

AP-101 Simulant Validation for Cesium Ion Exchange Processing Using SuperLig[®] 644

S. K. Fiskum
L. A. Snow
D. L. Blanchard, Jr.

August 2003

Prepared for Bechtel National, Inc.
under Contract No. 24590-101-TSA-W000-00004

LEGAL NOTICE

This report was prepared by Battelle Memorial Institute (Battelle) as an account of sponsored research activities. Neither Client nor Battelle nor any person acting on behalf of either:

MAKES ANY WARRANTY OR REPRESENTATION, EXPRESS OR IMPLIED, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, process, or composition disclosed in this report may not infringe privately owned rights; or

Assumes any liabilities with respect to the use of, or for damages resulting from the use of, any information, apparatus, process, or composition disclosed in this report.

References herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by Battelle. The views and opinions of authors expressed herein do not necessarily state or reflect those of Battelle.

**AP-101 Simulant Validation for
Cesium Ion Exchange Processing
Using SuperLig[®] 644**

S. K. Fiskum
L. A. Snow
D. L. Blanchard, Jr.

August 2003

Test specification: 24590-PTF-TSP-RT-02-002, Rev. 0
Test plan: TP-RPP-WTP-206, Rev. 0
Test exception: 24590-WTP-TEF-RT-02-090
R&T focus area: Pretreatment
Test Scoping Statement(s): B-42
Contract No. 24590-101-TSA-W000-00004

Battelle—Pacific Northwest Division
Richland, Washington 99352

COMPLETENESS OF TESTING

This report describes the results of work and testing specified by Test Specification 24590-PTF-TSP-RT-02-002, Rev. 0 and Test Plan TP-RPP-WTP-206, Rev. 0 and Test Exception 24590-WTP-TEF-RT-02-090. The work and any associated testing followed the quality assurance requirements outlined in the Test Specification/Plan. The descriptions provided in this test report are an accurate account of both the conduct of the work and the data collected. Test plan results are reported. Also reported are any unusual or anomalous occurrences that are different from expected results. The test results and this report have been reviewed and verified.

Approved:

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

Date

Summary

The U. S. Department of Energy is tasked with the disposition of high-level radioactive waste stored at the Hanford site. The waste is to be vitrified following specific pretreatment processing, separating the waste into a small-volume high-level waste fraction and a large-volume low-activity waste (LAW) fraction that can be contact-handled. This requires ^{137}Cs removal from the waste to reduce the LAW radiological dose. The River Protection Project-Waste Treatment Plant (RPP-WTP) baseline process for ^{137}Cs removal from Hanford high-level tank waste is ion exchange. The current pretreatment flowsheet includes the use of Cs-selective, elutable, organic ion exchange material, SuperLig[®] 644 (SL-644), for Cs removal from the aqueous waste fraction. This material has been developed and supplied by IBC Advanced Technologies, Inc., American Fork, UT. SL-644 has been shown to be effective in removing Cs from a variety of Hanford tank wastes. Testing with actual tank waste is expensive because of its high radiological dose and associated requisite containment facilities. In order to mitigate testing costs, Hanford tank waste simulants are used to test the ion exchanger.

Battelle—Pacific Northwest Division (PNWD) was contracted to develop a simulant of the supernatant waste in Hanford Tank 241-AP-101 (AP-101), diluted to 5 M Na,^(a) and to validate this simulant for use in Cs ion exchange studies under Contract 24590-101-TSA-W000-00004. The AP-101 simulant validation activity is defined in Appendix C of the *Research and Technology Plan*^(b) under Technical Scoping Statement B-42. The simulant will be used for Cs ion exchange studies to verify design and operating parameters for the RPP-WTP plant-scale ion exchange systems.

Objectives

The AP-101 simulant validation test objective was to assure that the AP-101 simulant (developed under Test Specification TSP-W375-01-00020) is valid for Cs ion exchange process testing and to validate its performance relative to batch-distribution coefficients. As specified in *Test Specification 24590-PTF-TSP-RT-02-002, Rev. 0*, successful validation of the AP-101 simulant is defined by batch-equilibrium distribution coefficients agreeing with actual waste AP-101 batch-distribution coefficients within $\pm 30\%$ or within 2-sigma uncertainty. All testing objectives were met.

Conduct of Test

Matching ion exchange behavior on SL-644 posed challenges to the validation task. Actual tank waste from AP-101 was not available for a side-by-side comparison to the simulant. The SL-644 ion exchange behavior has been shown to vary according to production batch, particle-size distribution, shelf-life (aging) [1], and chemical cycling [2]. The SL-644 material tested on the actual waste came from two different production lots [3]. Batch contacts were conducted with production batch 981112YK-N3-16/18 (16/18) at three Cs concentrations and batch 010319SMC-IV-73 (-73) resin using the 212- to 425- μm

(a) The AP-101 simulant development and verification has been reported (Russell et al. 2003).

(b) *Research and Technology Plan*, 24590-WTP-PL-RT-01-002, Rev. 1, April 2002 and Rev. 2, April 2003, S. Barnes, R. Roosa, R. Peterson, Bechtel National, Inc., Richland, WA.

particle-size distribution at one Cs concentration. Column testing was conducted with the same particle-size distribution of the -73 resin [3]. The existing stock (largely depleted) of the -73, 212- to 425- μm resin was aged two years in the washed H-form. Because of production-batch variations from the vendor, a new product identical to the -73 batch could not be assured. The existing resin beds and column system that were used for actual waste processing had been used on other wastes for a total of seven process cycles, and chemical-degradation effects on the breakthrough curve were likely to be evident.

The AP-101 simulant validation was conducted with batch-contact testing where the Cs equilibrium distribution ratios, K_d s, were determined and compared with the K_d values obtained for the actual AP-101 tank waste. Two approaches were taken and are summarized in Figure S.1. The first approach was to perform batch contacts with the residual stock of -73 resin; any loss of performance would be correlated with a benchmark material, AW-101 simulant [4]. The second approach was to compare the batch-distribution data with recently produced SL-644 resin, C-01-05-28-02-35-60 (“C02,” 94.6-L [25-gal] production batch). In either case, the batch-distribution results were to agree with the actual waste test results within $\pm 30\%$ or within 2-sigma uncertainty.

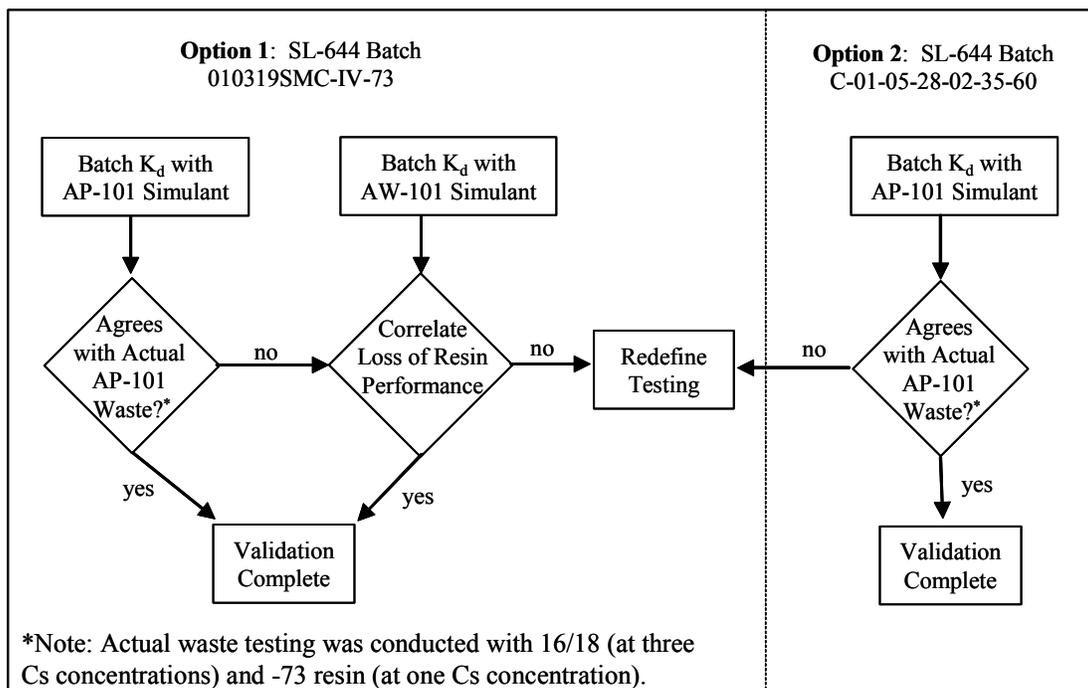


Figure S.1. Schematic of Simulant Validation Approach

This report summarizes testing of the AP-101 simulant using SL-644 in batch-contact studies. Batch contacts were performed with the AP-101 simulant at four Cs concentrations at a phase ratio of nominally 120 mL/g (liquid volume to exchanger mass). Resin test materials were taken from the production batch -73 and from production batch C02. An AW-101 simulant was tested in a side-by-side comparison with the AP-101 simulant. The AW-101 simulant had been tested over the last two years on resin batch -73. Because the SL-644 has shown evidence of deterioration with aging, the AW-101 simulant was the best

source as a benchmark degradation indicator. All batch-contact equilibrium coefficients (K_d , mL/g) were calculated relative to the mass of H-form SL-644 resin.

Results and Performance Against Objectives

The AP-101 simulant was validated for equilibrium Cs ion exchange. The simulant K_d results with -73 resin were compared to the actual waste, albeit only one actual AP-101 waste test was conducted with the -73 resin. The single Cs concentration tested on -73 compared well with the values obtained with 16/18 resin when contacted with actual AP-101 waste. The simulant K_d results were significantly below those of the actual waste, well outside of the $\pm 30\%$ criterion. However, when corrected for the aging effect (as determined from the AW-101 simulant testing), the AP-101 simulant results on the -73 resin were well within the $\pm 30\%$ criterion over a Na:Cs mole ratio range of $4E+3$ to $2E+6$. At Na:Cs mole ratios $< 4E+3$, the $\pm 30\%$ criterion was exceeded; however, this threshold is outside of the expected feed conditions, which are expected to be $> 1E+5$ in all cases. The AP-101 simulant K_d results for the C02 resin were also in good agreement with the actual waste K_d results and with the corrected -73 AP-101 simulant results. Thus the validation was achieved by two different paths.

The AP-101 simulant batch-contact results and best-fit curves are summarized in Figure S.2 where K_d is plotted as a function of the Na:Cs mole ratio. The AP-101 actual waste curve is also shown for reference with the $\pm 30\%$ threshold limits. The curve fits were used to calculate the feed condition (Na:Cs mole ratio equal to $1.10E+5$) K_d s shown in Table S.1.

Table S.1. Summary of Batch-Distribution Coefficients at the AP-101 Actual Waste Feed Condition

Parameter	Actual AP-101	Simulant AP-101	Simulant AP-101	Simulant AP-101
SL-644 Batch ID	16/18, (-73) ^(a)	C02	-73	-73 (corrected) ^(b)
K_d , mL/g at feed condition ^(c)	807	863	448	896
Deviation from actual	NA ^(d)	+6.8%	-44%	+11%
(a) Only one Cs concentration was tested with the -73 resin. (b) The corrected K_d values are based on measured performance of AW-101 simulant with -73 resin in 2001 and 2003. (c) Feed condition Na:Cs mole ratio of $1.10E+5$. (d) Not applicable.				

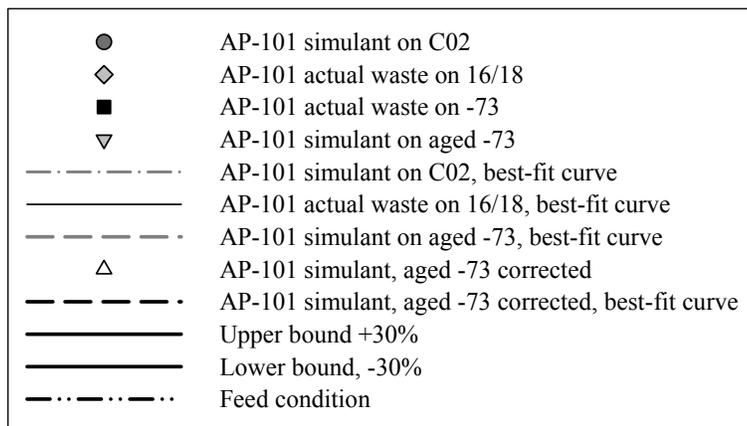
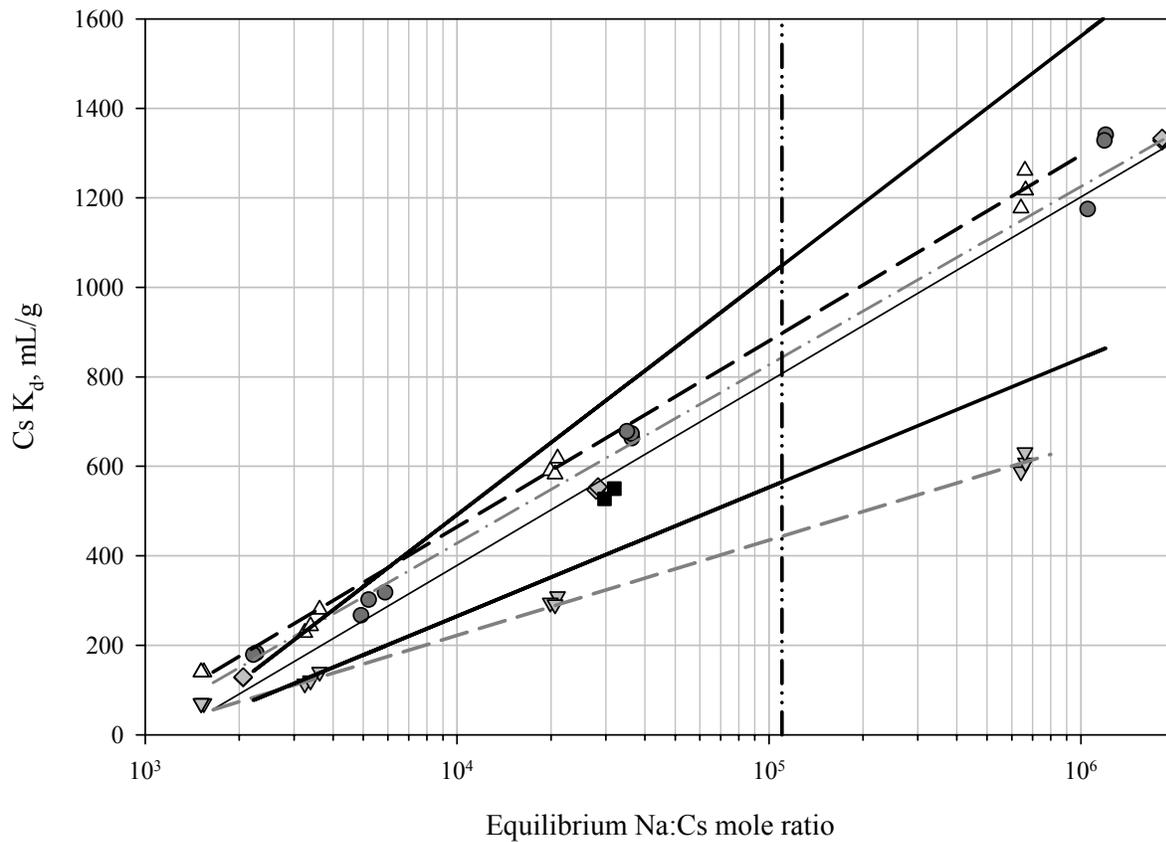


Figure S.2. Plot of K_{ds} for SL-644 Resins in AP-101 Simulant and Actual Waste

It is important to note that the batch-contact testing evaluated the equilibrium Cs ion exchange behavior. The rate of Cs ion exchange or kinetics is better evaluated through column testing. But differences in ion exchange kinetics are expected to arise more from differences in resin samples than from differences between the simulant and actual waste, provided a small set of matrix components (Na^+ , Cs^+ , K^+ , OH^- and total ionic strength) are accurately reproduced.

QA Requirements

PNWD implemented the RPP-WTP quality requirements by performing work in accordance with the PNWD Waste Treatment Plant Support Project (WTPSP) 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 are implemented through PNWD's *Waste Treatment Plant Support Project Quality Assurance Requirements and Description Manual* and to the approved Test Plan, TP-RPP-WTP-206, Rev. 0. The analytical requirements were implemented through PNWD's *Conducting Analytical Work in Support of Regulatory Programs*.

PNWD addressed internal verification 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 were traceable, that inferences and conclusions were soundly based, and that the reported work satisfied the Test Plan objectives.

Issues

None.

Terms and Abbreviations

16/18	SL-644 resin batch 981112YK-N3-16/18
-73	SL-644 resin batch 010319SMC-IV-73
AP-101	241-AP-101 Hanford tank waste, diluted to 5 M Na
ASR	Analytical Services Request
ASTM	American Society for Testing and Materials
BS	blank spike
C02	SL-644 resin batch C-01-05-28-02-35-60
CMC	Chemical Measurements Center
DI	deionized
EDTA	ethylenediaminetetraacetic acid
GEA	gamma energy analysis
HASQARD	Hanford Analytical Services Quality Assurance Requirements Document
IC	ion chromatography
ICP-AES	inductively-coupled plasma–atomic emission spectrometry
ICP-MS	inductively-coupled plasma–mass spectrometry
LAW	low-activity waste
MDL	minimum detection limit
MRQ	minimum reportable quantity
MS	matrix spike
NTA	nitrilotriacetic acid
PNWD	Battelle—Pacific Northwest Division
PSD	particle-size distribution
QAPjP	quality assurance project plan
QARDM	Quality Assurance Requirements and Description Manual
QC	quality control
RPD	relative percent difference
RPP-WTP	River Protection Project-Waste Treatment Plant
RSD	relative standard deviation
SL-644	SuperLig [®] 644
WTPSP	Waste Treatment Plant Support Project

Contents

Summary	iii
Terms and Abbreviations	ix
1.0 Introduction.....	1.1
1.1 Background.....	1.1
1.2 Objectives	1.2
1.3 Success Criterion	1.2
1.4 Validation Approach.....	1.2
2.0 Experimental.....	2.1
2.1 SL-644 Resin Properties—As Received.....	2.1
2.2 AP-101 Simulant and Actual Waste Composition	2.2
2.3 AW-101 Simulant Feed Preparation.....	2.2
2.4 SL-644 Resin Preparation.....	2.4
2.5 Batch Contacts.....	2.7
3.0 Results and Discussion	3.1
3.1 Equilibrium Test.....	3.1
3.2 AP-101 Simulant	3.2
3.3 AW-101 Simulant.....	3.5
3.4 AP-101 Simulant Validation.....	3.10
3.4.1 Validation Strategy Option 1	3.10
3.4.2 Validation Strategy Option 2	3.13
3.4.3 High Bias Discussion.....	3.16
3.5 Isotherms	3.18
4.0 Quality Control	4.1
4.1 Quality Assurance Requirements	4.1
4.2 Analytical Results.....	4.2

5.0	Conclusions.....	5.1
6.0	References.....	6.1
	Appendix A: AW-101 Simulant Preparation	A.1
	Appendix B: Resin Properties.....	B.1
	Appendix C: Batch Contacts Results	C.1

Figures

S.2. Plot of K_d s for SL-644 Resins in AP-101 Simulant and Actual Waste	vi
1.1. Actual AP-101 Waste Testing with SL-644 Resin	1.2
1.2. Schematic of Simulant Validation Approach	1.3
3.1. Comparison of $C_s K_d$ Values (resin mass in the H-form).....	3.4
3.2. AP-101 Simulant and Actual Waste $C_s K_d$ as a Function of Equilibrium C_s Concentration	3.5
3.3. AW-101 K_d Values as a Function of Na:Cs Mole Ratio, 2-Yr Test Range	3.7
3.4. AW-101 Simulant $C_s K_d$ as a Function of C_s Concentration	3.8
3.5. Successful AP-101 Simulant Validation Pathways	3.10
3.6. AP-101 Simulant Validation Strategy Option 1	3.14
3.7. AP-101 K_d Values with Corrected, Aged -73 Resin.....	3.16
3.8. Relative Difference Between K_d Values for Actual AP-101 Tank Waste Contacted with 16/18 and -73 Resins and Simulant AP-101 Contacted with C02 and -73 Resins	3.17
3.9. Isotherms for AP-101 Simulant and Actual Waste.....	3.19
3.10. AW-101 Simulant Isotherms	3.21

Tables

S.1. Summary of Batch-Distribution Coefficients at the AP-101 Actual Waste Feed Condition.....	v
2.1. Dry Particle-Size Weight-Percent Distribution of As-Received SL-644, Batches 16/18 and -73	2.1
2.2. AP-101 Simulant and Actual Waste Compositions	2.3
2.3. Targeted AW-101 Simulant Feed Composition	2.4
2.4. Feed AW-101 Simulant Compositions	2.5
2.5. AP-101 and AW-101 Feeds and Associated Tests	2.6
2.6. SL-644 Resin F-factors	2.6
2.7. Actual Cs Concentrations Used for the Batch-Distribution Tests	2.7
3.1. Batch Equilibrium K_d Values as a Function of Contact Time, First Test	3.1
3.2. Batch Equilibrium K_d Values as a Function of Time, Second Test	3.2
3.3. AP-101 Equilibrium Cs Concentrations and Batch Distribution Coefficients with SL-644.....	3.3
3.4. Equilibrium Cs K_d Values in AW-101 Simulant in Contact with -73 and C02 Resins	3.6
3.5. Predicted Cs K_d Values in AW-101 Simulant in Contact with -73 and C02 Resins.....	3.9
3.6. Comparison of Corrected AP-101 Simulant K_d Data on -73 Resin	3.12
3.7. Comparison of AP-101 Simulant K_d Data on C02 Resin	3.15
3.8. Equilibrium Cs Concentrations for AP-101 Simulant and Actual Waste	3.18
3.9. Equilibrium Cs Concentrations for AW-101 Simulant.....	3.20
4.1. ICP-AES Analysis of AW-101 Simulant.....	4.3
4.2. Anion Analysis of AW-101 Simulant.....	4.5
4.3. Cs Concentration in Spiked Stock Simulant Solutions.....	4.6
A.1. Simulant AW-101 (Envelope A) Preparations	A.1
B.1. F-Factor for SL-644	B.1

1.0 Introduction

The U. S. Department of Energy plans to vitrify tank wastes at the Hanford Site in preparation for permanent disposal. Before vitrification, tank wastes will be divided into low-activity and high-level fractions through specific pretreatment processes. The current flowsheet for pretreating the Hanford high-level tank wastes includes the use of Cs-selective SuperLig[®] 644 (SL-644) resin for ¹³⁷Cs removal from the aqueous waste fraction. IBC Advanced Technologies, Inc., American Fork, UT, developed and supplied this material. Valid simulant solutions for Hanford tank waste supernatants (diluted to 5 M Na) must be developed to minimize testing costs associated with Cs ion exchange studies conducted to assure that the River Protection Project – Waste Treatment Plant (RPP-WTP) will meet the design-basis operating and throughput requirements.

1.1 Background

The 241-AP-101 (AP-101) simulant has been formulated and tested extensively for chemical, physical, and rheological properties [5]. The chemical components, density, and rheological behavior matched well with an actual AP-101 composite sample. Once prepared and filtered, the simulant was also found to be stable with respect to continued precipitation reactions. This process concluded simulant verification activities as defined by Smith [6] by matching chemical concentrations and physical properties.

The AP-101 simulant requires validation for Cs ion exchange process testing. Validation confirms that the process behavior of the simulant adequately mimics the behavior of the actual waste [6]. Matching ion exchange behavior on SL-644 posed challenges to the validation task. Actual tank waste from AP-101 was not available for a side-by-side comparison to the simulant. The SL-644 ion exchange behavior has been shown to vary according to production batch, particle-size distribution, shelf-life (aging) [1], and chemical cycling [2]. The SL-644 material tested on the actual waste came from two different production lots [3]. Batch contacts were conducted with production batch 981112YK-N3-16/18 (16/18) at three Cs concentrations and batch 010319SMC-IV-73 (-73) resin using the 212- to 425- μm particle-size distribution at one Cs concentration. Column testing was conducted with the same particle size distribution of the -73 resin [3]. The existing stock (largely depleted) of the -73, 212- to 425- μm resin was aged two years in the washed H-form. Because of production batch variations from the vendor, an identical product to the -73 batch could not be assured. The existing resin beds and the column system that was used for actual waste processing had been used on other wastes for a total of seven process cycles, and chemical-degradation effects on the breakthrough curve were likely to be evident. The test materials applied to the actual waste are summarized in Figure 1.1.

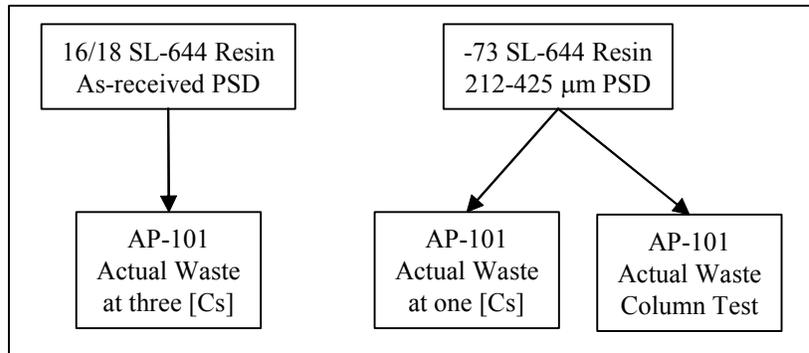


Figure 1.1 Actual AP-101 Waste Testing with SL-644 Resin

1.2 Objectives

The objective of this work was to validate the AP-101 simulant for use in Cs ion exchange process testing. This was accomplished by performing the following:

- determining Cs equilibrium distribution coefficients of SL-644 in contact with AP-101 simulant
- comparing Cs equilibrium distribution coefficients of actual AP-101 tank waste supernatant with simulant AP-101 supernatant on SL-644
- providing a basis for AP-101 simulant validation.

1.3 Success Criterion

The simulant validation is considered successful if the K_d data of the simulant matches the batch K_d of the actual waste within $\pm 30\%$ or within 2-sigma uncertainty.

1.4 Validation Approach

The simulant validation was conducted with batch-contact testing. The Cs equilibrium distribution ratios, K_{ds} , were determined and compared with the K_d values obtained for the actual AP-101 tank waste. Two approaches were taken and are summarized in Figure 1.2. The first approach was to perform batch contacts with the residual stock of -73 resin; any loss of performance would be correlated with a benchmark material, AW-101 simulant [4]. The second approach was to test the batch-distribution data with recently produced SL-644 resin, C-01-05-28-02-35-60 (C02). In either case, the batch-distribution results were to agree with the actual waste test results within $\pm 30\%$ or within 2-sigma uncertainty.

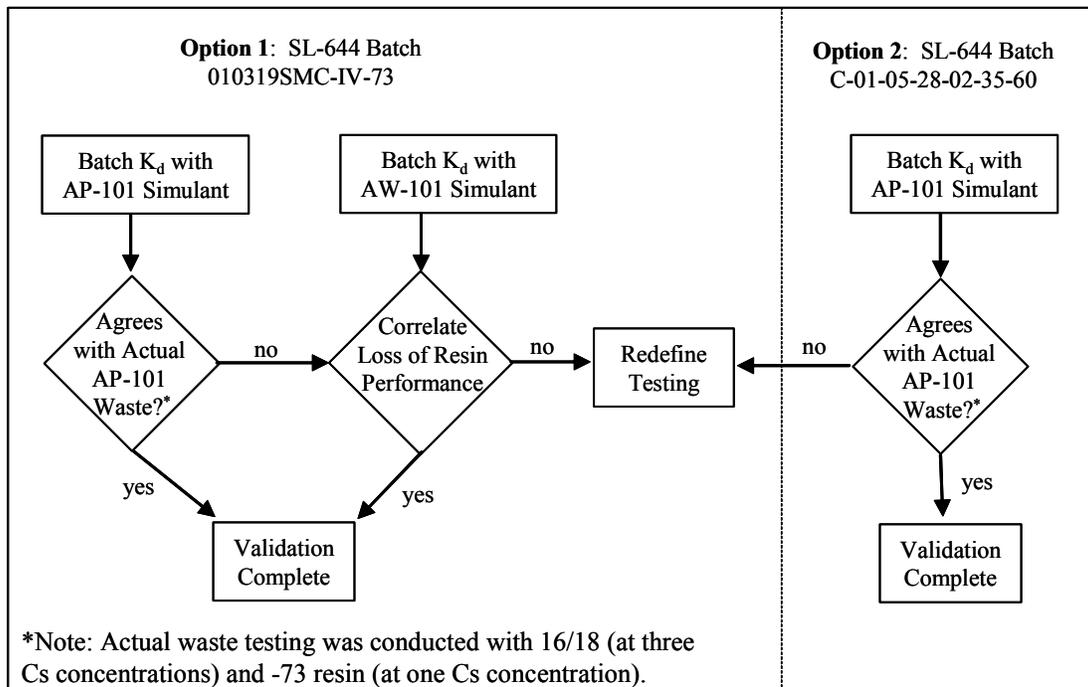


Figure 1.2. Schematic of Simulant Validation Approach

This report describes the results of batch-distribution contacts of the aged SL-644 (-73) and the more freshly produced SL-644 (C02) with Hanford tank waste AP-101 simulant and AW-101 simulant diluted to nominally 5 M Na. All work was conducted according to Test Specification 24590-PTF-TSP-RT-02-002, Rev. 0,^(a) Test Plan TP-RPP-WTP-206, Rev. 0,^(b) and Test Exception 24590-WTP-TEF-RT-02-090.

(a) *Ion Exchange Testing Validation and Verification of AP-101 Simulant*. J Toth. River Protection Project-Waste Treatment Plant, Bechtel National Inc., Richland, WA. July 31, 2002.

(b) *Ion Exchange Testing of AP-101 Simulant for Ion Exchange Validation*. S Fiskum. Battelle—Pacific Northwest Division. Richland, WA. January 2003.

2.0 Experimental

All experimental activities supporting the validation of AP-101 simulant were conducted according to test instruction TI-RPP-WTP-225, Rev. 0, *Batch Contact Testing of AP-101 Simulant with SL-644 for Simulant Validation*. All raw and reduced data are maintained in the project files at Battelle—Pacific Northwest Division (PNWD) under Project Number 42365. The following sections summarize resin properties, feed compositions, and experimental setup for batch-contact testing.

2.1 SL-644 Resin Properties—As Received

The SL-644 batch 16/18 (produced in 1998) was used for batch-contact testing at three Cs concentrations in actual AP-101 tank waste (diluted to 5 M Na) in 2001. This material batch had a distinct salt and pepper appearance with a significant light-gray fraction. It was received as a dry granular, free-flowing material in a ~1-L polyethylene bottle with approximately 50% gaseous headspace. The bottle had been periodically opened and shaken such that follow-on testing could evaluate the effect of aging on performance. The dry-sieve particle-size distribution has been previously reported [1] and is reproduced in Table 2.1. Batch-distribution studies with this SL-644 batch on AW-101 simulant indicated that it performed well, and it was used for actual waste AP-101 batch-distribution testing. Unfortunately, later simulant column testing proved this material inadequate [1], and its use was abandoned.

Table 2.1. Dry Particle-Size Weight-Percent Distribution of As-Received SL-644, Batches 16/18 and -73

Sieve Size ^(a)	Particle Size, (µm)	16/18 wt %	-73, wt %
18	>1000	1.78	0.06
30	600 - 1000	55.25	37.27
40	425 - 600	20.12	38.23
50	300 - 425	13.76	18.01
70	212 - 300	7.93	6.08
100	150 - 212	1.11	0.26
140	106 - 150	0.02	0.06
>140	<106	0.03	0.03

(a) Corresponding to ASTM E-11 specification.

The -73 resin, prepared at IBC on 3/19/01, exhibited a black-red appearance peppered with light-brown specks. It was received from IBC as a dry, granular, free-flowing material in a 1-L polyethylene bottle with an approximately 32% gaseous headspace. There was no indication that this headspace was filled with nitrogen or other inert gas, and no attempt was made to exclude air during storage. Table 2.1 reproduces the dry-sieve results of the resin batch that was previously reported [1]. The 212- to 425-µm fraction was forwarded for actual waste column testing; this fraction represented 24 wt% of the

as-received material.^(a) The resin had been batch-contact tested with AW-101 simulant in 2001 and 2002 [7] as well as in the current study. It was also used for a single Cs concentration batch-contact with, and column testing of, the actual AP-101 tank waste [3].

The C02 SL-644 resin batch was prepared by IBC in May 2002 as part of a 94.6-L (25-gal) production run. A nominal 19-L (5-gal) aliquot was delivered to PNWD in the Na form under water. This material had been previously sampled such that the gaseous head space was ambient air. The particle-size distribution for this material had not been characterized, but product specifications indicated it was 35 to 60 mesh (250- to 500- μm) in the expanded Na form. The material was granular and reddish-brown.

2.2 AP-101 Simulant and Actual Waste Composition

The AP-101 simulant was provided by the PNWD simulant development task from the 10-L scale-up preparation [5]. Its composition (except for Cs concentration) was well characterized and is reproduced in part (trace constituents are omitted) in Table 2.2. A sub-sample of the simulant was submitted to the Chemical Measurements Center (CMC) under Analytical Services Request (ASR) 6615 for Cs and Rb analysis by inductively coupled plasma-mass spectrometry (ICP-MS). Additional Rb was added to the simulant to better match the actual waste Rb concentration. The actual AP-101 supernatant diluted feed composition has also been reported [3] and is reproduced in part (trace constituents are omitted) in Table 2.2. The Cs concentration determined by ICP-MS appeared to be biased slightly low for the simulant. The as-prepared concentration for AP-101 simulant was calculated to be $4.50\text{E-}5$ M Cs (6.0 mg/L); the measured value was 17% low (5.0 mg/L). A similar situation appeared to be present with the actual waste analysis, in which case, a total Cs concentration of $4.5\text{E-}5$ M was calculated based on isotopic distribution and gamma-energy analysis. The Cs molarity of $4.5\text{E-}5$ in the AP-101 simulant was used for all subsequent data processing.

2.3 AW-101 Simulant Feed Preparation

Several batches of AW-101 simulant were prepared as previously described [4] to support the batch-contact and column ion exchange work over the past two years. The targeted composition is shown in Table 2.3. A 2-L batch of AW-101 simulant was prepared for the current study and was filtered before use. Aliquots were submitted for analysis by inductively-coupled plasma-atomic emission spectrometry (ICP-AES), ion chromatography (IC), ICP-MS, and acid titration for free hydroxide under ASR 6710. The composition of the AW-101 preparation is provided in Table 2.4 along with the 2001 and 2002 preparations. The relevant CMC ASR identifications for the current and previous AW-101 tests are also provided in Table 2.4. The data presented for AW-101 simulants 2001 and 2003 are from analytical results; the composition for 2002 simulant is calculated based on the masses of added ingredients.

(a) This particle-size distribution was used successfully in AW-101 simulant testing. The as-received particle-size distribution was shown not to meet the Cs decontamination specification (Fiskum, Blanchard, and Arm 2002).

Table 2.2. AP-101 Simulant and Actual Waste Compositions

Analyte	AP-101 Actual waste ^(a)	AP-101 Simulant ^(a)
<i>Physical property-density, g/mL</i>		
Density	1.256	1.257
<i>Cations, molarity</i>		
Na ⁺	4.97 E+0	4.83 E+0
K ⁺	7.61 E-1	6.56 E-1
Cs ⁺	3.68 E-5 ^(b)	3.72 E-5 ^(d)
Rb ⁺	4.13E-5	1.03E-5 (initial); 5.23E-5 (final) ^(e)
Uranyl	1.7 E-4	Not added
Na/Cs mole ratio	1.4 E+5 ^(b)	1.3 E+5 ^(d)
<i>Anions, molarity</i>		
AlO ₂ ⁻ ^(c)	2.59 E-1	2.56E-1
Cl ⁻	4.1 E-2	3.84 E-2
F ⁻	< 1.2 E-1	< 7 E-3
CO ₃ ⁻²	4.46 E-1	4.7 E-1
CrO ₄ ⁻² ^(c)	2.92 E-3	2.29E-3
NO ₂ ⁻	7.1 E-1	8.26 E-1
NO ₃ ⁻	1.68 E+0	1.66 E+0
OH ⁻ (free)	1.94 E+0	1.90 E+0
PO ₄ ⁻³ ^(c)	1.2 E-2	1.34E-2
SO ₄ ⁻²	4.8 E-2	4.00E-2
Oxalate	< 1 E-2	9.4 E-3
<i>Organics, g/L</i>		
Total organic carbon, g/L	1.64	1.03
<p>(a) The overall error is estimated to be within ±15%. Less-than values indicate that the analyte is less than the instrument detection limit or less than the lowest calibration standard. The dilution-corrected instrument detection limit is reported.</p> <p>(b) Total Cs reported by Goheen et al. [8] may be biased low. Reported value does not agree with ¹³⁷Cs determination by GEA (126 μCi/mL) and application of isotopic distribution (¹³³Cs 60.6 wt%, ¹³⁵Cs 15.4 wt%, ¹³⁷Cs 24.0 wt%) where a total Cs concentration of 6.04 μg/mL or 4.5 E-5 M is calculated (Na:Cs mole ratio = 1.1E+5).</p> <p>(c) Al, Cr, and P determined by ICP-AES. The anionic form is assumed on the basis of waste chemistry.</p> <p>(d) The as-prepared Cs concentration was calculated to be 5.99 μg/mL or 4.50E-5 M. The corresponding Na:Cs mole ratio is 1.1E+5.</p> <p>(e) The Rb concentration was measured before and after amendment.</p>		

Table 2.3. Targeted AW-101 Simulant Feed Composition

Cations, M		Anions, M	
Al	5.1 E-1	Cl ⁻	6.9 E-2
Ba	1.3 E-4	F ⁻	1.1 E-2
Ca	4.1 E-4	CO ₃ ⁻²	1.0 E-1
Cs	6.4 E-5	NO ₂ ⁻	7.9 E-1
Fe	5.0 E-5	NO ₃ ⁻	1.5 E+0
K	4.3 E-1	PO ₄ ⁻³	1.7 E-3
Li	5.5 E-4	SO ₄ ⁻²	2.4 E-3
Mg	1.5 E-3	Free OH ⁻	1.9 E+0
Mn	6.6 E-5	Organics, M	
Mo	2.9 E-4	Ethylenediamine tetraacetic acid	3.7 E-3
Na	5.0 E+0	Citrate	3.7 E-3
Ni	1.3 E-4	Gluconate	3.7 E-3
Rb	1.0 E-5	Nitrilotriacetic acid	3.7 E-3
Si	2.9 E-3	Iminodiacetic acid	3.7 E-3
Sr	1.3 E-5	Total organic carbon	1.86 g C/L
Mole Ratio		Density, g/mL	
Na/Cs	7.81 E+4	Density	1.23

2.4 SL-644 Resin Preparation

All resins in previous and current testing had been washed by contacting three times with 0.5 M HNO₃ and rinsed with deionized (DI) water to convert the resin to the H-form and remove inert production byproducts. The resins were dried in the H-form to a free-flowing state before sub-sampling for batch contacts.

The 16/18 resin was stored approximately two years in the as-received form (most likely the K-form) before conversion to the H-form. An aliquot of the -73 sieved resin fraction was washed approximately 5 days after production [9]. This resin was then air-dried and stored in a polyethylene bottle. The bottle had been periodically opened several times, and resin was sampled during the two years of storage. No additional pretreatment was conducted before batch-contact testing in 2001, 2002, and 2003.

An aliquot of the large-volume C02 resin was sampled according to American Society for Testing and Materials (ASTM) Method D 2687 *Standard Practices for Sampling Particulate Ion-Exchange Materials*. The aliquot was washed similarly to the -73 and 16/18 resins (contacted three times with 0.5 M HNO₃ and rinsing with DI water) but was dried under vacuum (63.5 cm [25 in.] Hg), with a low nitrogen flow, and at ambient temperature to constant mass. Sub-sampling and batch contacts occurred immediately after this drying stage.

Table 2.4. Feed AW-101 Simulant Compositions

<i>Preparation ID</i>	Feed 2001	Feed 2002	Feed 2003
<i>ASR ID</i>	6104	As Prepared^(a)	6710
<i>CMC ID</i>	01-0973	NA	03-0771
Analyte	µg/mL^(b)	µg/mL	µg/mL^(b)
Al	4.82E-1	5.08E-1	4.84E-1
B	1.46E-2	not added	<2.3E-5
Ba	1.32E-4	1.35E-4	1.27E-4
Ca	<7.7E-4	4.12E-4	5.54E-4
Cs	8.58E-5	6.40E-5	6.40E-5
Fe	[1.6E-4]	5.2E-5	6.8E-5
K	4.17E-1	4.30E-1	3.54E-1
Li	[6.9E-4]	5.6E-4	5.2E-4
Mg	[7.8E-4]	1.5E-3	[3.7E-5]
Mn	<1.3E-4	6.6E-5	6.0E-5
Mo	[2.6E-4]	2.91E-4	2.82E-4
Na	5.13E+0	5.04E+0	4.74E+0
Ni	[1.2E-4]	1.4E-4	1.4E-4
P	[1.9E-3]	1.7E-3	1.9E-3
Si	[6.2E-3]	2.93E-3	2.63E-3
Sr	<2.3E-5	1.4E-5	1.6E-5
F ⁻	1.63E-2	1.16E-2	1.72E-2
Cl ⁻	7.50E-2	6.94E-2	7.28E-2
NO ₃ ⁻	1.73E+0	1.52E+0	1.43E+0
NO ₂ ⁻	8.33E-1	7.89E-1	7.91E-1
PO ₄ ⁻³	<2.6E-3	1.73E-3	1.85E-3
SO ₄ ⁻²	<2.6E-3	2.36E-3	2.35E-3
Free OH ⁻ , M	NM	2.34E+0	2.10E+0
Density	1.234 g/mL	1.240 g/mL	1.239 g/mL
Na/Cs mole ratio	6.0 E+4	7.9E+4	7.4E+4
<p>(a) Calculated concentration based on preparation records, not analyzed. (b) The overall error is estimated to be within ±15%. Values in brackets are within 10 times the detection limit, and errors are likely to exceed ±15%. Less-than values indicate that the analyte is less than the instrument detection limit or less than the lowest calibration standard. The dilution-corrected instrument detection limit is reported. NA = not applicable NM = not measured</p>			

The simulants and actual waste tests with the associated resins and test dates are summarized in Table 2.5. Also included are the comparative batch-contact tests conducted in 2001 through 2003 with AW-101 simulant.

Table 2.5. AP-101 and AW-101 Feeds and Associated Tests

SL-644 Resin Batch	Feed	Test Start Date
981112YK-N3-16/18 (as-received particle-size distribution [PSD])	AP-101 actual waste	2/5/2001
010319SMC-IV-73 (212- to 425- μ m)	AW-101 simulant, 2001	3/28/2001
010319SMC-IV-73 (212- to 425- μ m)	AP-101 actual waste	6/7/2001
010319SMC-IV-73 (212- to 425- μ m)	AW-101 simulant, 2002	2/27/2002
010319SMC-IV-73 (212- to 425- μ m)	AW-101 simulant 2003	2/25/2003
C-01-05-28-02-35-60 (as-received PSD)		
010319SMC-IV-73 (212- to 425- μ m)	AP-101 simulant 2003	2/25/2003
C-01-05-28-02-35-60 (as-received PSD)		

The F-factors (ratio of dried resin to moist resin), were determined in duplicate at the same time aliquots were taken for the batch-contact tests. The F-factors were determined by drying nominally 0.3 g resin under vacuum at 50°C until constant mass was obtained. The F-factor was calculated according to Equation 2.1.

$$F - \text{factor} = \frac{M_d}{M_w} \quad (2.1)$$

where the F-factor is the fraction of dry resin, M_d is the mass of resin dried under vacuum at 50°C, and M_w is the starting mass of resin. The measured F-factors are summarized in Table 2.6; F-factor data is provided in Appendix B.

Table 2.6. SL-644 Resin F-factors

SL-644 Resin	Sample F-factor	Duplicate F-factor	Average F-factor	RPD, ^(b) %
-73 ^(a)	0.8216	0.8254	0.8235	0.46
C02	0.7581	0.7520	0.7551	0.81
(a) Stored for two years in the H-form.				
(b) RPD = relative percent difference				

2.5 Batch Contacts

Aliquots of the two simulants were prepared at four Cs concentrations. Aliquots of simulant were spiked with additional 0.5 M CsNO₃ stock solution, increasing the Cs concentrations as shown in Table 2.7. A ¹³⁷Cs tracer was added to each stock solution. The Cs concentrations were confirmed by ICP-MS measurement.

Table 2.7. Actual Cs Concentrations Used for the Batch-Distribution Tests

Solution	Cs Concentration mg/L	Cs Molarity	Na:Cs Mole Ratio
AW-101 Cs Spike 1	8.51	6.40 E-5	7.41E+4
AW-101 Cs Spike 2	111	8.35 E-4	5.68E+3
AW-101 Cs Spike 3	397	2.99E-3	1.59E+3
AW-101 Cs Spike 4	668	5.03E-3	9.43E+2
AP-101 Cs Spike 1	5.97	4.50 E-5	1.07E+5
AP-101 Cs Spike 2	109	8.17E-4	5.91E+3
AP-101 Cs Spike 3	386	2.91E-3	1.66E+3
AP-101 Cs Spike 4	669	5.03E-3	9.60E+2

The batch distribution tests were performed in triplicate. Nominally, 0.2 g of -73 SL-644 resin were contacted with 20 mL of simulant in a 30-mL glass vial. Nominally 0.5 g of C02 SL-644 resin were contacted with 50 mL of simulant in a 120-mL glass bottle. The resin mass was determined to an accuracy of 0.0002 g. The simulant volume was transferred by pipet; the actual volume was determined by mass difference and solution density. The targeted phase ratio (liquid volume to exchanger mass) was 100 mL/g. The obtained ratio was 120 mL/g because the residual water content in the resin was higher than anticipated.^(a) Sample-specific volumes and resin masses are given in Appendix C. The headspace above the simulant was purged with nitrogen gas just before capping.

Agitation was provided by a reciprocal shaker. Rigorous mixing was observed for all samples. The -73 resin materials were contacted for nominally 24 hours (consistent with actual waste testing); the C02 resin materials were contacted for nominally 140 hours.^(b) The temperature was not controlled, but was generally constant at 24 to 28°C during the contact period, as determined by a Fisher Thermo-Hygrometer. After contact, the samples were filtered through 0.45-µm nylon membrane syringe filters.

Samples were taken from the C02 resin contacted with 50-mL AP-101 Spike 4 triplicate and AW-101 Spike 1 triplicate samples at 42 hours and again at 66 hours to evaluate whether equilibrium had been

-
- (a) A similar phase ratio was obtained with the previous testing with -73 resin when the exchanger mass is considered in the H-form. The phase ratio for H-form 16/18 resin in contact with actual waste was nominally 106 mL/g; it had a higher F-factor.
- (b) The longer contact time was intended to allow equilibrium to be attained for the large particles characteristic of this resin batch. The Test Plan indicated 72 h contact time be tested; 140 h contact time was used instead.

reached. These analytical samples were counted and then recombined with the main contact sample, and agitation was resumed. The gaseous headspace was not flushed with N₂ after the periodic sub-sampling.

An additional test was conducted to better define the equilibrium kinetics of AP-101 simulant in contact with C02 resin while maintaining the original experimental parameters of having the headspace filled with N₂. In this case, separate duplicate samples were prepared for each of four contact times using AP-101 simulant spiked to 665 mg/L Cs. Each contact sample consisted of nominally 0.5 g of C02 SL-644 resin contacted with 50 mL of AP-101 simulant in a 120-mL glass bottle. The eight samples were prepared with the headspace back-filled with N₂. Duplicate samples were removed after 24, 42.5, 66, and 140 hours contact time, and the analytical samples were then counted.

Simulant-only samples (uncontacted aliquots) were used to determine the initial Cs (ICP-MS), Na, and K (ICP-AES) concentrations. The equilibrium Na concentration was assumed be equivalent to the feed Na concentration and was not measured. All solutions were analyzed by gamma-energy analysis (GEA) to determine the ¹³⁷Cs concentration. Final (equilibrium) Cs concentrations were calculated relative to the recovered ¹³⁷Cs tracer according to Equation 2.2.

$$C_{S_{Eq}} = C_{S_0} * \left(\frac{C_1}{C_0} \right) \quad (2.2)$$

where $C_{S_{Eq}}$ = equilibrium Cs concentration (µg/mL or M)
 C_{S_0} = initial Cs concentration (µg/mL or M)
 C_1 = equilibrium ¹³⁷Cs concentration (cpm/mL)
 C_0 = initial ¹³⁷Cs concentration (cpm/mL).

The equilibrium Na:Cs mole ratio was calculated relative to the measured feed Na concentration divided by the equilibrium Cs concentration.

The Cs batch-distribution coefficient (K_d) values were determined according to the standard formula shown in Equation 2.3. Errors were kept small because Cs tracer was used; samples with low Cs concentrations were counted longer to drive down counting error. The highest counting error was 5%; the average counting error was 2%.

$$K_d = \frac{(C_0 - C_1)}{C_1} * \frac{V}{M * F} \quad (2.3)$$

where K_d = batch-distribution coefficient (mL/g)
 C_0 = initial ¹³⁷Cs concentration (cpm/mL)
 C_1 = final (equilibrium) ¹³⁷Cs concentration (cpm/mL)
 V = volume of the liquid sample (mL)
 M = mass of H-form ion exchanger (g)
 F = mass of the dried resin divided by the mass of the as-received resin.

The mass increase attributed to Na was not considered for this test. A source of experimental uncertainty in the mass increase (I_{Na}) was reported by Fiskum, Blanchard, and Arm [1] for the 16/18 and -73 resins (I_{Na} equal to 1.29 and 1.25, respectively). In this case, the resins were dried at 25°C under vacuum; residual water in the resin would bias I_{Na} high. The mass increase for the C02 resin was found to be 1.10 where the resin was dried at 50°C under vacuum.

It is assumed that the mass increase factor is identical (within experimental error) for all of the SL-644 resins. Thus a comparison using the H-form mass basis of the resin is valid. Therefore, the elimination of the estimated I_{Na} factors eliminates a source of uncertainty and provides more accurate comparisons.

3.0 Results and Discussion

The following sections discuss the assessment of batch-contact equilibrium, equilibrium distribution coefficient determinations, isotherms, and comparison to actual waste testing.

3.1 Equilibrium Test

Achievement of batch-contact equilibrium was evaluated from two of the C02 resin contacts samples representing both a high and low Cs concentration in the contact solution, AW-101 at 8.5 mg/L Cs and AP-101 at 669 mg/L Cs. The samples were taken from the 50-mL batch-contact samples by measuring aliquots for ¹³⁷Cs at 42-h, 66-h, and 140-h processing times. The K_d results are summarized in Table 3.1 along with the K_d results for the corresponding sample and duplicate contacted for 140 hours.

Table 3.1. Batch Equilibrium K_d Values as a Function of Contact Time, First Test

Simulant	Initial Cs concentration, mg/L	TriPLICATE			Sample	Duplicate
		K _d , 42 h mL/g	K _d , 66 h mL/g	K _d , 140 h mL/g	K _d , 140 h mL/g	K _d , 140 h mL/g
AP-101 Spike 4	669	161	121	94	183	179
AW-101 Spike 1	8.5	1901	1351	1101	1956	1949

It is apparent that the experimental approach to evaluate equilibrium was not adequate. In both cases, the measured K_d values decreased with time, indicating that Cs was shifting back into solution. The K_d values obtained after a 42-h contact time were nearly identical to those of the sample and duplicate (which were not opened during the 140-h contact time). In the case of the low Cs concentration, 8.5 mg/L, the 42-h contact K_d (1901 mL/g) was only 3% lower than the average of the 140-h contact K_ds (1952 mL/g). For the high Cs concentration, 669 mg/L, the 42-h contact K_d (161 mL/g) was only 12% lower than the average of the 140-h contact K_ds (181 mL/g). Despite the generally large particle-size distribution of this material, this suggested that equilibrium was obtained in nearly 42 hours.

The K_d value decrease with repeated sampling for these two samples may be attributed to oxidative attack on the resin. All initial-contact container headspace was flushed with N₂. The triplicate samples were not flushed with N₂ after periodic sampling. Each time the sample bottle was opened for equilibrium sub-sampling, additional oxygen (from air) was allowed in to react with the resin.

An additional test was performed to evaluate equilibrium conditions using separate contact bottles (all head spaces inerted) for each time interval. In this case, AP-101 simulant spiked at an initial Cs concentration of 665 µg/mL was contacted with samples of the C02 resin batch. The K_d results, summarized in Table 3.2, show that equilibrium was established after a 24-h contact period, and no significant shift in equilibrium was observed over the 24- to 140-h contact time. Thus, all test results obtained at a 140-h contact time should be representative of equilibrium under the conditions tested.

Table 3.2. Batch Equilibrium K_d Values as a Function of Time, Second Test

Contact time, h	Sample K_d , mL/g	Duplicate K_d , mL/g	Average K_d , mL/g	RPD
24	207	220	213	6
42.5	199	181	190	10
66	178	193	186	8
140	206	195	201	5
Overall average			198	7 (RSD)

3.2 AP-101 Simulant

The experimentally derived K_d values for AP-101 simulant in contact with C02 and -73 resins are provided in Table 3.3 along with the K_d values previously reported for actual AP-101 waste [3]. Each group of triplicate distribution coefficients resulted in good precision for both the C02 and -73 resin contacts. The AP-101 Spike 4 triplicate sample was excluded from this calculation, however. It was used for equilibrium testing and its result, as discussed in Section 3.1, was suspected to have problems. The initial Na:Cs mole ratios were calculated based on the measured Na and Cs concentrations in the uncontacted simulant. The final Cs concentrations were calculated based on ^{137}Cs tracer recoveries according to Equation 2.2. The Na^+ concentrations were assumed to remain constant during the batch contacts.^(a)

The batch-distribution coefficients from Table 3.3 for AP-101 simulant and actual waste AP-101 diluted feed are plotted in Figure 3.1 (function of Na:Cs mole ratio). The best-fit curves derived from Excel Software (Microsoft Corp. Seattle, WA) are also provided in Figure 3.1, and the corresponding equations and correlation coefficients, where “x” is the Na:Cs mole ratio, are shown in Equations 3.1 through 3.3.

$$\begin{aligned} &\text{AP-101 simulant on C02} \\ &K_d = 180.0 \ln(x) - 1227 \quad R^2 = 0.992 \end{aligned} \quad (3.1)$$

$$\begin{aligned} &\text{AP-101 actual waste on 16/18} \\ &K_d = 178.8 \ln(x) - 1268 \quad R^2 = 0.996 \end{aligned} \quad (3.2)$$

$$\begin{aligned} &\text{AP-101 simulant on -73} \\ &K_d = 90.05 \ln(x) - 597.4 \quad R^2 = 0.997 \end{aligned} \quad (3.3)$$

(a) The H^+ form of the resin contains 2.2 meq H^+ per gram (Rapko et al. 2003). Thus, the moles of H^+ added with the resins was small relative to the moles of Na^+ in the contact solution (phase ratio of 120 mL of solution: gram of exchanger). In the 50-mL contact experiments, the simulant solutions were estimated to contain nominally 250 meq of Na^+ , while the resin aliquot contained 0.8 meq of H^+ . In the 20-mL contact experiments, the simulant solutions were estimated to contain nominally 100 meq of Na^+ , while the resin aliquot contained 0.35 meq H^+ .

Table 3.3. AP-101 Equilibrium Cs Concentrations and Batch Distribution Coefficients with SL-644

Simulant on C02 Resin					Actual Waste on 16/18 Resin					Simulant on-73 Resin				
Sample ID	Cs, mg/mL	Na:Cs mole ratio	Cs K _d , mL/g	RSD, %	Sample ID	Cs, mg/mL	Na:Cs mole ratio	Cs K _d , mL/g	RPD, %	Sample ID	Cs, mg/mL	Na:Cs mole ratio	Cs K _d , mL/g	RSD, %
225-AP-S1-C02	6.12E-4	1.05E+6	1175	7.2	AP101-644	3.62E-4	1.82E+6	1328	0.38	225-AP-S1-73	1.00E-3	6.42E+5	588	3.5
225-AP-S1-C02D	5.36E-4	1.20E+6	1341		AP101-644-D	3.63E-4	1.82E+6	1333		225-AP-S1-73D	9.67E-4	6.64E+5	608	
225-AP-S1-C02T	5.41E-4	1.19E+6	1328		AP101-S1-644	2.37E-2	2.79E+4	547	1.3	225-AP-S1-73T	9.70E-4	6.62E+5	631	
225-AP-S2-C02	1.77E-2	3.63E+4	663	1.1	AP101-S1-644-D	2.34E-2	2.83E+4	554	0.8	225-AP-S2-73	3.07E-2	2.10E+4	309	3.2
225-AP-S2-C02D	1.78E-2	3.62E+4	673		AP101-S2-644	3.21E-1	2.06E+3	128		225-AP-S2-73D	3.23E-2	1.99E+4	295	
225-AP-S2-C02T	1.84E-2	3.50E+4	678		AP101-S2-644-D	3.20E-1	2.06E+3	129	225-AP-S2-73T	3.11E-2	2.06E+4	291		
225-AP-S3-C02	1.24E-1	5.20E+3	302	8.8	Actual Waste on -73 Resin					225-AP-S3-73	1.77E-1	3.62E+3	140	11
225-AP-S3-C02D	1.30E-1	4.92E+3	267		AP101-S3-644	2.07E-2	3.19E+4	550	4.3	225-AP-S3-73D	1.97E-1	3.25E+3	114	
225-AP-S3-C02T	1.10E-1	5.87E+3	318		AP101-S3-644D	2.22E-2	2.97E+4	527		225-AP-S3-73T	1.89E-1	3.39E+3	121	
225-AP-S4-C02	2.83E-1	2.27E+3	183	2.2 ^(a)	No additional data.					225-AP-S4-73	4.18E-1	1.54E+3	70.1	0.16
225-AP-S4-C02D	2.89E-1	2.22E+3	179							225-AP-S4-73D	4.25E-1	1.51E+3	70.2	
225-AP-S4-C02T	3.90E-1	1.65E+3	94 ^(a)							NA	225-AP-S4-73T	4.26E-1	1.51E+3	

(a) The triplicate batch contact was sampled repeatedly for equilibrium testing; its data is neither plotted (Figure 3.1) nor calculated in the RSD; the RPD is calculated for the two samples.
Assigned Na:Cs mole ratio error is 14%, derived from uncertainty in measured Na concentration and as-prepared Cs concentration.
RPD = relative percent difference
RSD = relative standard deviation

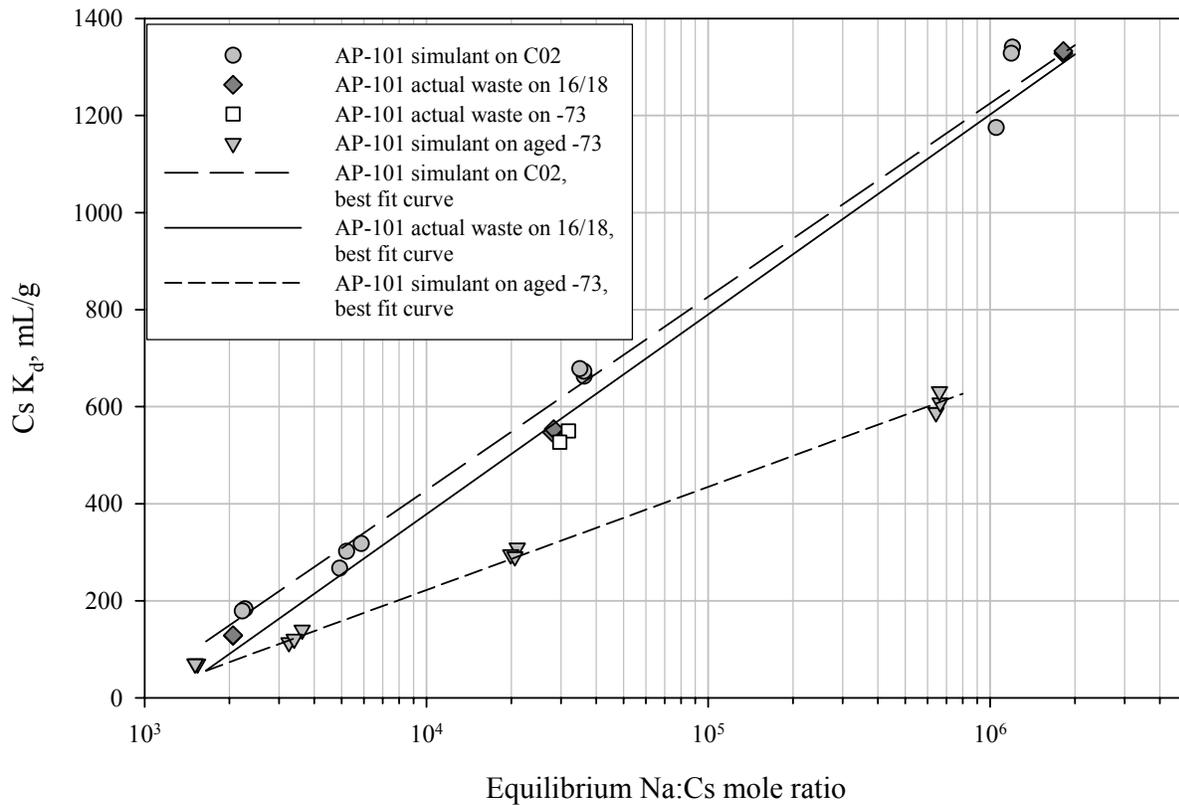


Figure 3.1. Comparison of Cs K_d Values (resin mass in the H-form)

The -73 resin K_d results with AP-101 simulant were significantly lower than the K_d values obtained with actual waste on 16/18 and -73 resins. It is possible the -73 resin had lost performance over time. Simulant comparison to actual waste with this resin may require correction based on the relative performance of AW-101 simulant over the 2-yr storage period.

The AP-101 simulant in contact with C02 resin tracked closely to the actual waste with a nearly parallel slope. Figure 3.2 summarizes the same K_d data as a function of Cs concentration. These results support the Option 2 validation strategy.

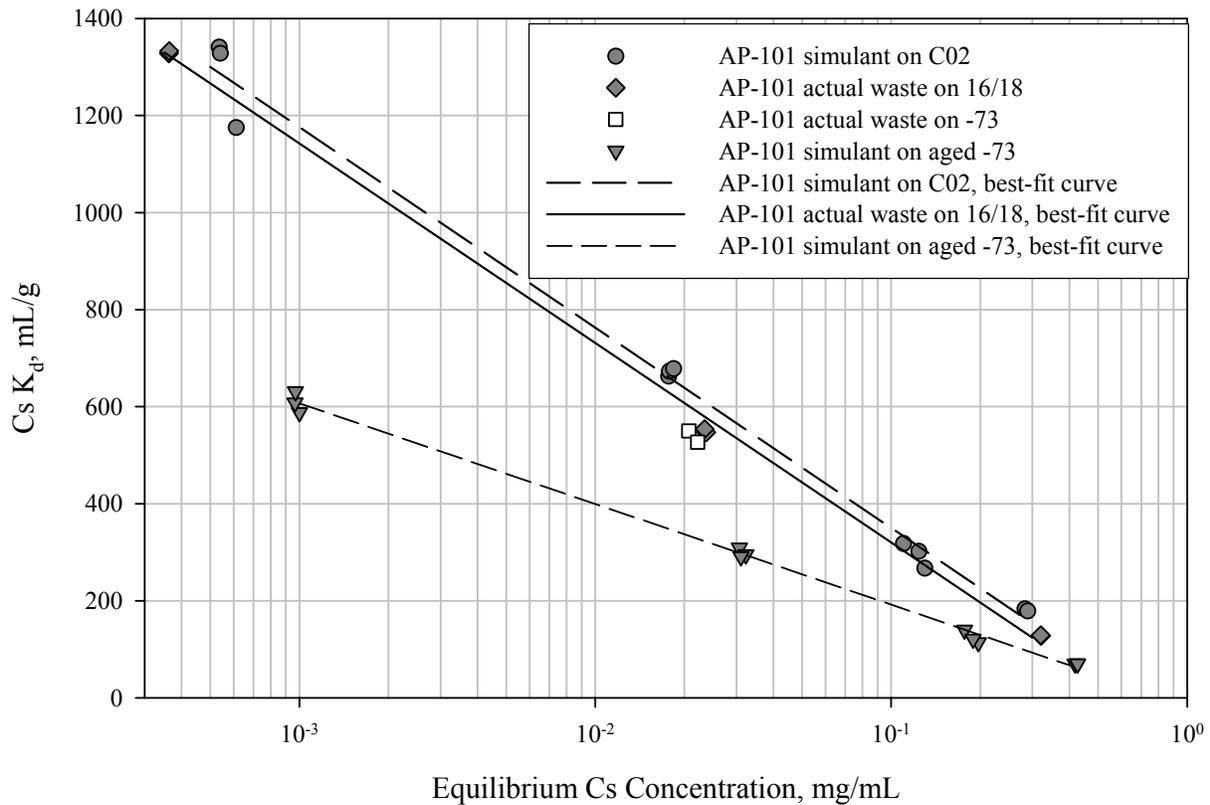


Figure 3.2. AP-101 Simulant and Actual Waste Cs K_d as a Function of Equilibrium Cs Concentration

3.3 AW-101 Simulant

The K_d results for the AW-101 simulant on -73 resin for 2001, 2002, and 2003 are summarized in Table 3.4, along with the results for the C02 resin contact. Each group of duplicate and triplicate samples resulted in good precision of the distribution coefficients. The AW-101 Spike 1 triplicate sample was excluded from the precision measure because its result was suspect, as discussed in Section 3.1.

The steady decline in K_d values over two years with test results from 2001, 2002, and 2003 are clearly demonstrated in Figure 3.3. The difference may be due to oxidative attack or other forms of degradation to the dry H-form -73 resin during the 2-yr storage period. The K_d values obtained with the C02 resin agreed well with those of the -73 fresh resin (2001) batch contacts. The data were fit to an exponential curve with Excel software. The best-fit curves are provided in Figure 3.3, and their corresponding equations and correlation coefficients are given in Equations 3.4 through 3.7.

Table 3.4. Equilibrium Cs K_d Values in AW-101 Simulant in Contact with -73 and C02 Resins

Sample ID ^(a)	Na:Cs mole ratio	Cs, mg/mL	-73 Resin, 2001 K _d , mL/g	RPD, %	Sample ID ^(b)	Na:Cs mole ratio	Cs, mg/mL	-73 Resin, 2002 K _d , mL/g	RPD, %
SimA-NH	1.36E+6	4.91E-4	1877	7.6	S-TI164-S0-73	1.10E+6	6.03E-4	1650	0.73
SimA-NHD	1.43E+6	4.64E-4	2025		S-TI164-S0-73-D	1.08E+6	6.17E-4	1638	
SimA-NH100	4.83E+4	1.38E-2	1101	6.7	S-TI164-S1-73	2.86E+4	2.32E-2	634	0.0
SimA-NH100D	6.26E+4	1.06E-2	1177		S-TI164-S1-73-D	2.78E+4	2.39E-2	634	
SimA-N600H	3.44E+3	1.93E-1	292	11.8	S-TI164-S2-73	2.32E+3	2.86E-1	166	7.0
SimA-N600HD	3.70E+3	1.80E-1	328		S-TI164-S2-73-D	2.41E+3	2.76E-1	178	
Sample ID	Na:Cs mole ratio	Cs, mg/mL	-73 resin, 2003 K _d , mL/g	RSD, %	Sample ID	Na:Cs mole ratio	Cs, mg/mL	C02 resin, 2003 K _d , mL/g	RSD, %
225-AW-S1-73	5.85E+5	1.08E-3	829	5.1	225-AW-S1-C02	1.20E+6	5.23E-4	1956	0.36 ^(c)
225-AW-S1-73D	6.35E+5	9.93E-4	911		225-AW-S1-C02D	1.24E+6	5.09E-4	1949	
225-AW-S1-73T	6.31E+5	9.99E-4	901		225-AW-S1-C02T	7.21E+5	8.74E-4	1101 ^(b)	
225-AW-S2-73	2.35E+4	2.68E-2	377	8.6	225-AW-S2-C02	4.76E+4	1.33E-2	993	5.9
225-AW-S2-73D	2.39E+4	2.63E-2	381		225-AW-S2-C02D	5.15E+4	1.22E-2	1039	
225-AW-S2-73T	2.64E+4	2.39E-2	438		225-AW-S2-C02T	5.34E+4	1.18E-2	1114	
225-AW-S3-73	3.71E+3	1.70E-1	160	2.4	225-AW-S3-C02	6.28E+3	1.00E-1	394	4.8
225-AW-S3-73D	3.80E+3	1.66E-1	168		225-AW-S3-C02D	6.00E+3	1.05E-1	359	
225-AW-S3-73T	3.80E+3	1.66E-1	166		225-AW-S3-C02T	6.09E+3	1.03E-1	385	
225-AW-S4-73	1.65E+3	3.83E-1	88	10.1	225-AW-S4-C02	2.32E+3	2.71E-1	200	3.9
225-AW-S4-73D	1.55E+3	4.06E-1	78		225-AW-S4-C02D	2.41E+3	2.62E-1	211	
225-AW-S4-73T	1.69E+3	3.74E-1	95		225-AW-S4-C02T	2.32E+3	2.72E-1	195	
<p>(a) [1] (b) [3] (c) The triplicate batch contact was sampled repeatedly for equilibrium testing; its data are neither plotted (Figure 3.3 and Figure 3.4) nor calculated in the RSD; the RPD is calculated for the two samples. RPD = relative percent difference; RSD = relative standard deviation; NA = not applicable</p>									

$$\begin{aligned} &\text{AW-101 simulant 2001} \\ &K_d = 274.5 \ln(x) - 1907 \quad R^2 = 0.994 \end{aligned} \tag{3.4}$$

$$\begin{aligned} &\text{AW-101 simulant 2002} \\ &K_d = 242.7 \ln(x) - 1766 \quad R^2 = 0.990 \end{aligned} \tag{3.5}$$

$$\begin{aligned} &\text{AW-101 simulant 2003} \\ &K_d = 135.5 \ln(x) - 941 \quad R^2 = 0.991 \end{aligned} \tag{3.6}$$

$$\begin{aligned} &\text{AW-101 simulant 2003 with C02 resin} \\ &K_d = 285.8 \ln(x) - 2058 \quad R^2 = 0.996 \end{aligned} \tag{3.7}$$

The same K_d data are plotted in Figure 3.4 as a function of equilibrium C_s concentration. Again, the C02 resin K_d s were nearly identical to those obtained on fresh -73 resin.

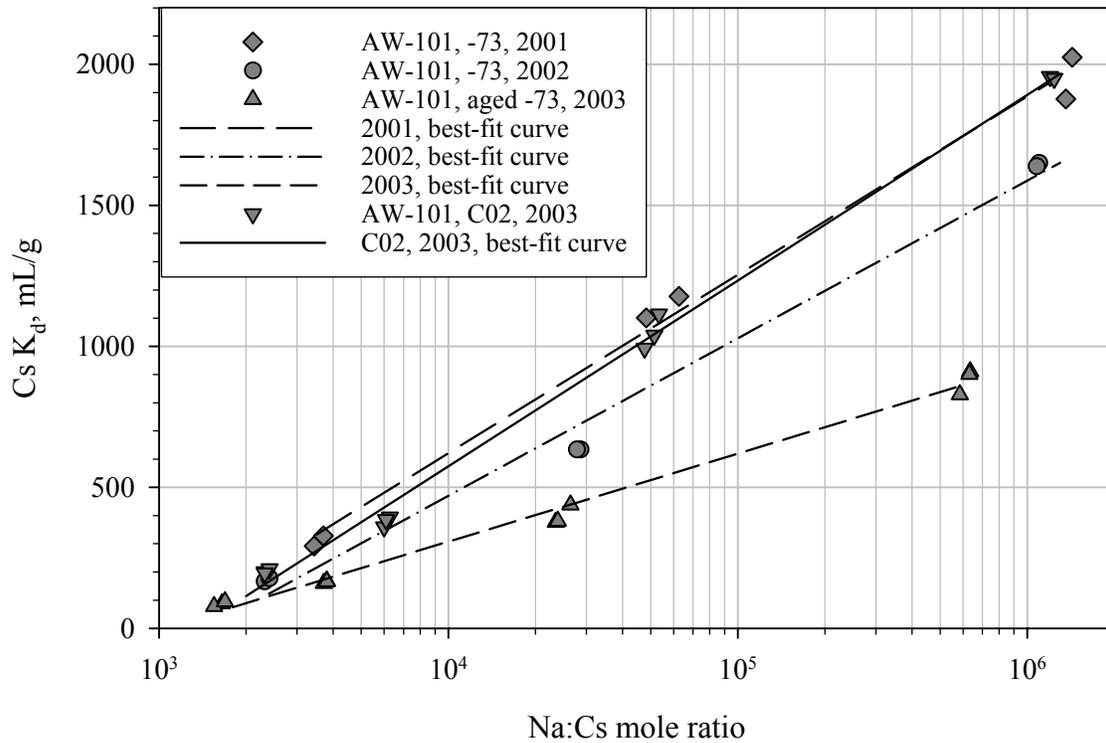


Figure 3.3. AW-101 Simulant K_d Values as a Function of Na:Cs Mole Ratio, 2-Yr Test Range

The relative changes in the AW-101 simulant K_d s on the -73 resin were evaluated over the 2-yr storage period. Table 3.5 summarizes the predicted K_d s as a function of equilibrium Na:Cs mole ratios using the best-fit curve definitions defined in Equations 3.4 through 3.7. The differences between the K_d values represented by the simulant varied by a factor of 2.0 (202%) from 2001 to 2003 over a broad range of Na:Cs mole ratios. Therefore, the correction factor was 2.0 for the K_d values obtained in 2003 with -73 resin. This correction factor can be applied to the AP-101 simulant results on the -73 resin to correlate loss of resin performance as shown in the validation strategy Option 1.

The K_d s calculated for the -73 resin contacted in 2001 with AW-101 simulant were virtually identical to those of the C02 resins contacted in 2003 with AW-101 simulant where the Na:Cs mole ratio was $\geq 6E+3$. The experimental conditions were different; however, equilibrium was assumed for each condition. This was an indication that the resins had similar selectivity and were not a probable source for K_d variation.

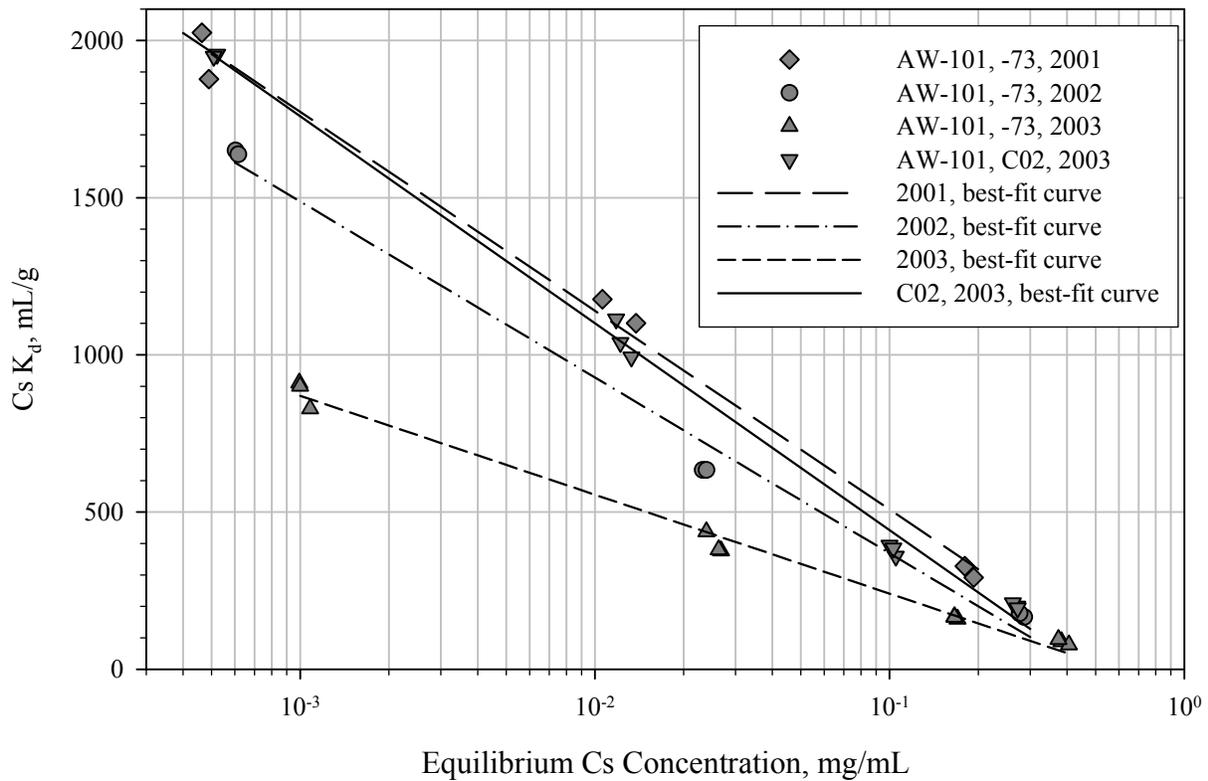


Figure 3.4. AW-101 Simulant Cs K_d as a Function of Cs Concentration

Table 3.5. Predicted Cs K_d Values in AW-101 Simulant in Contact with -73 and C02 Resins

Equilibrium Cs Concentration, µg/mL	Input Equilibrium Na:Cs Mole Ratio	Calculated K _d Values				Ratios		
		-73 Resin			C02 Resin	2001 (-73) to 2002 (-73)	2001 (-73) to 2003 (-73)	2001 (-73) to 2003 (C02)
		2001 K _d , mL/g ^(a)	2002 K _d , mL/g ^(b)	2003 K _d , mL/g ^(c)	2003 K _d , mL/g ^(d)			
315	2.00E+03	179	79	89	114	2.28	2.01	1.57
210	3.00E+03	291	177	144	230	1.64	2.02	1.26
105	6.00E+03	481	345	238	428	1.39	2.02	1.12
63.0	1.00E+04	621	469	307	574	1.32	2.02	1.08
12.6	5.00E+04	1063	860	525	1034	1.24	2.02	1.03
6.30	1.00E+05	1253	1028	619	1232	1.22	2.02	1.02
1.26	5.00E+05	1695	1419	837	1692	1.19	2.03	1.00
0.630	1.00E+06	1885	1587	931	1890	1.19	2.03	1.00

(a) K_d = 274.5*Ln(x) - 1907
 (b) K_d = 242.7*Ln(x) - 1766
 (c) K_d = 135.5*Ln(x) - 941
 (d) K_d = 285.8*Ln(x) - 2058
 where x = Na:Cs mole ratio

3.4 AP-101 Simulant Validation

Both validation strategies, Option 1 and 2, succeeded. The progression (or pathway) of success is shown in Figure 3.5 as shaded boxes and heavy lines.

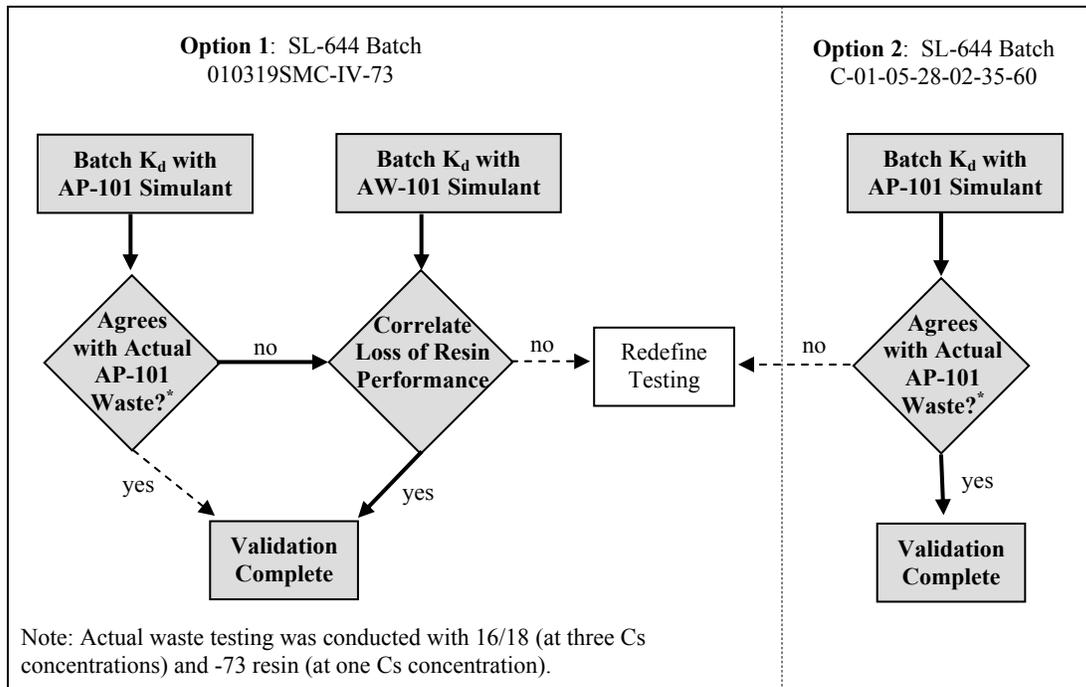


Figure 3.5 Successful AP-101 Simulant Validation Pathways

3.4.1 Validation Strategy Option 1

For the -73 resin batch, the AP-101 simulant K_d results were very different from the K_d results obtained with actual waste (see Figure 3.1 and Figure 3.2). To account for aging effects, the relative change from 2001 to 2003 in the AW-101 simulant K_d was used as a basis for correcting the K_d response of the -73 resin in AP-101 simulant.

The relative loss of the -73 resin performance from 2001 to 2003 was clearly demonstrated with the AW-101 simulant. A K_d correction factor of 2.0 was derived for a broad range of K_d values in AW-101 simulant. This correction factor was used as a basis for correcting the K_d values of the -73 resin in AP-101 simulant. The corrected K_d result was calculated by multiplying the experimentally obtained -73 K_d results by 2.0 according to Equation 3.8.

$$K_d' = K_d * 2.0 \quad (3.8)$$

where K_d' = AP-101 K_d value on -73 resin corrected for 2-yr aging effect
 K_d = experimentally obtained K_d on -73 resin aged 2-yr
 2.0 = correction factor.

The percent difference for the -73 resin corrected K_d (K_d') and actual waste was calculated according to the Equation 3.9.

$$\%D = \left(\frac{S_c}{A_c} - 1 \right) * 100 \quad (3.9)$$

where $\%D$ = percent difference for AP-101 simulant -73 resin and actual waste on -73 and 16/18 resins
 S_c = AP-101 simulant K_d'
 A_c = actual waste K_d calculated at the sample Na:Cs mole ratio according to
 $178.8 \ln(x) - 1268$ (Equation 3.2)
 x = Na:Cs mole ratio.

The corrected AP-101 simulant results on -73 resin are shown in Table 3.6 with the calculated actual waste K_d s. Reasonably good agreement with the actual AP-101 waste (calculated relative to the best-fit curve for the input Na:Cs mole ratio) was obtained for Cs concentrations lower than 130 mg/L (Na:Cs mole ratios higher than 5E+3). The actual AP-101 waste Na:Cs mole ratio was recently found to be 1.1E+5 [3]. The current plan for plant operation is to dilute the waste prior to Cs ion exchange to nominally 5 M Na. A dilute NaOH solution will probably be used to prevent precipitation of waste components, which would raise the Na:Cs ratio prior to Cs ion exchange. The current Cs ion exchange system design is for three columns in series, and the current operational plan is to load only the first (lead) column to significant Cs breakthrough. The second (lag) and third (polishing) columns will accordingly see even higher Na:Cs ratios. Processing that decreases the AP-101 Na:Cs ratio prior Cs ion exchange is not anticipated. Therefore agreement at Na:Cs ratios greater than 1.1E+5 is most important.

Table 3.6. Comparison of Corrected AP-101 Simulant K_d Data on -73 Resin

Equilibrium Na:Cs Mole Ratio	Equilibrium Cs Concentration, $\mu\text{g/mL}$	Original -73 K_d , mL/g	Corrected -73 K_d , mL/g	Calculated AP-101 Actual Waste K_d , mL/g ^(a)	% D, Corrected Simulant to Actual Waste
6.42E+5	1.00	588	1177	1123	4.8
6.64E+5	0.967	608	1217	1129	7.8
6.62E+5	0.970	631	1261	1128	12
2.10E+4	30.6	309	618	511	21
1.99E+4	32.3	295	590	502	18
2.06E+4	31.2	291	582	508	15
3.62E+3	177	140	280	197	42
3.25E+3	198	114	228	178	29
3.39E+3	189	121	243	185	31
1.54E+3	417	70.0	140	44	218
1.51E+3	425	70.2	140	40	247
1.51E+3	425	70.0	140	40	246

(a) Calculated according to $K_d = 178.8 \cdot \ln(x) - 1268$

A graphical representation of the corrected AP-101 simulant in contact with -73 resin K_d data is provided in Figure 3.6 with the $\pm 30\%$ acceptance criterion. The agreement between the actual AP-101 waste on -73 and 16/18 resins and corrected -73 resin K_d values in AP-101 simulant satisfied acceptance criteria for Na:Cs mole ratios greater than 5000 which encompasses solutions of practical interest to plant operations. The corrected -73 K_d data were curve-fitted using Excel to produce the relationship summarized in Equation 3.10,

$$K_d = 180.1 \ln(x) - 1195 \quad (3.10)$$

where x is the Na:Cs mole ratio. Above the Na:Cs mole ratio of $5E+3$, the %D is within the acceptance criterion, but with a slightly high bias. The large deviation less than $5E+3$ Na:Cs mole ratio may be the result of an inadequate curve fit in this region, as this is the region of non-linearity of the isotherm (see Section 3.5). The $5E+3$ Na:Cs mole ratio represents a Cs concentration of 0.001M (130 mg/L) and is not likely to be seen in the AP-101 waste feed at the WTP, as discussed above.

3.4.2 Validation Strategy Option 2

Relative agreements (percent differences) between the experimentally obtained simulant results and the predicted actual tank waste results (based on the best-fit curve equation) were calculated according to Equation 3.11.

$$\%D' = \left(\frac{S}{A_c} - 1 \right) * 100 \quad (3.11)$$

where $\%D'$ = percent difference between AP-101 simulant with C02 resin and actual waste with -73 and 16/18 resins

S = AP-101 simulant experimental K_d on C02 resin

A_c = actual waste K_d calculated at the sample Na:Cs mole ratio according to Equation 3.2 ($178.8 \ln(x) - 1268$, where x = Na:Cs mole ratio).

The % differences were generally well within the $\pm 30\%$ criterion where Na:Cs mole ratios exceeded $4E+3$. Table 3.7 summarizes the experimental K_{ds} for C02 resin in contact with AP-101 simulant and expected K_{ds} for 16/18 resin in contact with actual AP-101 waste according to the best-fit curve equation. The differences between the K_d values from high Na:Cs mole ratios of $>2E+6$ to low ratios of $4E+3$ are within the acceptance criterion of $\pm 30\%$. As discussed in the previous section, agreement for Na:Cs ratios of approximately $1.1E+5$ and higher is most important.

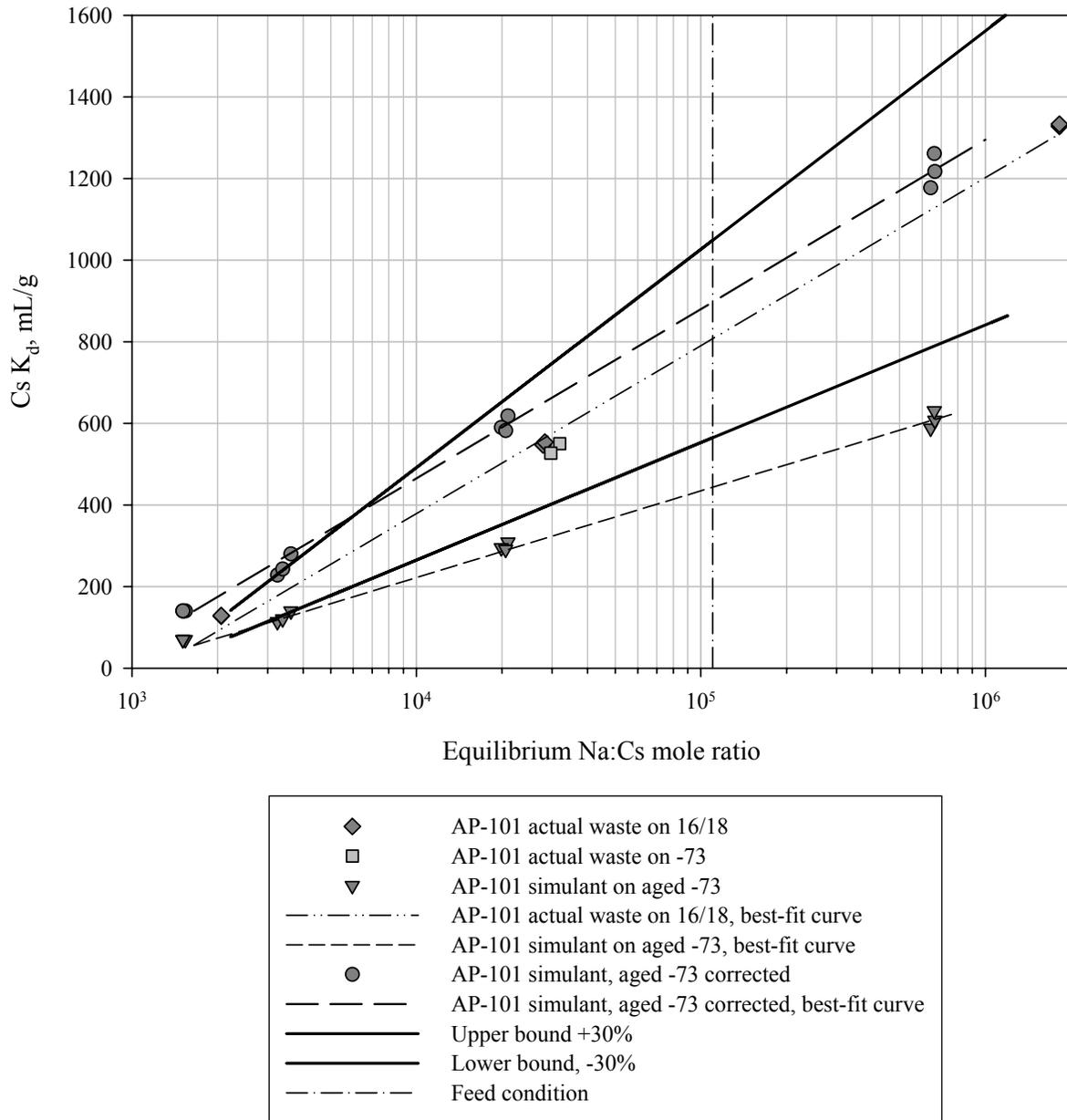


Figure 3.6. AP-101 Simulant Validation Strategy Option 1

A graphical representation of the AP-101 simulant in contact with C02 resin K_d data is provided in Figure 3.7 along with the ±30% acceptance criterion. Relative agreement between K_d values of AP-101 simulant on C02 resin, corrected K_d values with AP-101 simulant on -73 resin, and K_d values of AP-101 actual waste satisfied acceptance criteria for Na:Cs mole ratios greater than 5000 which encompasses solutions of practical interest to plant operations.

Table 3.7. Comparison of AP-101 Simulant K_d Data on C02 Resin

Na:Cs Mole Ratio	C02 with Simulant K_d , mL/g	16/18 with Actual Waste, Calculated K_d , mL/g	% D
	Experimental	$K_d = 178.8\ln(x) - 1268$	
1.05E+6	1175	1211	-3.0
1.20E+6	1341	1234	8.6
1.19E+6	1328	1233	7.8
3.63E+4	663	609	8.9
3.62E+4	673	608	11
3.50E+4	678	602	13
5.20E+3	302	262	16
4.92E+3	267	252	6.1
5.87E+3	318	283	12
2.27E+3	183	113	62
2.22E+3	179	110	64
1.10E+5 ^(a)	863 ^(b)	807	6.8

(a) AP-101 feed condition Na:Cs mole ratio.
(b) The C02 K_d at the feed condition was calculated according to the formula:
 $K_d = 180.0*\ln(x) - 1227$.
x = Na:Cs mole ratio.

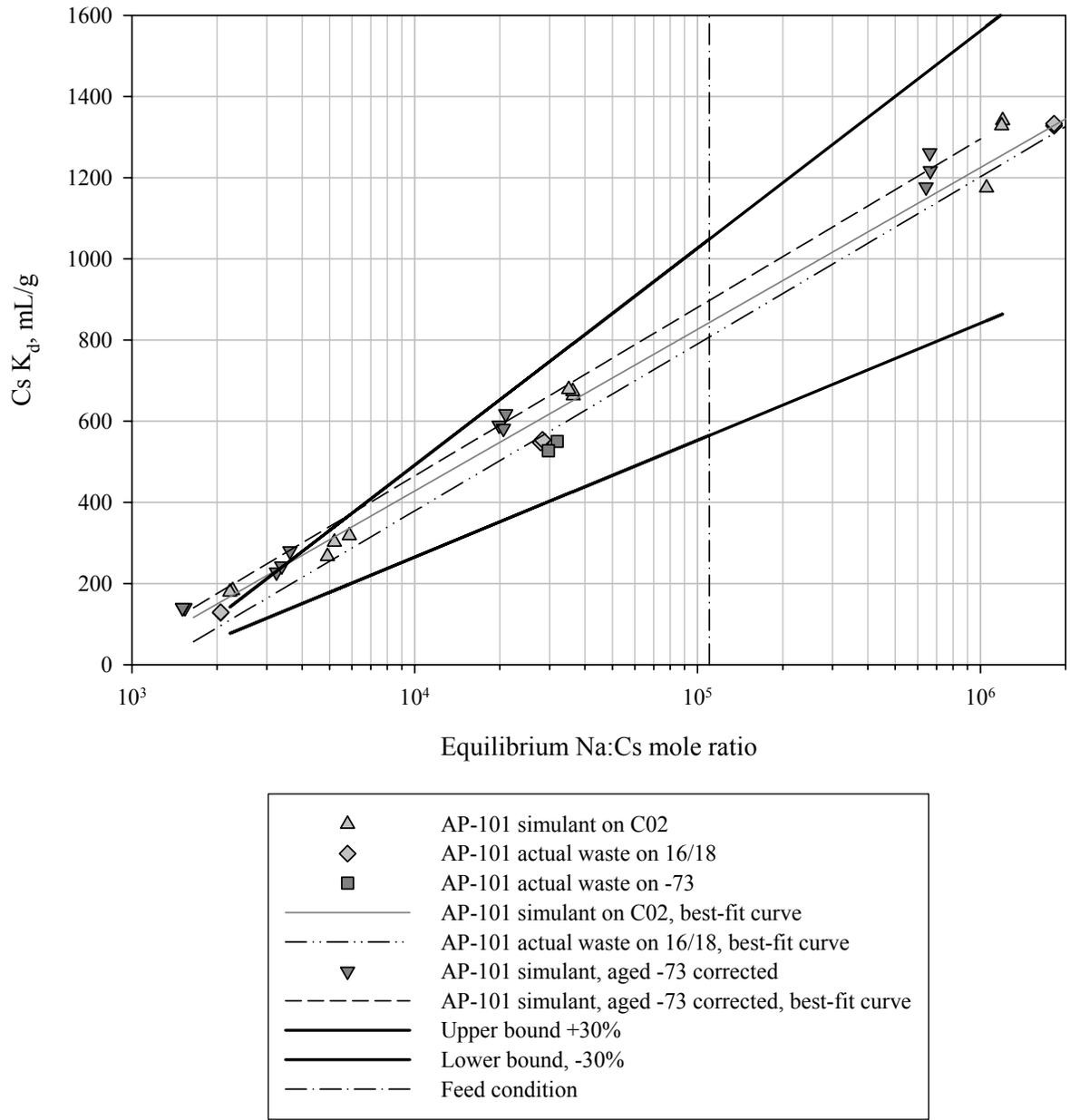


Figure 3.7. AP-101 K_d Values with Corrected, Aged -73 Resin

3.4.3 High Bias Discussion

The AP-101 simulant resulted in higher K_d s than those of the actual waste. Figure 3.8 summarizes the relative percent differences between the simulant and actual waste K_d results for both resins tested. At

low Na:Cs mole ratios (high Cs concentrations), the curve fit may not apply well resulting in high %D. At higher Cs concentrations, the %D dropped to <30% but remained positive.

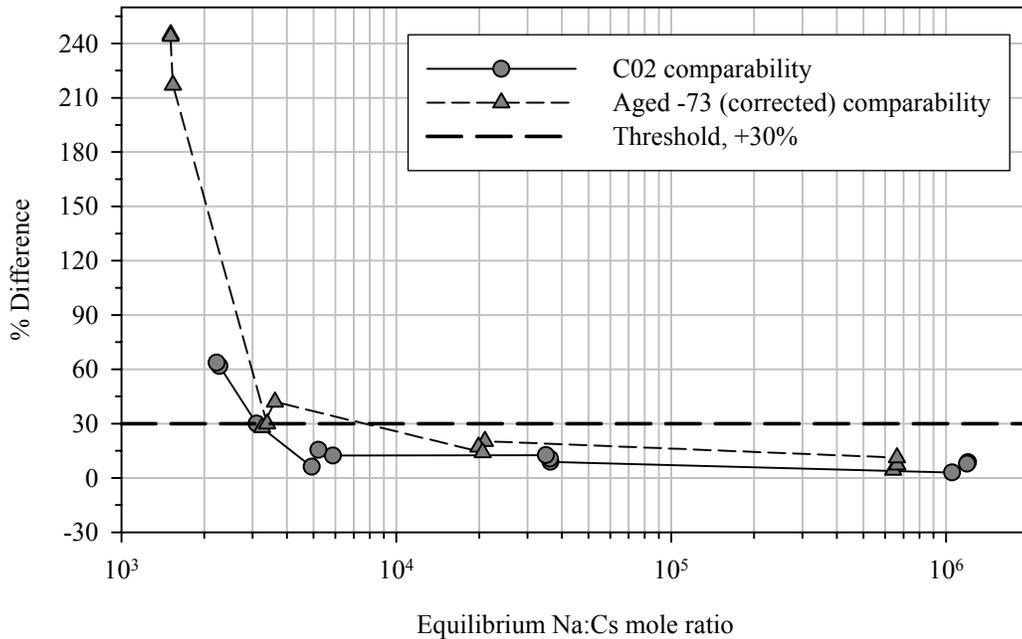


Figure 3.8. Relative Difference Between K_d Values for Actual AP-101 Tank Waste Contacted with 16/18 and -73 Resins and Simulant AP-101 Contacted with C02 and -73 Resins

The overall slightly high bias of the AP-101 simulant $K_{d,s}$ (-73 corrected and C02 resins) relative to those of the actual waste may be due to differences in the resin batches used (C02 versus -73), differences between the simulant and actual waste, or other experimental differences. Even after correction for aging, the -73 batch may exhibit a different total Cs capacity than the C02 resin. This effect would be most pronounced at the high Cs loadings, where a large fraction of the available sites are occupied. An example of the differences between the simulant and the actual waste is the presence of U in the actual waste. Uranium was present at nominally 41 mg/L in the actual AP-101 diluted feed and was found to exchange nearly quantitatively onto the resin during actual waste testing [3]. Uranium was purposely not added to the simulant formulation because non-radioactive simulants are required by the WTP. The exchange behavior of U may slightly decrease the Cs K_d 's by occupying some of the exchange sites. This effect could also be most pronounced at high Cs loadings. Other experimental differences include the effect of oxygen degradation (eliminated from the most recent simulant contacts, but not from the actual waste contacts), and the transferability of the correction factor determined using the AW-101 simulant to the AP-101 simulant/actual waste comparison for the -73 resin.

It must be emphasized again that the AP-101 feed Na:Cs mole ratio is expected to always be greater than 1E+5, where the observed agreement is excellent.

3.5 Isotherms

The isotherms for the AP-101 simulant in contact with C02 resin and actual waste in contact with 16/18 resin were determined. The equilibrium Cs concentrations in supernatant and resin are shown in Table 3.8. The associated isotherms are plotted in Figure 3.9.

Table 3.8. Equilibrium Cs Concentrations for AP-101 Simulant and Actual Waste

AP-101 Simulant on C02			AP-101 Actual Waste on 16/18 and -73		
Sample ID	mg/mL Cs	mg/g Cs ⁽¹⁾	Sample ID	mg/mL Cs	mg/g Cs ⁽¹⁾
225-AP-S1-C02	6.12E-4	7.18E-1	AP101-644	3.62E-4	4.82E-1
225-AP-S1-C02D	5.36E-4	7.18E-1	AP101-644-D	3.63E-4	4.85E-1
225-AP-S1-C02T	5.41E-4	7.18E-1	AP101-S1-644	2.37E-2	1.29E+1
225-AP-S2-C02	1.77E-2	1.17E+1	AP101-S1-644-D	2.34E-2	1.29E+1
225-AP-S2-C02D	1.78E-2	1.20E+1	AP101-S3-644	2.07E-2	1.14E+1
225-AP-S2-C02T	1.84E-2	1.24E+1	AP101-S3-644D	2.22E-2	1.17E+1
225-AP-S3-C02	1.24E-1	3.73E+1	AP101-S2-644	3.21E-1	4.12E+1
225-AP-S3-C02D	1.30E-1	3.48E+1	AP101-S2-644-D	3.20E-1	4.15E+1
225-AP-S3-C02T	1.10E-1	3.48E+1	No data		
225-AP-S4-C02	2.83E-1	5.18E+1			
225-AP-S4-C02D	2.89E-1	5.18E+1			

(1) The Cs resin loading is in terms of mg Cs per gram of dry H-form resin.

The C02 resin contacted with the AP-101 simulant has an effective Cs capacity of 0.39 mmoles/g dry H-form resin at nominally 0.29 mg/mL equilibrium Cs solution concentration. Making a rough (visual) interpolation of the 16/18 resin/actual AP-101 contact data gives an effective Cs capacity of approximately 0.30 mmoles/g dry resin at this same equilibrium Cs solution concentration.. The difference is approximately 0.09 mmoles/g resin, and may be due to differences between the two resin batches used, differences between the simulant and the actual waste, or other experimental differences, as discussed in the previous section. One difference discussed previously is the presence of uranyl in the actual waste (present at 40 mg/L), which may have occupied some ion exchange sites. The total U available to the actual waste batch-contact sample was nominally 0.0017 mmoles, corresponding to ~0.018 mmoles/g dry resin. It is possible that other aspects of the actual waste test (such as oxidative attack from air in the headspace) may decrease effective Cs exchange capacity.

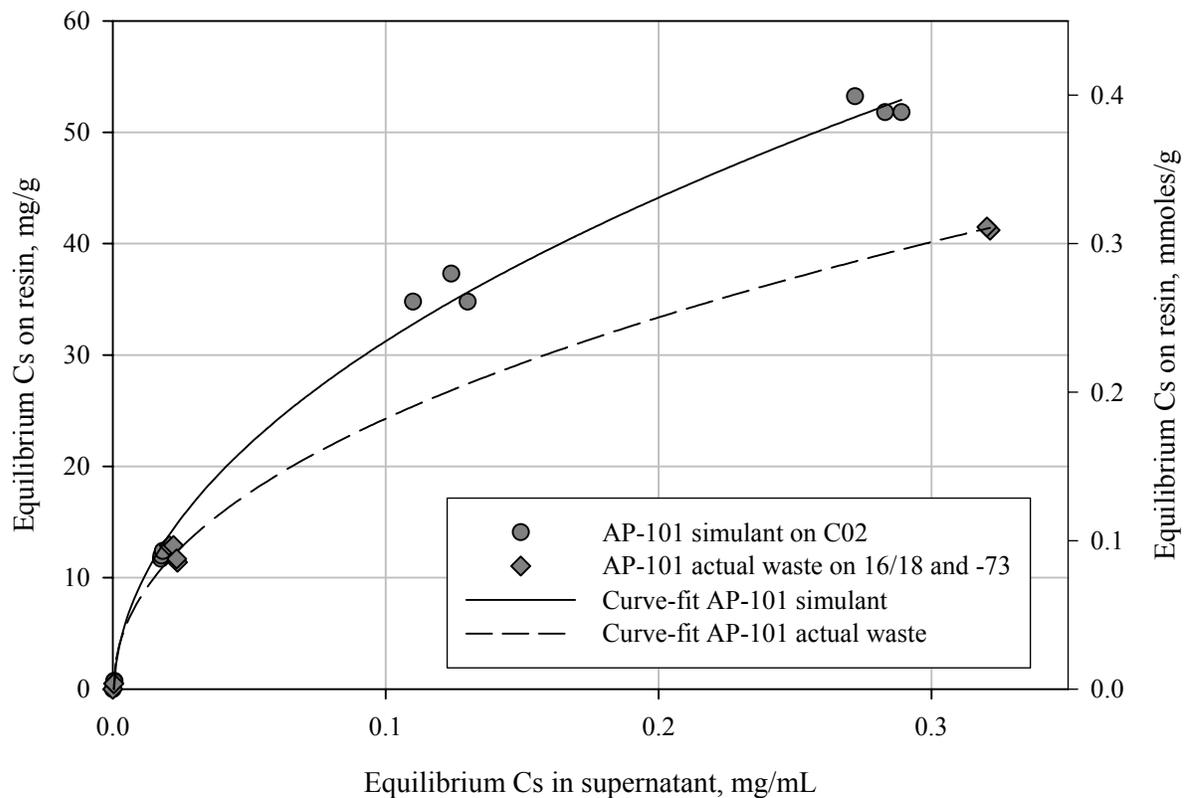


Figure 3.9. Isotherms for AP-101 Simulant and Actual Waste

For comparison, the AW-101 isotherm data are provided in Table 3.9, and the corresponding isotherms are plotted in Figure 3.10. Again it is clear that the capacity of the aged SL-644 was greatly affected by aging. The effective Cs capacity of the fresh -73 resin at an equilibrium solution Cs concentration of approximately 0.18 mg/mL was nominally 0.4 mmoles/g of H-form resin, whereas the aged material exhibited an effective Cs capacity of about 0.15 mmoles/g at similar equilibrium Cs solution concentrations. Based on the shapes of the curves, the total capacity of the aged -73 appears to be not much greater than 0.2 – 0.25 mmoles/g, while the total capacity of the fresh -73 resin looks like it could be significantly higher than the 0.4 mmoles/g observed at the highest solution Cs concentration tested.

Table 3.9. Equilibrium Cs Concentrations for AW-101 Simulant

-73 Resin, 2001			Aged -73 Resin, 2003			C02 Resin, 2003		
Sample ID	Cs mg/mL	Cs mg/g ⁽¹⁾	Sample ID	Cs mg/mL	Cs mg/g ⁽¹⁾	Sample ID	Cs mg/mL	Cs mg/g ⁽¹⁾
SimA-NH	4.91E-4	9.21E-1	225-AW-S1-73	1.08E-3	8.93E-1	225-AW-S1-C02	5.24E-4	1.02E+0
SimA-NHD	4.64E-4	9.40E-1	225-AW-S1-73D	9.93E-4	9.05E-1	225-AW-S1-C02D	5.09E-4	9.91E-1
SimA-NH100	1.38E-2	1.52E+1	225-AW-S1-73T	9.99E-4	9.00E-1	Data intentionally excluded		
SimA-NH100D	1.06E-2	1.25E+1	225-AW-S2-73	2.68E-2	1.01E+1	225-AW-S2-C02	1.33E-2	1.31E+1
SimA-N600H	1.93E-1	5.63E+1	225-AW-S2-73D	2.63E-2	1.00E+1	225-AW-S2-C02D	1.22E-2	1.27E+1
SimA-N600HD	1.80E-1	5.90E+1	225-AW-S2-73T	2.39E-2	1.05E+1	225-AW-S2-C02T	1.18E-2	1.32E+1
No data			225-AW-S3-73	1.70E-1	2.72E+1	225-AW-S3-C02	1.00E-1	3.95E+1
			225-AW-S3-73D	1.66E-1	2.78E+1	225-AW-S3-C02D	1.05E-1	3.78E+1
			225-AW-S3-73T	1.66E-1	2.75E+1	225-AW-S3-C02T	1.03E-1	3.98E+1
			225-AW-S4-73	3.83E-1	3.36E+1	225-AW-S4-C02	2.71E-1	5.42E+1
			225-AW-S4-73D	4.06E-1	3.15E+1	225-AW-S4-C02D	2.62E-1	5.51E+1
			225-AW-S4-73T	3.74E-1	3.55E+1	225-AW-S4-C02T	2.72E-1	5.31E+1

(1) The Cs resin loading is in terms of mg Cs per gram of dry H-form resin.

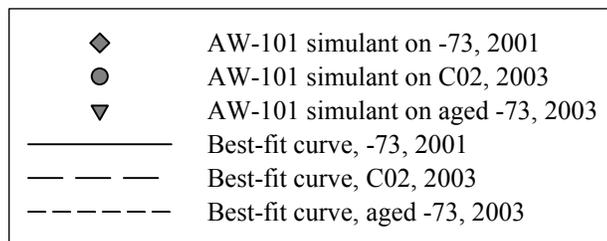
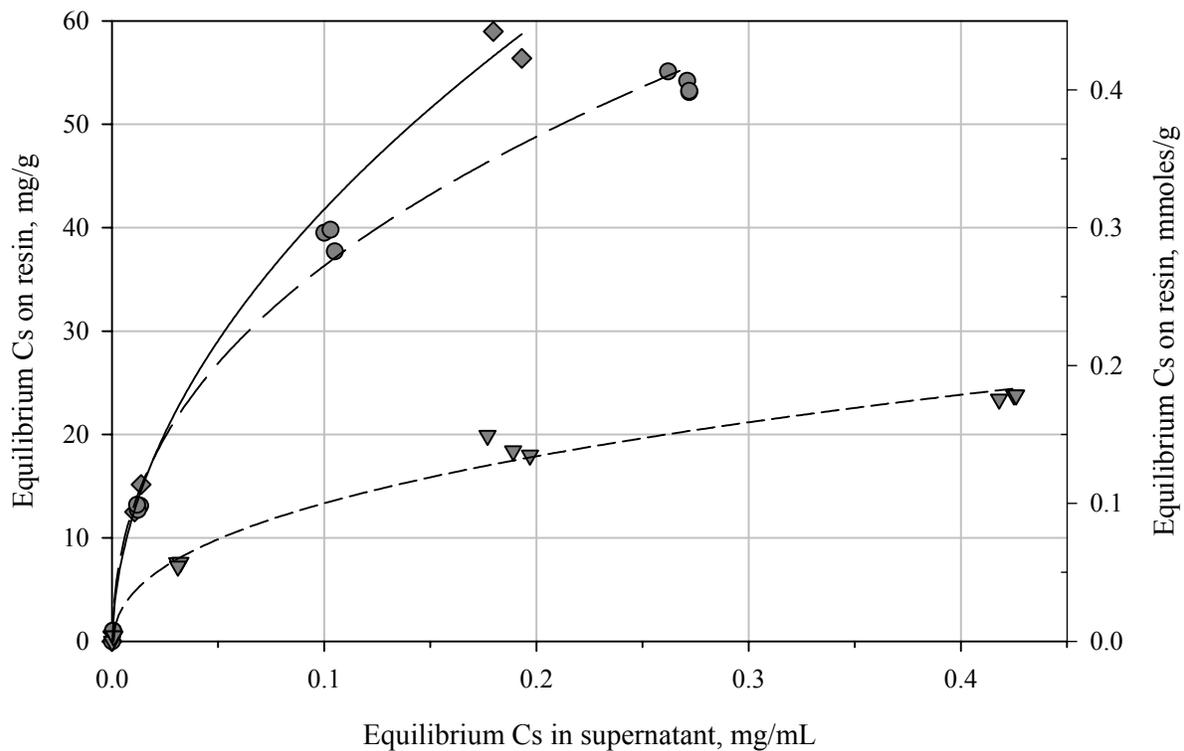


Figure 3.10. AW-101 Simulant Isotherms

4.0 Quality Control

The following sections describe the quality assurance and quality control requirements and implementation.

4.1 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, Subpart 2.7. These quality requirements were implemented through PNWD's *Waste Treatment Plant Support Project (WTPSP) Quality Assurance Requirements and Description Manual* and to the approved Test Plan, TP-RPP-WTP-206, Rev. 0. The analytical requirements were implemented through PNWD's *Conducting Analytical Work in Support of Regulatory Programs* requirements document.

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 in Test Specification 24590-PTF-TSP-RT-02-002, Rev. 0, *Ion Exchange Testing Validation and Verification of AP-101 Simulant*, BNI's QAPjP, PL-24590-QA00001, Rev. 0, was not applicable since the work was not performed in support of environmental/regulatory testing, and the data should not be used as such.

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 were traceable, that inferences and conclusions were soundly based, and that the reported work satisfied the test plan objectives. This review procedure is part of PNWD's *WTPSP Quality Assurance Requirements and Description Manual*.

Analytical processes were performed in accordance with the requirements in PNWD's *Conducting Analytical Work in Support of Regulatory Programs*. Gamma counting was performed by the use of a multichannel analyzer and a suitable detector, such as a high-purity germanium detector. The CMC measured ^{137}Cs in the 50-mL batch-contact samples. The CMC gamma counting was conducted according to procedure PNL-ALO-450, Rev. 0. Additional gamma measurements (for the 20-mL batch contact samples) were taken on a benchtop GEA for comparative measurements (i.e., indication). The equipment was user-calibrated to determine that the equipment was working properly. Known standards of the tracer were counted along with the samples. The gamma counter was energy-calibrated with a vendor-supplied control sample. Because relative measurements were taken, absolute efficiency calibration of the portable gamma counter was not required; however, system stability was required. Detector stability was established each day this system was in use by counting the control samples before

and after the associated sample set. Batch-contact duplicate controls and triplicate samples were processed for each simulant at each Cs concentration. The results and measure of precision (RPD and RSD) are reported in previous sections.

Additional equipment included a thermometer, clock, and balances. The thermometer that was used for monitoring the batch-contact temperature and the timepiece that established contact times were standard laboratory equipment for use as indicators only. Balances are calibrated annually by an NQA-1 qualified contractor, QC Services, Portland, OR. Balance operations were checked each day of use with check weights.

4.2 Analytical Results

The AW-101 simulant was acid digested according to Procedure PNL-ALO-128 *HNO₃-HCl Acid Extraction of Liquids for Metals Analysis Using a Dry-Block Heater*. Aliquots were distributed for analysis by ICP-AES for metals according to Procedure PNNL-ALO-211, *Determination of Elements by Inductively Coupled Argon Plasma Atomic Emission Spectrometry (ICP-AES)* and ICP-MS for Rb and Cs according to Procedure PNL-SC01, Rev. 1, *Inductively-Coupled Plasma Mass Spectrometric (ICP-MS) Analysis*. The simulant was diluted with DI water for analysis by IC for anions according to Procedure PNL-ALO-212, *Determination of Inorganic Anions by Ion Chromatography*. The hydroxide concentration was determined on a direct sample according to PNL-ALO-228, *Hydroxide and Alkalinity Determination*. The characterization of the AP-101 simulant was already reported [5]. After adding Cs to simulant aliquots, aliquots of all spiked solutions were acid digested and analyzed by ICP-MS for Cs. Analytical instrument calibrations and continuing calibrations were conducted in accordance with PNWD's *Conducting Analytical Work in Support of Regulatory Programs*.

Batch and instrument quality control (QC) requirements were met except for phosphate determination by IC where the RPD was 28% (exceeding the 15% criterion). Because the quantity present in solution (180 mg/L) was below the required minimum reportable quantity (MRQ) (1000 mg/L), re-analysis was not required and the analytical results for phosphate were qualified as estimated. Additionally, all phosphorous was added as phosphate so total P determined by ICP-AES could be compared to the IC results. Good agreement was obtained between the two techniques where the total P analysis resulted in 59 mg/L (6% RPD), which corresponds to 181 mg/L phosphate, and the IC average phosphate result was 176 mg/L.

The fluoride measured by IC must be considered an upper bound. Evidence of peak distortion was observed on the fluoride peak, indicative of possible co-eluting anions. Therefore, the results were flagged as estimated.

All test plan-specified MRQs were met. Analytical results and batch QC results are summarized in Table 4.1 through Table 4.3. All raw and reduced data are maintained in data files under Project 42365 at PNWD.

Table 4.1. ICP-AES Analysis of AW-101 Simulant

Analyte	MRQ	Process Blank 1		Sample		Duplicate		RPD	BS Recovery	MS Recovery	Serial Dilution
		EQL	03-00771-PB	EQL	03-00771	MDL	03-00771-DUP				
	µg/mL	µg/mL ^(a)		µg/mL ^(a)		µg/mL ^(a)		%	%	%	%
<i>Criteria:</i>								<15 ^(b)	80 - 120	75 - 125	<10
<i>ICP-AES Test Specification Analytes</i>											
Al	750	11.3	nd	57	13,300	56	12,800	3.8	97	nr	3.6
Ba	12	0.3	[0.041]	1.3	17.7	1.3	17.1	3.3	100	94	—
Ca	310	11.4	nd	11	21.9	11	22.4	2.2	98	95	—
Fe	30	2.5	[0.3]	2.5	3.79	2.5	3.90	2.9	102	94	—
K	750	250	nd	1,270	14,100	1,257	13,600	3.7	98	nr	1.2
Mg	130	8.5	nd	8.5	[0.71]	8.4	[1.1]	—	100	95	—
Mo	60	1.4	nd	7.2	27.8	7.2	26.4	5.1	99	94	—
Na	750	22.0	nd	111	111,000	109	107,000	3.6	102	nr	5.1
Ni	40	3.3	nd	3.3	8.28	3.3	8.34	0.7	101	94	—
P	130	6.0	nd	30	60.9	30	57.4	6.1	99	97	—
<i>Opportunistic Analytes Measured^(c)</i>											
Ag		1.7	nd	1.8	[0.21]	1.7	[0.26]	—	—	—	—
As		9.1	nd	9.2	nd	9.0	nd	—	—	—	—
B		0.8	nd	0.79	nd	0.78	nd	—	99	91	—
Be		0.051	nd	0.05	[0.008]	0.050	[0.009]	—	100	96	—
Bi		6.3	nd	6.4	[2.4]	6.3	[2.3]	—	103	96	—
Cd		1.0	[0.72]	1.0	1.82	0.95	[0.88]	—	99	91	—
Ce		10.1	nd	10.2	nd	10	[1.5]	—	97	92	—
Co		1.3	nd	1.3	[0.33]	1.3	[0.38]	—	—	—	—
Cr		1.5	nd	1.5	[0.45]	1.5	[0.42]	—	98	91	—
Cu		1.8	[0.21]	1.8	[0.64]	1.8	[0.46]	—	102	93	—
Dy		2.5	nd	2.5	nd	2.5	nd	—	—	—	—
Eu		1.3	nd	1.3	nd	1.3	nd	—	—	—	—
La		3.3	nd	3.3	nd	3.3	[0.47]	—	99	92	—
Li		1.5	nd	1.5	3.57	1.5	3.71	3.8	99	93	—
Mn		0.30	nd	1.5	3.38	0.30	3.26	1.9	100	98	—
Nd		10	nd	10	[1.2]	10	[1.7]	—	99	91	—
Pb		6.7	nd	6.7	[1.2]	6.6	[1.5]	—	96	92	—
Pd		32	nd	32	nd	31	nd	—	—	—	—
Rh		13	nd	13	nd	13	[2.0]	—	—	—	—
Ru		5.1	nd	5.1	[0.72]	5.0	[0.87]	—	—	—	—

Table 4.1 (cont'd)

Analyte	MRQ	Process Blank 1		Sample		Duplicate		RPD	BS Recovery	MS Recovery	Serial Dilution
		EQL	03-00771-PB	EQL	03-00771	EQL	03-00771-DUP				
	µg/mL	µg/mL ^(a)		µg/mL ^(a)		µg/mL ^(a)		%	%	%	%
Sb		7.1	nd	7.1	[0.88]	7.0	[0.95]	—	—	—	—
Se		9.1	nd	9.2	nd	9.0	nd	—	—	—	—
Si		7.5	nd	38	74.5	7.5	73.1	1.8	103	105	—
Sn		31	nd	31	[6.9]	31	[9.3]	—	—	—	—
Sr		0.38	nd	0.38	1.34	0.38	1.37	1.7	101	93	—
Te		13	nd	13	[2.8]	13	[3.0]	—	—	—	—
Th		7.0	nd	7.1	nd	7.0	nd	—	98	93	—
Ti		0.63	nd	0.64	[0.12]	0.63	[0.14]	—	98	89	—
Tl		5.3	nd	5.3	[2.3]	5.3	[2.3]	—	—	—	—
U		126	nd	126	[16]	125	[23]	—	98	88	—
V		1.0	nd	1.0	[0.13]	1.0	[0.17]	—	97	89	—
W		3.3	nd	3.3	nd	3.3	nd	—	102	97	—
Y		0.51	nd	0.51	nd	0.50	nd	—	—	—	—
Zn		1.8	nd	1.8	[0.48]	1.8	[0.35]	—	101	95	—
Zr		1.1	nd	1.1	nd	1.1	[0.13]	—	96	88	—

Analytes detected by ICP-AES are bolded for clarity and better readability.

- (a) The overall error for bolded values without brackets is estimated to be within ±15% (analytes greater than the EQL). Bracketed values identify sample concentrations that are <EQL but ≥MDL, and errors likely exceed 15%. The MDL is typically a factor of 10 lower than the EQL.
- (b) Required Na RPD <5%.
- (c) Opportunistic analytes are reported for information only; quality control requirements do not apply to these analytes.

BS = blank spike

EQL = estimated quantitation limit

MDL = minimum detection limit

MRQ = minimum reportable quantity

MS = matrix spike

nd = not detected

nr = not recovered; spike concentration less than 20% of sample concentration; serial dilution test used to assess accuracy.

RPD = relative percent difference

“—” indicates calculation is not required

Data are from ASR 6710, RPL Sample ID = 03-00771

Table 4.2. Anion Analysis of AW-101 Simulant

Analyte	MRQ	Process Blank 1		Sample		Duplicate		RPD	BS Recovery	MS Recovery
		EQL	03-00771-PB	EQL	03-00771	EQL	03-00771-DUP			
	µg/mL	µg/mL ^(a)		µg/mL ^(a)		µg/mL ^(a)		%	%	%
<i>Criteria:</i>								<15	80 - 120	75 - 125
<i>Test Specification Analytes</i>										
Cl ⁻	300	0.13	nd	63	2,650	63	2,500	6	96	98
F ⁻	250	0.13	nd	63	336^(b)	63	317^(b)	6	99	98
NO ₂ ⁻	3000	0.25	nd	1,300	36,300	1300	36,500	1	100	103
NO ₃ ⁻	3000	0.25	nd	1,300	88,500	1300	89,400	1	97	92
PO ₄ ³⁻	1000	0.25	nd	130	201^(c)	130	152^(c)	28	99	99
SO ₄ ²⁻	1000	0.25	nd	130	230	130	222	4	98	98
OH ⁻	75,000	^(d)	nd	NA	35,600	NA	35,800	0.55	95	95
<i>Other Analytes Measured^(e)</i>										
Br ⁻	NA	0.13	nd	630	nd	630	nd	—	99	95
C ₂ O ₄ ²⁻	NA	0.25	nd	130	nd	130	nd	—	99	99
Analytes detected are bolded for clarity and better readability. (a) The overall error is estimated to be within ±15% or better for non-complex aqueous samples that are free of interference. (b) Fluoride results should be considered the upper bound concentration. Peak distortion of the F peak was observed suggesting the presence of co-eluting anion(s), possibly formate or acetate. Therefore, these results are qualified as estimated. (c) The RPD acceptance criteria for phosphate was exceeded; therefore, the results are qualified as estimated. (d) For the OH ⁻ blank, no inflection point was detected. (e) Opportunistic analytes are reported for information only; quality control requirements do not apply to these analytes. NA = not applicable BS = blank spike EQL = estimated quantitation limit MDL = minimum detection limit (note: the MDL is a factor of ten less than the EQL) MRQ = minimum reportable quantity MS = matrix spike nd = not detected RPD = relative percent difference “—“ indicates calculation is not required. Data are from ASR 6710.										

Table 4.3. Cs Concentration in Spiked Stock Simulant Solutions

Sample ID	RPL Number	Cs-133		Rb-85	
		MDL	Sample	MDL	Sample
		µg/mL		µg/mL	
<i>ASR 6615</i>					
Process Blank	NA	0.039	< 0.39	0.018	< 0.18
AP-101 ^(a)	03-0082	0.04	4.92	0.018	0.856
AP-101 DUP ^(a)	03-0082 Duplicate	0.04	4.98	0.018	0.912
RPD, %	NA	1.2		6.3	
BS Recovery, %	NA	84		85	
MS Recovery, %	NA	102		90	
<i>ASR 6710</i>					
Process Blank	NA	0.098	< 0.98	0.024	< 0.24
TI-225-AP-S2	03-0772	0.97	110	0.024	4.57
TI-225-AP-S3	03-0773	2.8	378	0.023	4.40
TI-225-AP-S4	03-0774	4.9	663	0.024	4.43
TI-225-F0-AW101	03-0771	0.094	8.28	0.023	2.21
TI-225-AW-S2	03-0775	0.97	111	0.024	2.18
TI-225-AW-S3	03-0776	2.9	377	0.024	2.16
TI-225-AW-S4	03-0777	4.7	652	0.023	2.13
TI-225-AW-S4 DUP	03-0777 Duplicate	4.7	656	0.023	2.11
RPD, %	NA	0.65		0.8	
BS Recovery, %	NA	94		102	
MS Recovery, %	NA	103		100	
<p>(a) After analysis, Rb was added to the AP-101 simulant stock to correct for incorrect initial concentration [5].</p> <p>Criteria:</p> <p>RPD < 15%</p> <p>BS recovery: 80 – 120%</p> <p>MS recovery: 75 – 125%</p> <p>Cs MRQ: 1.5 µg/mL</p> <p>Notes:</p> <p>NA = not applicable</p> <p>BS = blank spike</p> <p>MDL = minimum detection limit</p> <p>MRQ = minimum reportable quantity</p> <p>MS = matrix spike</p> <p>RPD = relative percent difference</p>					

5.0 Conclusions

The AP-101 simulant was validated for Cs ion exchange behavior.

- The Cs batch-distribution coefficients of SL-644 2-yr aged batch -73 resin in contact with AP-101 simulant were determined.
 - Simulant AP-101 Cs ion exchange behaviors were compared to that of the actual AP-101 waste.
 - The SL-644 batch -73 resin simulant batch-distribution coefficients were about a factor of two lower than the actual waste. Applying a nominal correction factor generated from AW-101 simulant to account for resin aging over the time between the actual and simulant waste tests resulted in AP-101 simulant K_d values within the allowed tolerance ($\pm 30\%$ for simulant validation) to those of the actual waste.
- The Cs batch-distribution coefficients of SL-644 batch C02 resin in contact with AP-101 simulant were determined.
 - SL-644 batch C02 resin simulant batch-distribution coefficients compared well (within $\pm 30\%$ tolerance) with those from the actual AP-101 waste and those from the -73 resin, as corrected.
 - The batch equilibrium distribution data provide a basis of comparison with the larger production run of SL-644 and previous lab-scale testing of the -73 resin. The consistency showed that the actual waste -73 results were applicable to expected WTP performance with production-scale resin.

6.0 References

1. Fiskum SK, DL Blanchard, and ST Arm. 2002. *Aging Study and Small Column Ion Exchange Testing of SuperLig® 644 for Removal of ¹³⁷Cs from Simulated AW-101 Hanford Tank Waste*. PNWD-3195, Battelle—Pacific Northwest Division, Richland, WA.
2. Arm, ST, DL Blanchard, SK Fiskum, DR Weier. 2003. *Chemical Degradation of SuperLig®644 Ion Exchange Resin*. WTP-RPT-046, Battelle—Pacific Northwest Division, Richland, WA.
3. Fiskum SK, ST Arm, DL Blanchard, and BM Rapko. 2002. *Small Column Ion Exchange Testing of Superlig® 644 for Removal of ¹³⁷Cs from Hanford Waste Tank 241-AP-101 Diluted Feed (Envelope A)*. PNWD-3198, Battelle—Pacific Northwest Division, Richland, WA.
4. Golcar GR, NG Colton, JG Darab, and HD Smith. 2000. *Hanford Tank Waste Simulants Specification and Their Applicability for the Retrieval, Pretreatment, and Vitrification Processes*. PNWD-2455, Pacific Northwest National Laboratory, Richland, WA.
5. Russell, RL, SK Fiskum, LK Jagoda, AP Poloski. 2003. *AP-101 Diluted Feed (Envelope A) Simulant Development Report*. PNWD-3248, Battelle—Pacific Northwest Division, Richland, WA.
6. Smith GL. 2002. *R&T Simulant Development, Approval, Validation, and Documentation*. River Protection Project-Waste Treatment Plant, Bechtel National, Inc. Richland, WA.
7. Fiskum SK, DL Blanchard, and ST Arm. 2003. *Small Column Ion Exchange Testing of SuperLig® 644 for Removal of ¹³⁷Cs from Hanford Waste Tank 241-AZ-102 Concentrate (Envelope B)*. PNWD-3267, Battelle—Pacific Northwest Division, Richland, WA.
8. Goheen, SC, PR Bredt, OT Farmer, III, SK Fiskum, KA Gaither, LR Greenwood, LK Jagoda, AP Poloski, RD Scheele, CZ Soderquist, RG Swoboda, MP Thomas, MW Urie, JJ Wagner. 2002. *Chemical Analysis and Physical Property Testing of Diluted 241-AP-101 Tank Waste*. PNWD-3174, Battelle—Pacific Northwest Division, Richland, WA.
9. Rapko BM, DL Blanchard Jr, KJ Carson, JR DesChane, RL Sell, RG Swoboda. 2003. *Batch Contact Testing of SuperLig®-644*. PNWD-3265, Battelle—Pacific Northwest Division, Richland, WA.

APPENDIX A

AW-101 Simulant Preparation

Appendix A: AW-101 Simulant Preparation

Table A.1. Simulant AW-101 (Envelope A) Preparations

Compound	Targeted M	FW	AW-101 2001 (Feed 4)		AW-101 2002		AW-101 2003	
			Mass used g	Calculated M	Mass used g	Calculated M	Mass used g	Calculated M
EDTA	3.70E-3	292.24	2.1652	3.70E-3	1.0818	3.70E-3	2.1629	3.70E-3
Citric acid	3.70E-3	210.14	1.5577	3.71E-3	0.7778	3.70E-3	1.5553	3.70E-3
Na ₃ HEDTA-2H ₂ O	3.70E-3	344.00	2.5459	3.70E-3	1.2733	3.70E-3	2.5458	3.70E-3
Na ₃ NTA	3.70E-3	257.10	1.9027	3.70E-3	0.9518	3.70E-3	1.9030	3.70E-3
NaGluconate	3.70E-3	218.00	1.6130	3.70E-3	0.8068	3.70E-3	1.6113	3.70E-3
Na ₂ Iminodiacetate	3.70E-3	177.07	1.3104	3.70E-3	0.6559	3.70E-3	1.3121	3.71E-3
Fe(NO ₃) ₃ -9H ₂ O	5.00E-5	404.02	0.0409	5.06E-5	0.0208	5.15E-5	0.0404	5.00E-5
Mg(NO ₃) ₂ -6H ₂ O	1.50E-3	256.40	0.7691	1.50E-3	0.3847	1.50E-3	0.7707	1.50E-3
Mn(NO ₃) ₂ , 50%	6.63E-5	4.30 M	0.0308 mL	6.62E-5	0.0154 mL	6.62E-5	0.0308 mL	6.62E-5
MoO ₃	2.86E-4	143.95	0.0828	2.88E-4	0.0418	2.90E-4	0.0820	2.85E-4
Ni(NO ₃) ₂ -6H ₂ O	1.33E-4	290.80	0.0774	1.33E-4	0.0392	1.35E-4	0.0771	1.33E-4
SiO ₂	2.93E-3	60.08	0.3523	2.93E-3	0.1763	2.93E-3	0.3522	2.93E-3
BaNO ₃	1.33E-4	261.38	0.0693	1.33E-4	0.0353	1.35E-4	0.0694	1.33E-4
Ca(NO ₃) ₂	4.13E-4	236.16	0.1952	4.13E-4	0.0974	4.12E-4	0.1947	4.12E-4
Sr(NO ₃) ₂	1.30E-5	211.65	0.0056	1.32E-5	0.0028	1.32E-5	0.0055	1.30E-5
RbNO ₃	1.00E-5	147.47	0.0030	1.02E-5	0.0015	1.02E-5	0.0030	1.02E-5
CsNO ₃	6.40E-5	194.92	0.0243	6.23E-5	0.0125	6.41E-5	0.0250	6.41E-5
LiNO ₃	5.51E-4	69.00	0.0761	5.51E-4	0.0385	5.58E-4	0.0753	5.46E-4
KOH	4.30E-1	56.11	56.22 ^(a)	5.01E-1	24.1298	4.30E-1	48.28	4.30E-1
NaOH	3.89E+0	40.00	356.53 ^(a)	4.46E+0	157.5	3.94E+0	311.4	3.89E+0
Al(NO ₃) ₃ -9H ₂ O	5.06E-1	375.15	403.2 ^(a)	5.37E-1	189.83	5.06E-1	379.6	5.06E-1
Na ₂ CO ₃	1.00E-1	105.99	21.199	1.00E-1	10.599	1.00E-1	21.198	1.00E-1
Na ₂ SO ₄	2.36E-3	142.05	0.6705	2.36E-3	0.3353	2.36E-3	0.6708	2.36E-3
NaHPO ₄ -7H ₂ O	1.73E-3	268.07	0.9280	1.73E-3	0.4636	1.73E-3	0.9281	1.73E-3
NaCl	6.93E-2	58.45	8.0850	6.92E-2	4.051	6.93E-2	8.1004	6.93E-2
NaF	1.10E-2	41.99	0.9234	1.10E-2	0.4624	1.10E-2	0.9236	1.10E-2
NaNO ₂	7.90E-1	69.00	109.00	7.90E-1	54.51	7.90E-1	109.01	7.90E-1
Final Volume			2-L		1-L		2-L	

(a) Additional reagent was added to increase molarity, hygroscopic nature biased the mass low
EDTA = ethylenediaminetetraacetic acid

APPENDIX B

Resin Properties

Appendix B: Resin Properties

Table B.1. F-factor for SL-644

Vial ID	Date/Time	Vial Mass (inc. cap)	Vial+cap+ resin mass (g)	Resin mass (g)	F-Factor	Average F-Factor
SL-644 Batch ID 010319SMC-IV-73						
225-73-F1	2/24/2003 12:15	17.0977	17.3808	0.2831	NA	
	2/26/2003 15:20		17.3382	0.2405	0.8495	
	2/27/2003 20:10		17.3358	0.2381	0.8410	
	3/3/2003 10:10		17.3313	0.2336	0.8252	
	3/4/2003 14:40		17.3319	0.2342	0.8273	
	3/5/2003 16:00		17.3303	0.2326	0.8216	
225-73-F2 (duplicate)	2/24/2003 12:15	16.9967	17.2940	0.2973	NA	0.8235
	2/26/2003 15:20		17.2501	0.2534	0.8523	
	2/27/2003 20:10		17.2473	0.2506	0.8429	
	3/3/2003 10:10		17.2418	0.2451	0.8244	
	3/4/2003 14:40		17.2416	0.2449	0.8237	
	3/5/2003 16:00		17.2421	0.2454	0.8254	
SL-644 Batch ID C-01-05-28-02-35-60						
225-CO2-F1	2/24/2003 12:15	16.8345	17.2351	0.4006	NA	
	2/26/2003 15:20		17.1415	0.3070	0.7664	
	2/27/2003 20:10		17.1414	0.3069	0.7661	
	3/3/2003 10:10		17.1374	0.3029	0.7561	
	3/4/2003 14:40		17.1364	0.3019	0.7536	
	3/5/2003 16:00		17.1382	0.3037	0.7581	
225-CO2-F2 (duplicate)	2/24/2003 12:15	17.0885	17.4861	0.3976	NA	0.7551
	2/26/2003 15:20		17.3933	0.3048	0.7666	
	2/27/2003 20:10		17.3928	0.3043	0.7653	
	3/3/2003 10:10		17.3884	0.2999	0.7543	
	3/4/2003 14:40		17.3879	0.2994	0.7530	
	3/5/2003 16:00		17.3875	0.2990	0.7520	
NA = not applicable Bold values indicate the values used to calculate the average F-factor.						

APPENDIX C

Batch Contacts Results

Appendix C: Batch Contacts Results

Data for Resin 010319SMC-IV-73
 Samples were contacted for nominally 24 h
 AW-101 Na concentration: 4.74 M

AW-101 Simulant Controls

Sample ID	Cs conc., mg/L	Cs conc., M	Resin mass, g	Simulant volume ^(a) mL	¹³⁷ Cs cpm/ mL	Avg ¹³⁷ Cs cpm/mL	RPD
225-AW-S1-C	8.51	6.40E-5	none	20.21	171.6	170.1	-1.7
225-AW-S1-CD	8.51	6.40E-5	none	20.23	168.6		
225-AW-S2-C	111	8.35E-4	none	20.18	173.8	172.8	-1.1
225-AW-S2-CD	111	8.35E-4	none	20.19	171.9		
225-AW-S3-C	397	2.99E-3	none	20.12	164.4	168.1	4.4
225-AW-S3-CD	397	2.99E-3	none	20.12	171.8		
225-AW-S4-C	668	5.03E-3	none	20.13	155.7	164.1	10.2
225-AW-S4-CD	668	5.03E-3	none	20.12	172.6		

AW-101 Simulant Batch Contacts

Sample ID	IX Material	Resin mass, g	F factor	Corrected resin mass, g	Simulant volume ^(a) , mL	¹³⁷ Cs cpm/ mL	Fraction Cs in solution	Equil. Cs molarity	Equil. Cs, mg/mL	Equil. Cs in resin, mg/g	Na/Cs mole ratio	K _d , mL/g
225-AW-S1-73	010319SMC-IV-73	0.2007	0.8235	0.1653	19.85	21.5	0.127	8.11E-6	1.08E-3	8.93E-1	5.85E+5	829
225-AW-S1-73D	010319SMC-IV-73	0.2003	0.8235	0.1650	19.86	19.8	0.117	7.47E-6	9.93E-4	9.05E-1	6.35E+5	911
225-AW-S1-73T	010319SMC-IV-73	0.1999	0.8235	0.1646	19.72	20.0	0.117	7.51E-6	9.99E-4	9.00E-1	6.31E+5	901
225-AW-S2-73	010319SMC-IV-73	0.1998	0.8235	0.1645	19.75	41.8	0.242	2.02E-4	2.68E-2	1.01E+1	2.35E+4	377
225-AW-S2-73D	010319SMC-IV-73	0.2028	0.8235	0.1670	19.75	41.0	0.237	1.98E-4	2.63E-2	1.00E+1	2.39E+4	381
225-AW-S2-73T	010319SMC-IV-73	0.2001	0.8235	0.1648	19.79	37.2	0.215	1.80E-4	2.39E-2	1.05E+1	2.64E+4	438
225-AW-S3-73	010319SMC-IV-73	0.2004	0.8235	0.1650	19.75	71.9	0.428	1.28E-3	1.70E-1	2.72E+1	3.71E+3	160
225-AW-S3-73D	010319SMC-IV-73	0.2000	0.8235	0.1647	19.74	70.1	0.417	1.25E-3	1.66E-1	2.78E+1	3.80E+3	168
225-AW-S3-73T	010319SMC-IV-73	0.2017	0.8235	0.1661	19.72	70.1	0.417	1.25E-3	1.66E-1	2.75E+1	3.80E+3	166
225-AW-S4-73	010319SMC-IV-73	0.2011	0.8235	0.1656	19.54	94.1	0.573	2.88E-3	3.83E-1	3.36E+1	1.65E+3	88
225-AW-S4-73D	010319SMC-IV-73	0.1987	0.8235	0.1636	19.60	99.6	0.607	3.05E-3	4.06E-1	3.15E+1	1.55E+3	78
225-AW-S4-73T	010319SMC-IV-73	0.1988	0.8235	0.1637	19.70	91.7	0.559	2.81E-3	3.74E-1	3.55E+1	1.69E+3	95

(a) AW101 simulant volumes were determined based on the density given below. The slight dilution attributed to spiking was considered inconsequential.
 AW-101 density: 1.239 g/mL

Data for Resin 010319SMC-IV-73
 AP-101 Na concentration: 4.83 M
 Samples were contacted for nominally 24 hrs

AP-101 Simulant Controls

Sample ID	Cs conc., mg/L	Cs conc., M	Resin mass, g	Simulant volume ^(a) mL	¹³⁷ Cs cpm/mL	Avg ¹³⁷ Cs cpm/mL	RPD
225-AP-S1-C	5.97	4.50E-5	none	20.13	165.7	170.9	6.0
225-AP-S1-CD	5.97	4.50E-5	none	20.13	176.0		
225-AP-S2-C	109	8.17E-4	none	20.12	172.4	169.5	-3.3
225-AP-S2-CD	109	8.17E-4	none	20.00	166.7		
225-AP-S3-C	386	2.91E-3	none	20.12	173.4	171.4	-2.3
225-AP-S3-CD	386	2.91E-3	none	20.08	169.5		
225-AP-S4-C	669	5.03E-3	none	20.13	169.1	164.1	-6.1
225-AP-S4-CD	669	5.03E-3	none	20.13	159.1		

AP-101 Simulant Batch Contacts

Sample ID	IX Material	Resin mass, g	F factor	Corrected resin mass, g	Simulant volume ^(a) , mL	¹³⁷ Cs cpm/mL	Fraction Cs in solution	Equil. Cs molarity	Equil. Cs, mg/mL	Equil. Cs in resin, mg/g	Na/Cs mole ratio	K _d , mL/g
225-AP-S1-73	010319SMC-IV-73	0.2024	0.8235	0.1667	19.71	28.6	0.167	7.52E-6	1.00E-3	5.89E-1	6.42E+5	588
225-AP-S1-73D	010319SMC-IV-73	0.2035	0.8235	0.1676	19.66	27.6	0.162	7.27E-6	9.67E-4	5.88E-1	6.64E+5	608
225-AP-S1-73T	010319SMC-IV-73	0.1952	0.8235	0.1608	19.61	27.7	0.162	7.29E-6	9.69E-4	6.11E-1	6.62E+5	631
225-AP-S2-73	010319SMC-IV-73	0.1978	0.8235	0.1629	19.80	47.8	0.282	2.30E-4	3.07E-2	9.47E+0	2.10E+4	309
225-AP-S2-73D	010319SMC-IV-73	0.1937	0.8235	0.1595	19.92	50.4	0.297	2.43E-4	3.23E-2	9.52E+0	1.99E+4	295
225-AP-S2-73T	010319SMC-IV-73	0.2045	0.8235	0.1684	19.67	48.6	0.286	2.34E-4	3.11E-2	9.05E+0	2.06E+4	291
225-AP-S3-73	010319SMC-IV-73	0.2022	0.8235	0.1665	19.80	78.7	0.459	1.33E-3	1.77E-1	2.48E+1	3.62E+3	140
225-AP-S3-73D	010319SMC-IV-73	0.2000	0.8235	0.1647	19.63	87.6	0.511	1.48E-3	1.97E-1	2.25E+1	3.25E+3	114
225-AP-S3-73T	010319SMC-IV-73	0.2050	0.8235	0.1688	19.67	84.0	0.490	1.42E-3	1.89E-1	2.29E+1	3.39E+3	121
225-AP-S4-73	010319SMC-IV-73	0.2036	0.8235	0.1677	19.51	102.4	0.624	3.14E-3	4.18E-1	2.92E+1	1.54E+3	70.0
225-AP-S4-73D	010319SMC-IV-73	0.1955	0.8235	0.1610	19.63	104.1	0.634	3.19E-3	4.25E-1	2.98E+1	1.51E+3	70.2
225-AP-S4-73T	010319SMC-IV-73	0.1953	0.8235	0.1608	19.67	104.4	0.636	3.20E-3	4.26E-1	2.98E+1	1.51E+3	70.0

(a) AP-101 simulant volumes were determined based on the densities given below. The slight dilution attributed to spiking was considered inconsequential.
 AP-101 density: 1.257 g/mL

Data for Resin C-01-05-28-02-35-60
 Samples were contacted for 139.5 hrs

AW-101 Na Concentration: 4.74 M

Sample ID	Cs conc., mg/L	Cs conc., M	Resin mass, g	Simulant volume ^(a) mL	¹³⁷ Cs cpm/mL	Avg ¹³⁷ Cs cpm/mL	RPD
225-AW-S1-C	8.51	6.40E-5	none	20.21	1988.4	2027.0	3.8
225-AW-S1-CD	8.51	6.40E-5	none	20.23	2065.6		
225-AW-S2-C	111	8.35E-4	none	20.18	1597.3	1622.9	3.2
225-AW-S2-CD	111	8.35E-4	none	20.19	1648.5		
225-AW-S3-C	397	2.99E-3	none	20.12	2043.8	2067.1	2.3
225-AW-S3-CD	397	2.99E-3	none	20.12	2090.5		
225-AW-S4-C	668	5.03E-3	none	20.13	2008.6	2015.5	0.7
225-AW-S4-CD	668	5.03E-3	none	20.12	2022.5		

AW-101 Simulant Batch Contacts

Sample ID	IX Material	Resin mass, g	F factor	Corrected resin mass, g	Simulant volume ^(a) , mL	¹³⁷ Cs cpm/mL	Fraction Cs in solution	Equil. Cs molarity	Equil. Cs, mg/mL	Equil. Cs in resin, mg/g	Na/Cs mole ratio	K _d , mL/g
225-AW-S1-C02	C-01-05-28-02-35-60	0.5025	0.7551	0.3794	48.63	124.6	0.0615	3.94E-6	5.24E-4	1.02E+0	1.20E+6	1956
225-AW-S1-C02D	C-01-05-28-02-35-60	0.4997	0.7551	0.3773	46.72	121.1	0.0597	3.82E-6	5.09E-4	9.91E-1	1.24E+6	1949
225-AW-S1-C02T	C-01-05-28-02-35-60	0.5043	0.7551	0.3808	47.96	208.1	0.1027	6.57E-6	8.74E-4	9.62E-1	7.21E+5	1101
225-AW-S2-C02	C-01-05-28-02-35-60	0.4998	0.7551	0.3774	50.76	193.7	0.1193	9.97E-5	1.33E-2	1.31E+1	4.76E+4	993
225-AW-S2-C02D	C-01-05-28-02-35-60	0.5081	0.7551	0.3836	49.38	178.9	0.1102	9.21E-5	1.22E-2	1.27E+1	5.15E+4	1039
225-AW-S2-C02T	C-01-05-28-02-35-60	0.4928	0.7551	0.3721	49.35	172.6	0.1063	8.88E-5	1.18E-2	1.32E+1	5.34E+4	1114
225-AW-S3-C02	C-01-05-28-02-35-60	0.4928	0.7551	0.3721	49.55	521.9	0.2525	7.55E-4	1.00E-1	3.95E+1	6.28E+3	394
225-AW-S3-C02D	C-01-05-28-02-35-60	0.4944	0.7551	0.3733	48.23	546.7	0.2645	7.90E-4	1.05E-1	3.78E+1	6.00E+3	359
225-AW-S3-C02T	C-01-05-28-02-35-60	0.4943	0.7551	0.3732	50.56	538.2	0.2603	7.78E-4	1.03E-1	3.98E+1	6.09E+3	385
225-AW-S4-C02	C-01-05-28-02-35-60	0.4937	0.7551	0.3728	50.93	817.7	0.4057	2.04E-3	2.71E-1	5.42E+1	2.32E+3	200
225-AW-S4-C02D	C-01-05-28-02-35-60	0.4996	0.7551	0.3772	51.11	788.8	0.3913	1.97E-3	2.62E-1	5.51E+1	2.41E+3	211
225-AW-S4-C02T	C-01-05-28-02-35-60	0.4911	0.7551	0.3708	49.72	820.6	0.4072	2.05E-3	2.72E-1	5.31E+1	2.32E+3	195

(a) AW-101 simulant volumes were determined based on the AW-101 simulant density. The slight dilution attributed to spiking was considered inconsequential. Shaded batch contact sample was used for monitoring equilibrium.

Data for Resin C-01-05-28-02-35-60
 Samples were contacted for 139.5 hrs
 AP-101 Na concentration: 4.83 M

AP-101 Simulant Controls

Sample ID	Cs conc., mg/L	Cs conc., M	Resin mass, g	Simulant volume ^(a) mL	¹³⁷ Cs cpm/mL	Avg ¹³⁷ Cs cpm/mL	RPD
225-AP-S1-C	5.97	4.50E-5	none	20.13	2098.0	2105.8	0.7
225-AP-S1-CD	5.97	4.50E-5	none	20.13	2113.6		
225-AP-S2-C	109	8.17E-4	none	20.12	1621.7	1638.5	2.0
225-AP-S2-CD	109	8.17E-4	none	20.00	1655.3		
225-AP-S3-C	386	2.91E-3	none	20.12	2094.4	2107.4	1.2
225-AP-S3-CD	386	2.91E-3	none	20.08	2120.4		
225-AP-S4-C	669	5.03E-3	none	20.13	2006.1	2022.2	1.6
225-AP-S4-CD	669	5.03E-3	none	20.13	2038.2		

AP-101 Simulant Batch Contacts

Sample ID	IX Material	Resin mass, g	F factor	Corrected resin mass, g	Simulant volume ^(a) mL	¹³⁷ Cs cpm/mL	Fraction Cs in solution	Equil. Cs molarity	Equil. Cs, mg/mL	Equil. Cs in resin, mg/g	Na/Cs mole ratio	K _d , mL/g
225-AP-S1-C02	C-01-05-28-02-35-60	0.5030	0.7551	0.3798	50.87	215.5	0.1024	4.60E-6	6.12E-4	7.18E-1	1.05E+6	1175
225-AP-S1-C02D	C-01-05-28-02-35-60	0.4944	0.7551	0.3733	49.26	188.7	0.0896	4.03E-6	5.36E-4	7.18E-1	1.20E+6	1341
225-AP-S1-C02T	C-01-05-28-02-35-60	0.4937	0.7551	0.3728	49.27	190.6	0.0905	4.07E-6	5.41E-4	7.18E-1	1.19E+6	1328
225-AP-S2-C02	C-01-05-28-02-35-60	0.5001	0.7551	0.3776	48.81	267.2	0.1631	1.33E-4	1.77E-2	1.17E+1	3.63E+4	663
225-AP-S2-C02D	C-01-05-28-02-35-60	0.4988	0.7551	0.3766	49.57	268.0	0.1635	1.34E-4	1.78E-2	1.20E+1	3.62E+4	673
225-AP-S2-C02T	C-01-05-28-02-35-60	0.4939	0.7551	0.3729	51.48	277.2	0.1692	1.38E-4	1.84E-2	1.24E+1	3.50E+4	678
225-AP-S3-C02	C-01-05-28-02-35-60	0.4967	0.7551	0.3750	53.25	674.1	0.3199	9.29E-4	1.24E-1	3.73E+1	5.20E+3	302
225-AP-S3-C02D	C-01-05-28-02-35-60	0.4878	0.7551	0.3683	50.17	711.5	0.3376	9.81E-4	1.30E-1	3.48E+1	4.92E+3	267
225-AP-S3-C02T	C-01-05-28-02-35-60	0.5003	0.7551	0.3778	47.50	597.3	0.2834	8.23E-4	1.10E-1	3.48E+1	5.87E+3	318
225-AP-S4-C02	C-01-05-28-02-35-60	0.4966	0.7551	0.3750	50.37	855.5	0.4231	2.13E-3	2.83E-1	5.18E+1	2.27E+3	183
225-AP-S4-C02D	C-01-05-28-02-35-60	0.5029	0.7551	0.3797	51.76	873.3	0.4318	2.17E-3	2.89E-1	5.18E+1	2.22E+3	179
225-AP-S4-C02T	C-01-05-28-02-35-60	0.4980	0.7551	0.3760	49.68	1179.0	0.5830	2.93E-3	3.90E-1	3.68E+1	1.65E+3	94

(a) AP-101 simulant volumes were determined based on the AP-101 simulant density. The slight dilution attributed to spiking was considered inconsequential. Shaded batch contact sample was used for monitoring equilibrium.

Distribution

**No. of
Copies**

**No. of
Copies**

OFFSITE

ONSITE

7 Savannah River Technology Site

Russ Eibling
PO Box 616, Road 1
Building 999-W
Aiken, South Carolina 29808

Larry Hamm
PO Box 616, Road 1
Building 773-42A
Aiken, South Carolina 29808

Neguib Hassan
PO Box 616, Road 1
Building 773-A
Aiken, South Carolina 29808

Jim Marra
PO Box 616, Road 1
Building 773-43A
Aiken, South Carolina 29808

Charles Nash
PO Box 616, Road 1
Building 773-42A
Aiken, South Carolina 29808

Robert Pierce
PO Box 616, Road 1
Building 773-A
Aiken, South Carolina 29808

Harold Sturm
PO Box 616, Road 1
Building 773-A
Aiken, South Carolina 29808

12 Battelle—Pacific Northwest Division

D. L. Blanchard P7-25
L. A. Bray P7-22
S. K. Fiskum (3) P7-22
D. E. Kurath P7-28
L. A. Snow P7-22
J. J. Toth H4-02
Project File (2) P7-28
Information Release (2) K1-06

7 Bechtel National, Inc.

S. M. Barnes H4-02
W. L. Graves H4-02
H. R. Hazen H4-02
R. A. Peterson H4-02
M. R. Thorson H4-02
W. L. Tamosaitis H4-02
WTP PDC Coordinator H4-02