.19E+03	40
1.21E+03	43
1.20E+03	42

Table A28. Acid Form Dry in Nitrogen at 40^{o}C (40DNH6)

Equilibrium Sodium-to-Cesium Molar Ratio	Equilibrium Distribution Coefficient (mL/g sodium-form resin)
9.91E+05	677
1.02E+06	668
1.08E+06	698
1.42E+04	254
1.46E+04	257
1.50E+04	258
1.65E+03	81
1.65E+03	84
1.56E+03	56

Table A29. Sodium Form Submerged in Air at Ambient Temperature (20WAN6)

Equilibrium Sodium-to-Cesium Molar Ratio	Equilibrium Distribution Coefficient (mL/g sodium-form resin)
1.23E+06	787
1.31E+06	852
1.34E+06	856
1.36E+04	184
1.47E+04	200
1.45E+04	196
1.92E+03	77
1.99E+03	82
1.86E+03	76

Table A30. Sodium Form Submerged in Air at 40^{o}C (40WAN6)

Equilibrium Sodium-to-Cesium Molar Ratio	Equilibrium Distribution Coefficient (mL/g sodium-form resin)
1.28E+06	801
1.19E+06	774
1.12E+06	738
1.37E+04	180
1.61E+04	239
1.76E+04	250
1.82E+03	72
1.94E+03	77
1.92E+03	80

Table A31. Acid Form Submerged in Air at Ambient Temperature (20WAH6)

Equilibrium Sodium-to-Cesium Molar Ratio	Equilibrium Distribution Coefficient (mL/g sodium-form resin)
2.39E+06	1568
2.49E+06	1563
2.23E+06	1493
4.07E+04	697
4.54E+04	732
4.14E+04	719
3.30E+03	200
3.49E+03	203
3.61E+03	215

Table A32. Acid Form Submerged in Air at 40°C (40WAH6)

Equilibrium Sodium-to-Cesium Molar Ratio	Equilibrium Distribution Coefficient (mL/g sodium-form resin)
2.39E+06	1507
2.49E+06	1511
2.37E+06	1472
4.51E+04	727
4.29E+04	691
3.91E+04	675
3.27E+03	194
3.26E+03	195
3.38E+03	203

Table A33. Sodium Form Submerged in Nitrogen at Ambient Temperature (20WNN6)

Equilibrium Sodium-to-Cesium Molar Ratio	Equilibrium Distribution Coefficient (mL/g sodium-form resin)
1.13E+06	783
1.13E+06	775
1.15E+06	802
1.69E+04	255
1.83E+04	276
1.85E+04	276
1.97E+03	88
2.13E+03	102
2.06E+03	88

Table A34. Sodium Form Submerged in Nitrogen at 40°C (40WNN6)

Equilibrium Sodium-to-Cesium Molar Ratio	Equilibrium Distribution Coefficient (mL/g sodium-form resin)
1.13E+06	785
1.13E+06	772
1.18E+06	782
1.57E+04	239
1.74E+04	255
1.63E+04	250
1.91E+03	81
1.82E+03	75
1.97E+03	83

Table A35. Acid Form Submerged in Nitrogen at Ambient Temperature (20WNH6)

Equilibrium Sodium-to-Cesium Molar Ratio	Equilibrium Distribution Coefficient (mL/g sodium-form resin)
2.97E+06	1916
2.99E+06	1956
3.22E+06	2099
4.23E+04	729
4.64E+04	762
5.09E+04	881
3.46E+03	210
3.57E+03	212
3.37E+03	207

Table A36. Acid Form Submerged in Nitrogen at 40°C (40WNH6)

Equilibrium Sodium-to-Cesium Molar Ratio	Equilibrium Distribution Coefficient (mL/g sodium-form resin)
2.82E+06	1780
2.75E+06	1704
2.57E+06	1678
4.08E+04	694
4.03E+04	675
4.00E+04	671
3.25E+03	193
3.23E+03	192
3.31E+03	197

Table A37. As-Received Form Submerged in Air at 40^{o}C (40WAAR6)

Equilibrium Sodium-to-Cesium Molar Ratio	Equilibrium Distribution Coefficient (mL/g sodium-form resin)
1.39E+06	1108
1.36E+06	1065
1.32E+06	1013
2.13E+04	397
1.93E+04	359
2.05E+04	376
2.02E+03	104
1.98E+03	103
1.94E+03	102

Appendix B

Statistical Analysis of Batch-Contact Results

Appendix B: Statistical Analysis of Batch-Contact Results

Analysis of Equilibrium Distribution Coefficient Data

The data listed in Table B.1 were used in the analyses to be discussed. The first four columns, labeled Resin Form, Medium, Atmosphere, and Temperature, refer to conditions under which the resin can be stored before use. Their impact on the subsequent performance of the resin is of interest. Note three different “factor levels” in the Resin Form factor (Acid, Sodium, and As-received), and only two levels for the other three factors. The fifth column, Month, is the number of months the resin is stored before use. While the first four factors are of the “categorical” type, Month is a continuous quantity and can therefore be treated as a regression variable. The “EqDistCoeff“ column gives the observed response “Equilibrium-Distribution Coefficient” that measures the resin performance in testing and is potentially influenced by the factor levels given earlier in each row. Maximizing this response is desirable.

The first model described that was fit to the data used only the “main effects” as listed in the table above. That is, no “interaction effects” were initially used. Note that the factor Month was included both as linear and quadratic (squared) terms since the performance was expected to fall off relatively quickly with storage time, but then level out. Figure B.1 is a plot of the actual values observed (vertical axis and the last column above) against the values predicted from the model (horizontal axis). A very good model fit would result in all the points lying close to the diagonal line centered between the curved lines. The degree of spread of the curved lines reflects the inability of the model to explain all the variability in the response. The model fit is reasonable, but the points that lay well outside the curved bands show the experimental results that are difficult to explain.

Table B.2, labeled Effect Tests, follows for this initial main-effects model. It gives the statistical significance for the individual terms in the factors in the model rather than for the model as a whole (as was the case in the Analysis of Variance table—Table B.3). The larger the F Ratio values are, and the smaller the Prob>F values are, as listed in the last two columns, the more useful the associated factors are in explaining the variability in the data. Therefore, the ordered importance of the factors is Resin Form, then Medium, then Month, and then Month-squared. Atmosphere and Temperature, with the large Prob>F values, are adding little to the model. The subsequent Prediction Profiler figure (Figure B.2) shows these results graphically. Note that the response decreases with Month, first rapidly and then leveling out as expected. Acid appears to be the optimal level for Resin Form and Wet for Medium. Note the minimal impact of Atmosphere and Temperature indicated by the nearly flat lines.

An obvious improvement that can be made to the main-effects model discussed to this point is to also include interaction terms. This means, for example, that how the Resin Form level affects the response may actually depend on what Medium is used. Perhaps with Medium level “Dry,” one Resin Form level is best, but with Medium level “Wet,” a different Resin Form level would be best. Relationships like this would indicate that interactions of factors are important in explaining the experimental results. In this case, the Prediction Profiler become more complex since the relative shape of the lines can change, depending on the levels considered for a different factor. The next model therefore includes all the two-way interactions of the main effects. Interactions with Month-squared are not included since insufficient combinations of experimental conditions were run to allow the estimation of all the resulting effects.

Table B.1. Conditions Under Which Resin Can be Stored Before Use, the Time of Storage, and the Observed Response

Test identification	Resin Form	Medium	Atmosphere	Temperature	Month	EqDistCoeff
Reference-H	Acid	Wet	Air	ambient	0	1460
20DAH1	Acid	Dry	Air	ambient	1	1310
20DAH2	Acid	Dry	Air	ambient	2	580
20DAH3	Acid	Dry	Air	ambient	3	610
20DAH6	Acid	Dry	Air	ambient	6	480
40DAH3	Acid	Dry	Air	40	3	380
40DAH6	Acid	Dry	Air	40	6	300
20DNH6	Acid	Dry	Nitrogen	ambient	6	630
40DNH6	Acid	Dry	Nitrogen	40	6	420
20WAH6	Acid	Wet	Air	ambient	6	830
40WAH1	Acid	Wet	Air	40	1	1460
40WAH6	Acid	Wet	Air	40	6	810
20WNH6	Acid	Wet	Nitrogen	ambient	6	930
40WNH6	Acid	Wet	Nitrogen	40	6	830
Reference-N	Sodium	Wet	Air	ambient	0	520
20DAN3	Sodium	Dry	Air	ambient	3	330
20DAN6	Sodium	Dry	Air	ambient	6	300
40DAN3	Sodium	Dry	Air	40	3	340
40DAN6	Sodium	Dry	Air	40	6	330
20DNN6	Sodium	Dry	Nitrogen	ambient	6	210
40DNN1	Sodium	Dry	Nitrogen	40	1	550
40DNN6	Sodium	Dry	Nitrogen	40	6	220
20WAN6	Sodium	Wet	Air	ambient	6	430
20WAN1	Sodium	Wet	Air	ambient	1	470
40WAN6	Sodium	Wet	Air	40	6	420
20WNN6	Sodium	Wet	Nitrogen	ambient	6	450
40WNN1	Sodium	Wet	Nitrogen	40	1	550
40WNN6	Sodium	Wet	Nitrogen	40	6	440
Reference-AR	As-received	Wet	Air	ambient	0	790
20DAAR3	As-received	Dry	Air	ambient	3	400
20DAAR6	As-received	Dry	Air	ambient	6	380
40DAAR3	As-received	Dry	Air	40	3	490
40DAAR6	As-received	Dry	Air	40	6	430
20DNAR1	As-received	Dry	Nitrogen	ambient	1	1040
40WAAR6	As-received	Wet	Air	40	6	590
20WNAR1	As-received	Wet	Nitrogen	ambient	1	490
40WNAR1	As-received	Wet	Nitrogen	40	1	560

Table B.2. Effect Tests

Source	DF	Sum of Squares	F Ratio	Prob > F
Month	1	188823.5	4.4326	0.0440
Month*Month	1	105147.9	2.4683	0.1270
Resin Form	2	1176494.7	13.8090	<.0001
Medium	1	133133.9	3.1253	0.0876
Atmosphere	1	443.3	0.0104	0.9195
Temperature	1	1615.5	0.0379	0.8470

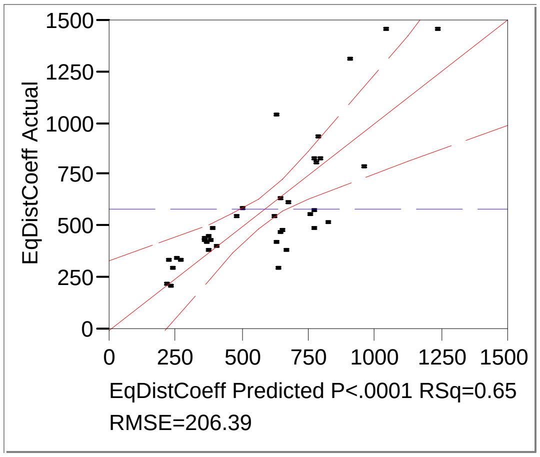

Figure B.1. Actual by Predicted Plot (main effects only)

Table B.3. Analysis of Variance

Source	**DF**	**Sum of Squares**	**Mean Square**	**F Ratio**
Model	7	2298599.9	328371	7.7085
Error	29	1235367.7	42599	Prob > F
C. Total	36	3533967.6		<0.0001

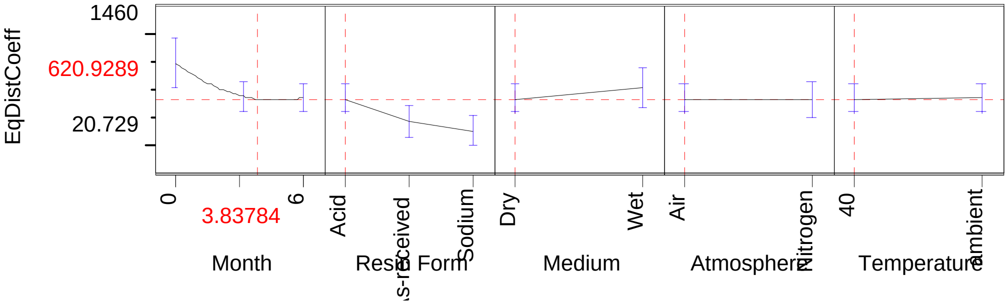

Figure B.2. Prediction Profiler

The resulting better fit of the actual and predicted values for this new model is shown in Figure B.3. The r-square value is increased from 0.65 to 0.93 with 93% of the variability explained, and the RMSE value is decreased from 206.39 to 128.06. The F Ratio value in the subsequent Analysis of Variance table (Table B.4) is also increased. All of these quantities indicate that this is an improved model over the main effects model.

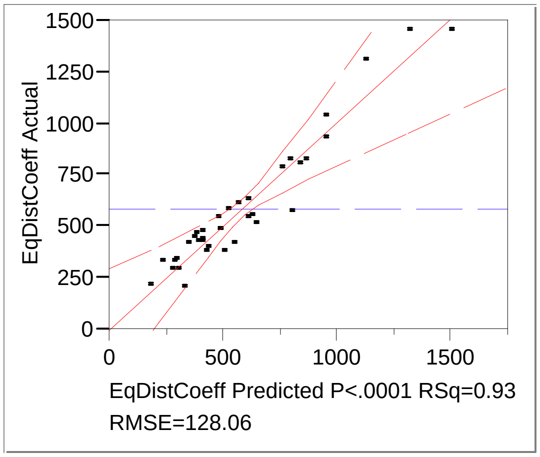

**Figure B.3. EqDistCoeff (with interaction terms)
Actual by Predicted Plot**

Table B.4. Analysis of Variance

Source	**DF**	**Sum of Squares**	**Mean Square**	**F Ratio**
Model	21	3287974.3	156570	9.5472
Error	15	245993.3	16400	Prob > F
C. Total	36	3533967.6		<.0001

Note in the Effects Tests (Table B.5) that all the effects that involve Atmosphere and Temperature, either as main effects or in interaction effects, generally have large significance-level values in the rightmost column (the only exception is the moderate value of the Medium*Temperature interaction). This continues to show that these two effects contribute very little to the model. This is again shown on the Prediction Profiler figures that follow (Figure B.4 and Figure B.6). Therefore, the next model investigated does not include these effects at all.

Table B.5. Effect Tests

Source	**DF**	**Sum of Squares**	**F Ratio**	**Prob > F**
Month	1	287710.21	17.5438	0.0008
Month*Month	1	189210.63	11.5375	0.0040
Resin Form	2	375967.93	11.4627	0.0010
Medium	1	46442.22	2.8319	0.1131
Resin Form*Medium	2	241262.39	7.3558	0.0059
Atmosphere	1	157.03	0.0096	0.9233
Resin Form*Atmosphere	2	34150.26	1.0412	0.3772
Medium*Atmosphere	1	2662.00	0.1623	0.6927
Temperature	1	10315.88	0.6290	0.4401
Resin Form*Temperature	2	22779.52	0.6945	0.5147
Medium*Temperature	1	53389.19	3.2555	0.0913
Atmosphere*Temperature	1	26051.28	1.5885	0.2268
Resin Form*Month	2	118342.53	3.6081	0.0526
Medium*Month	1	122977.11	7.4988	0.0152
Atmosphere*Month	1	409.82	0.0250	0.8765
Temperature*Month	1	12111.73	0.7385	0.4037

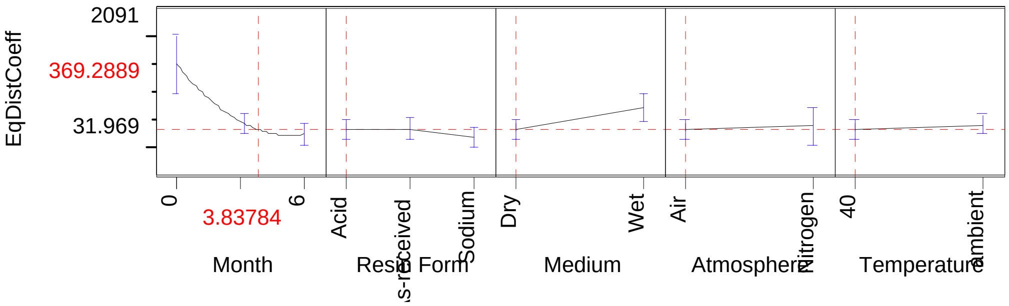

Figure B.4. Prediction Profiler

The model results obtained when Atmosphere and Temperature are not included follow. With the fewer model terms, the interaction with Month-squared can now be included. Note that the r-square value drops from the previous 0.93 to 0.92. However, this is not a statistically significant change when one considers how many terms were omitted from the previous model. In going from the previous model to this new model, nine terms are dropped while only two are added. The modestly larger r-square in the previous model is not worth the added model complexity, and the r-square gain from it is not statistically significant. That is why, even though r-square is decreased in the following model, the RMSE value is actually decreased (107.91 now compared to 128.06 before). As a result, the following model (Figure B.5) is preferred.

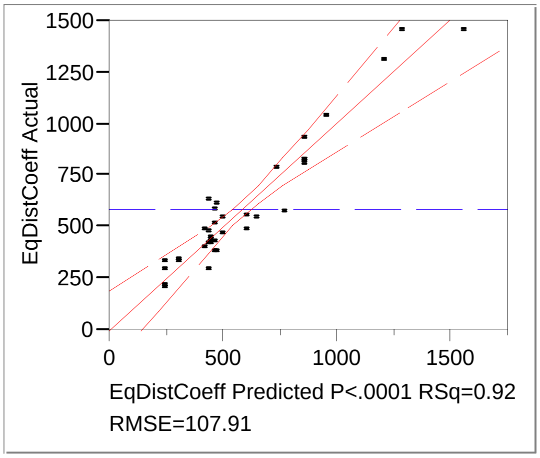

Figure B.5. EqDistCoeff (Atmosphere and Temperature not included) Actual by Predicted Plot

The remaining summary tables follow for this last model. Note the larger F Ratio value in the Analysis of Variance (Table B.6). Note also the significance indicated by the Effect Tests Prob>F values (Table B.7); the terms are generally all quite significant.

Table B.6. Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	13	3266127.6	251241	21.5746
Error	23	267840.0	11645	Prob > F
C. Total	36	3533967.6		<.0001

Table B.7. Effect Tests

Source	DF	Sum of Squares	F Ratio	Prob > F
Month	1	297440.22	25.5418	<.0001
Month*Month	1	164229.32	14.1027	0.0010
Resin Form	2	639019.54	27.4370	<.0001
Medium	1	125365.91	10.7654	0.0033
Resin Form*Medium	2	163447.43	7.0178	0.0042
Resin Form*Month	2	104448.49	4.4846	0.0227
Medium*Month	1	95698.99	8.2179	0.0087
Month*Month*Resin Form	2	66739.17	2.8655	0.0774
Month*Month*Medium	1	60267.61	5.1753	0.0326

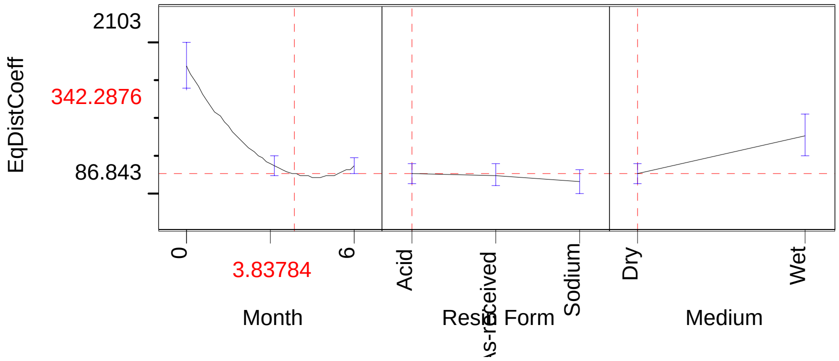

Figure B.6. Prediction Profiler

The Parameter Estimates in Table B.8 will be used below to show how predicted values can be obtained from this model. Consider the last line of the initial data table as shown in the following:

Resin Form	Medium	Atmosphere	Temperature	Month	EqDistCoeff
As-received	Wet	Nitrogen	40	1	560

Given this set of experimental conditions, what response would be expected based on the estimated model? The following Parameter Estimates can be used for this purpose. Note that the values for Atmosphere and Temperature are not used since they were not included in the final model.

First start with the Intercept term. Its estimate is approximately 1145.32 as shown in the first line in the Parameter Estimates (Table B.8).

For Resin Form (As-received), the Parameter Estimate indicates the subtraction of 76.95. And Medium(Wet) results in subtracting 221.99.

Month is different since it is a continuous effect. The value -305.83 listed in the Parameter Estimates is a slope that would be multiplied by the number of months. For the example case being discussed, this is 1, so -305.83 × 1 = -305.83 is the impact. Similarly, for Month-squared, 32.80 × 1 × 1 = 32.80 is added.

Then come the interaction terms. For Resin Form(As-received)*Medium(Wet), 104.87 is subtracted.

For Resin Form(As-received)*Month, the adjustment is –16.10 × 1 = -16.10. For Month-squared* Resin Form(As-received), 1 × 1 × 4.21 = 4.21 is added.

Table B.8. Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	1145.3201	67.65674	16.93	<.0001
Month	-305.8305	60.51384	-5.05	<.0001
Month*Month	32.801163	8.734492	3.76	0.0010
Resin Form[Acid]	530.14306	78.43151	6.76	<.0001
Resin Form[As-received]	-76.95166	81.25586	-0.95	0.3535
Resin Form[Sodium]	-453.1914	78.07055	-5.80	<.0001
Medium[Dry]	221.98673	67.65674	3.28	0.0033
Medium[Wet]	-221.9867	67.65674	-3.28	0.0033
Resin Form[Acid]*Medium[Dry]	-109.5736	30.07198	-3.64	0.0014
Resin Form[Acid]*Medium[Wet]	109.57359	30.07198	3.64	0.0014
Resin Form[As-received]*Medium[Dry]	104.86517	35.74464	2.93	0.0075
Resin Form[As-received]*Medium[Wet]	-104.8652	35.74464	-2.93	0.0075
Resin Form[Sodium]*Medium[Dry]	4.7084142	29.25032	0.16	0.8735
Resin Form[Sodium]*Medium[Wet]	-4.708414	29.25032	-0.16	0.8735
Resin Form[Acid]*Month	-166.9977	68.84507	-2.43	0.0235
Resin Form[As-received]*Month	-16.09951	72.88791	-0.22	0.8271
Resin Form[Sodium]*Month	183.09723	69.15069	2.65	0.0144
Medium[Dry]*Month	-173.6693	60.58194	-2.87	0.0087
Medium[Wet]*Month	173.66932	60.58194	2.87	0.0087
Month*Month*Resin Form[Acid]	17.596457	9.78714	1.80	0.0853
Month*Month*Resin Form[As-received]	4.214838	10.32179	0.41	0.6868
Month*Month*Resin Form[Sodium]	-21.81129	9.836734	-2.22	0.0368
Month*Month*Medium[Dry]	19.91022	8.752011	2.27	0.0326
Month*Month*Medium[Wet]	-19.91022	8.752011	-2.27	0.0326

And finally for Medium(Wet)*Month, 173.67 × 1 = 173.67 is added, and for Month-squared*Medium(Wet), 1 × 1 × -19.91 = -19.91 is the impact.

In summary from the previous statements, the Parameter Estimates suggest a predicted value for the case considered as:

$$1145.32 - 76.95 - 221.99 - 305.83 + 32.80 - 104.87 - 16.10 + 4.21 + 173.67 - 19.91 = +610.35$$

But for round-off error, this is the source of the value 610.361 in the final line and third last column of the following data table (Table B.9). Predicted values for the other experimental combinations would be obtained in the same manner. They are listed in Table B.9 and are plotted on the horizontal axis of Figure B.5.

Note that interpolated predicted values for Months other than those used in the experimental trials can be obtained in this manner. However, extrapolating outside the experimental range is not advisable. The range 0 to 6 months was used in the experimentation. Extrapolating to less than zero is nonsensical. At greater than 6, since a quadratic polynomial was used, the influence of Month would turn upwards as part of a parabola, and this too would be inappropriate. This is already observable in the final Prediction

Profiler figure for Month shown for the final model above. Predictions should not be made beyond 6 months with this model.

The predicted values given in Table B.9 are point estimates that do not indicate the uncertainty in the model caused by its inability to perfectly fit all the observed experimental results. This uncertainty is reflected in the RMSE value of 107.91. The average response expected for the experimental conditions used is given by the predicted values. An uncertainty range for such averages is given in the final two columns. If many repeated experiments were performed for a given set of conditions, their average result would be expected to fall into the 95% confidence interval shown. Any individual experimental result could range over an even wider interval roughly approximated by the predicted value ± twice the RMSE.

Table B.9. Data Table

Test Identification	**Resin Form**	**Medium**	**Atmosphere**	**Temperature**	**Month**	**EqDistCoeff**	**Predicted EqDistCoeff**	**Lower 95% Mean EqDistCoeff**	**Upper 95% Mean EqDistCoeff**
Reference-H	Acid	Wet	Air	ambient	0	1460	1563.04	1366.34	1759.75
20DAH1	Acid	Dry	Air	ambient	1	1310	1211.68	1052.06	1371.31
20DAH2	Acid	Dry	Air	ambient	2	580	776.112	664.111	888.113
20DAH3	Acid	Dry	Air	ambient	3	610	481.154	347.019	615.288
20DAH6	Acid	Dry	Air	ambient	6	480	439.973	332.302	547.643
40DAH3	Acid	Dry	Air	40	3	380	481.154	347.019	615.288
40DAH6	Acid	Dry	Air	40	6	300	439.973	332.302	547.643
20DNH6	Acid	Dry	Nitrogen	ambient	6	630	439.973	332.302	547.643
40DNH6	Acid	Dry	Nitrogen	40	6	420	439.973	332.302	547.643
20WAH6	Acid	Wet	Air	ambient	6	830	865.642	758.004	973.281
40WAH1	Acid	Wet	Air	40	1	1460	1294.37	1134.56	1454.19
40WAH6	Acid	Wet	Air	40	6	810	865.642	758.004	973.281
20WNH6	Acid	Wet	Nitrogen	ambient	6	930	865.642	758.004	973.281
40WNH6	Acid	Wet	Nitrogen	40	6	830	865.642	758.004	973.281
Reference-N	Sodium	Wet	Air	ambient	0	520	465.433	271.580	659.286
20DAN3	Sodium	Dry	Air	ambient	3	330	307.716	159.888	455.544
20DAN6	Sodium	Dry	Air	ambient	6	300	252.811	145.745	359.877
40DAN3	Sodium	Dry	Air	40	3	340	307.716	159.888	455.544
40DAN6	Sodium	Dry	Air	40	6	330	252.811	145.745	359.877
20DNN6	Sodium	Dry	Nitrogen	ambient	6	210	252.811	145.745	359.877
40DNN1	Sodium	Dry	Nitrogen	40	1	550	653.321	485.111	821.530
40DNN6	Sodium	Dry	Nitrogen	40	6	220	252.811	145.745	359.877
20WAN6	Sodium	Wet	Air	ambient	6	430	449.917	342.606	557.227
20WAN1	Sodium	Wet	Air	ambient	1	470	507.449	374.607	640.290
40WAN6	Sodium	Wet	Air	40	6	420	449.917	342.606	557.227
20WNN6	Sodium	Wet	Nitrogen	ambient	6	450	449.917	342.606	557.227
40WNN1	Sodium	Wet	Nitrogen	40	1	550	507.449	374.607	640.290
40WNN6	Sodium	Wet	Nitrogen	40	6	440	449.917	342.606	557.227
Reference-AR	As-received	Wet	Air	ambient	0	790	741.516	547.612	935.420
20DAAR3	As-received	Dry	Air	ambient	3	400	420.758	272.913	568.603
20DAAR6	As-received	Dry	Air	ambient	6	380	470.968	323.790	618.146
40DAAR3	As-received	Dry	Air	40	3	490	420.758	272.913	568.603
40DAAR6	As-received	Dry	Air	40	6	430	470.968	323.790	618.146
20DNAR1	As-received	Dry	Nitrogen	ambient	1	1040	956.547	781.028	1132.06
40WAAR6	As-received	Wet	Air	40	6	590	467.760	273.934	661.585
20WNAR1	As-received	Wet	Nitrogen	ambient	1	490	610.361	474.502	746.220
40WNAR1	As-received	Wet	Nitrogen	40	1	560	610.361	474.502	746.220

Summary: A very reasonable model that relies only on Resin Form, Medium, and Month has been derived. This model explains about 92% of the variation in the experimental results for Equilibrium-Distribution Coefficient. The additional factors Atmosphere and Temperature do not provide statistically significant contributions, so they would add very little to the prediction capability and were not included in the recommended model.

Additional investigation, not discussed in the previous pages, showed no patterns in the model residuals that would suggest the need for model improvement. The assumptions of equal variance and the normal distribution of residuals were also investigated and determined to be appropriate. A log transformation of the response was also modeled, primarily to accommodate the influence of Month in place of the quadratic term use, but appropriate models on the transformed data did not perform as well as the final model proposed here.

Appendix C

Column Test Results

Appendix C: Column Test Results

Reference As-received Form Resin

Table C1. Breakthrough Results

Bed volumes of simulated LAW processed	Breakthrough (%)
10.2	0.001
23.1	0.066
30.2	0.092
40.3	0.073
50.3	0.006
60.2	0.047
70.4	0.010
80.6	0.185
90.6	0.200
101.0	0.353
110.7	0.659
120.7	0.902
130.7	1.31
140.5	2.29
150.8	3.63
160.9	5.63
170.9	9.65
180.5	14.76

Table C2. Elution Results

Bed volumes of eluate generated	Eluate to simulated LAW feed cesium concentration ratio
0.960	0.0001
1.955	8.16
2.966	48.7
3.991	69.3
5.013	46.6
6.042	35.0
7.068	6.873
8.085	0.764
9.097	0.316
10.111	0.212
11.115	0.112
12.123	0.065
13.128	0.038
14.132	0.022
15.141	0.014

Reference Acid Form Resin

Table C3. Breakthrough Results

Bed volumes of simulated LAW processed	Breakthrough (%)
9.7	0.023
19.4	0.001
29.0	0.011
38.7	0.013
48.4	0.043
58.1	0.023
67.7	0.041
77.3	0.048
87.3	0.056
96.6	0.121
106.4	0.335
115.9	0.924
125.8	2.12
135.6	3.76
144.8	5.81
154.6	7.26
164.4	10.8
173.4	12.9

Table C4. Elution Results

Bed volumes of eluate generated	Eluate to simulated LAW feed cesium concentration ratio
0.869	0.002
1.831	0.004
2.823	58.5
3.820	71.5
4.807	65.7
5.798	12.0
6.786	1.19
7.800	0.370
8.764	0.224
9.753	0.137
10.742	0.090
11.735	0.058
12.729	0.037
13.712	0.029
14.700	0.023

Reference Sodium Form Resin

Table C5. Breakthrough Results

Bed volumes of simulated LAW processed	Breakthrough (%)
9.5	0.0004
19.8	0.014
30.1	0.053
40.5	0.181
50.8	0.421
61.2	0.813
71.5	1.38
81.9	1.81
91.2	3.37
101.6	5.08
112.0	8.37
122.3	9.53
132.7	11.1
143.0	13.9
153.4	16.1
164.5	18.8
174.8	23.3
185.1	27.0

Table C6. Elution Results

Bed volumes of eluate generated	Eluate to simulated LAW feed cesium concentration ratio
1.049	0.002
1.982	0.079
3.024	50.0
4.075	58.8
5.135	52.8
6.196	30.1
7.260	9.85
8.325	1.41
9.389	0.249
10.450	0.130
11.503	0.075
12.552	0.048
13.602	0.030
14.628	0.026
15.644	0.018

6-month Stored Acid Form Resin

Table C7. Breakthrough Results

Bed volumes of simulated LAW processed	Breakthrough (%)
10.7	0.019
21.0	0.138
31.4	0.649
41.7	2.12
51.9	5.54
62.2	11.8
72.1	19.2
82.2	29.6
92.6	44.4
103.0	55.8
113.4	66.1
123.7	76.1
133.4	82.6
142.8	85.7
152.4	86.7
162.6	95.2
172.9	95.0
183.7	94.6

Table C8. Elution Results

Bed volumes of eluate generated	Eluate to simulated LAW feed cesium concentration ratio
0.753	0.135
1.477	0.040
2.286	0.049
3.040	0.073
3.805	40.1
4.551	121
5.285	53.5
6.012	8.88
6.734	0.974
7.451	0.534
8.169	0.361
8.881	0.269
9.582	0.231
10.277	0.212
11.014	0.206
18.162	0.062
22.133	0.041
22.846	0.023
23.544	0.014
24.274	0.010
25.068	0.008
25.752	0.005
26.364	0.002

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