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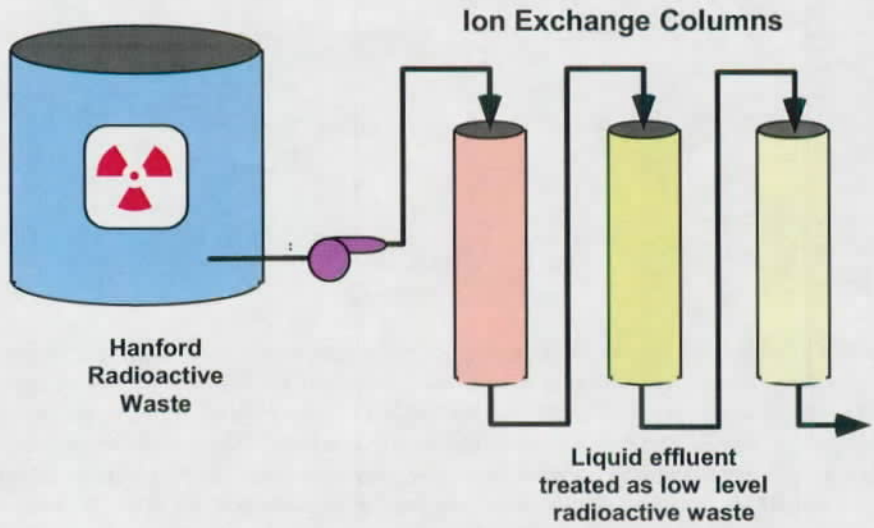
Revision 0

Ion Exchange Modeling for Removal of Cesium from Hanford Waste Using SuperLig® 644 Resin



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Ion Exchange Modeling for Removal of Cesium from Hanford Waste Using SuperLig® 644 Resin

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1.0 Executive Summary

The expected performance of a proposed ion exchange column using SuperLig® 644 resin for the removal of cesium from Hanford high level radioactive alkaline waste is discussed. This report represents a final report on our ability and knowledge with regard to modeling the Cesium-SuperLig® 644 resin ion exchange system. Only the loading phase of the cycle process is addressed within this report. Pertinent bench-scale column tests and batch equilibrium experiments are addressed. The methodology employed and sensitivity analyses are also included (i.e., existing methodology employed is referenced to prior developmental efforts while updated methodology is discussed). Pilot-scale testing is not assessed since no pilot-scale testing was available at the time of this report. Column performance predictions are made considering three selected feed compositions under nominal operating conditions. The sensitivity analyses provided help to identify key parameters that aid in resin procurement acceptance criteria. The methodology and application presented within this report reflect the expected behavior of SuperLig® 644 resin manufactured at the production-scale (i.e., 250 gallon batch size level).

1.1 Objectives

The details associated with this task are identified within the technical and quality assurance plan for the ion exchange computer model upgrades (Hamm et al., 2002a), performed in support of the River Protection Program Waste Treatment Plant ion exchange process. The original scope of this task is provided in the Test Specification 24590-PTF-TSP-RT-01-004, Rev 0 (Toth, 2002a). The primary objective of this work was, through modeling and verification based on experimental assessments, to predict the cesium removal performance of SuperLig® 644 resin for application in the RPP pretreatment facility.

Based on necessary scope reductions that occurred during the life of this task plan, only the performance of SuperLig® 644 resin is being addressed within this document. Also, the planned 16 LAW feeds were not addressed individually, but were addressed by looking at just three limiting/composite feed compositions (i.e., referred to as Hot Commissioning Operation, Envelope B Operation, and Subsequent Operation). These alterations in task plan objectives were the result of WTP guidance as discussed in Toth (2003), where feed compositions and product purity criteria were established.

The column performance predictions presented within this report reflect expected performance behavior for SuperLig® 644 resin manufactured at the production scale (i.e., the 250 gallon batch size scale whose batch ID is C-01-11-05-02-35-60, Bruening [2002]). Data taken for earlier batches (e.g., 1 gallon and 25 gallon batches) were not incorporated into the final modeling assessment phase presented within this report. The isotherm database focused on the 20-30 sieve cut of the 250 gallon batch.

The specific objectives pertinent to this report, as outlined in the test specification, of this activity are:

Test Objective	Objective Met (Y/N)	Discussion
Refine the algebraic equations representing adsorption isotherms for cesium on SuperLig® 644 (SL-644) and pertechnetate on SuperLig® 639 (SL-639) required by the column transport models, including the development of appropriate multi-component isotherms (Na/Cs, NO_2/Tc, K/Cs) based on more detailed equilibrium models and binary databases. The isotherm refinement is based on prior isotherm development for SuperLig® 639 and SuperLig® 644.	Met objective partially	Experimental equilibrium distribution, particle loading kinetics, and material property measurements were also measured under this Task Plan to support this analysis effort using the most recent production scale resin (i.e., 250 gallon batch). Due to scope reductions, no SL639 pertechnetate isotherm models are being provided within this report. Only limited algebraic isotherm models for the specific feed compositions are being provided since only limited isotherm data and feed stream definitions were provided.
Refine the development of the VERSE-LC models for the removal of cesium by SL-644 and pertechnetate by SL-639.	Met objective partially	Due to scope reductions, no SuperLig® 639 VERSE-LC models are being provided within this report.
Correlate model predictions with small-scale test results from both actual waste samples and simulant testing with particular emphasis on Envelopes B and C (update Envelope A analyses where appropriate). Assess and benchmark column models to pending pilot-scale tests (Toth, 2001)	Met objective partially	Pilot-scale testing was not performed and no assessment data were available for analysis. However, pilot-scale performance should be consistent with full-scale predictions provided.
Provide predictions of anticipated lead, lag, and polishing column performance, particularly in reference to anticipated process conditions for each of the waste tanks. These predictions should be based on the planned initial feed sequencing for the facility and provide an indication of the anticipated performance for each tank waste.	Met objective partially	Scope reduction was provided to look at only three LAW feeds, not the 16 LAW feeds individually. The feeds chosen are: The AP-101 LAW; an Envelope B LAW; and a composite feed from the remaining LAW feeds.
Provide sensitivity results for model predictions illustrating the impact of the key process variables associated with the waste envelopes. These predictions should, where feasible, assess the dynamics of the full-scale column including the feed distribution; i.e. feed distributor 3-dimensional flow impact.	Yes	3D flow impact was addressed in a previous report (Aleman and Hamm, 2002). Impact of resin chemical plus radiological degradation is addressed within this report by use of a fixed degradation factor based on batch contact measurements of the 250 gallon resin used in the large-scale (24 inch diameter) column referred to as the "ALL-IN Test Rig."

Test Objective	Objective Met (Y/N)	Discussion
Provide ongoing guidance and perspective for experimental efforts to ensure data of sufficient quality and applicability are obtained in the most efficient manner.	Yes	No comment.
Develop an understanding of the importance of key resin characteristics on column performance, including, but not limited to: particle size, porosity and effective diffusivity.	Yes	No comment.

1.2 Test Exceptions

No official written test exceptions were imposed on this activity. Various alterations in modeling objectives were made based upon WTP requests to eliminate scope in order to retrieve budget for other budget shortfalls within the overall project.

1.3 Results and Performance Against Success Criteria

The following table lists the various success criteria being considered:

Success Criteria	Discussion
Creation of multi-component isotherms that fit the experimental data to within experimental uncertainty (i.e., both the detailed equilibrium and algebraic models).	Due to scope reductions, no pertechnetate isotherm models are being provided within this report. Only limited algebraic isotherm models for three specific feed compositions are being provided since only limited isotherm data and feed stream definitions were provided. Insufficient isotherm database exists to adequately establish uncertainty bounds.
Development of dynamic column models that predict lead and lag column performance with both simulants and actual waste to within experimental uncertainty.	Due to scope reductions, no SuperLig® 639 VERSE-LC models are being provided within this report. Additional guard column model included to reflect process design change to a three column carrousel configuration (i.e., lead, lag, and guard columns modeled).

Success Criteria	Discussion
Correlate model predictions with small-scale test results from both actual waste samples and simulant testing with particular emphasis on Envelopes B and C (update Envelope A analyses where appropriate). Assess and benchmark column models to pending pilot-scale tests (Toth, 2001)	Due to scope reductions, no SuperLig® 639 VERSE-LC model assessments are being provided within this report. Small-scale column assessments were made to all pertinent tests available. Pilot-scale testing was not performed since no assessment data were available for such an analysis.
Provide predictions of anticipated lead, lag, and polishing column performance, particularly in reference to anticipated process conditions for each of the waste tanks. These predictions should be based on the planned initial feed sequencing for the facility and provide an indication of the anticipated performance for each tank waste.	Due to scope reductions, no full-scale SuperLig® 639 VERSE-LC model predictions are being provided within this report. Scope reduction was provided to look at only three LAW feeds, not the 16 LAW feeds individually. For the three specific feeds provided both fresh resin and degraded resin performance was considered.
Provide sensitivity results for model predictions illustrating the impact of the key process variables associated with the waste envelopes. These predictions should, where feasible, assess the dynamics of the full-scale column including the feed distribution; i.e. feed distributor 3-dimensional flow impact.	Due to scope reductions, no full-scale SuperLig® 639 VERSE-LC model predictions are being provided within this report. 3D flow impact was addressed in a previous report. Impact of resin degradation is addressed within this report by use of a fixed degradation factor based on batch contact measurements of the 250 gallon resin used in the large-scale (24 inch diameter) column referred to as the "ALL-IN Test Rig." A sensitivity study based on a star-pattern approach was performed where the nominal feed was assumed and degraded resin behavior.
Provide ongoing guidance and perspective for experimental efforts to ensure data of sufficient quality and applicability are obtained in the most efficient manner.	Throughout the life of the effort numerous VERSE-LC and isotherm model predictions were made and used to provide insight into the experimental pragmatic efforts.
Develop an understanding of the importance of key resin characteristics on column performance, including, but not limited to: particle size, porosity and effective diffusivity.	Where data were available, the impact of key resin characteristics on column performance are assessed through the sensitivity simulations. Effective diffusivity is very sensitive to sodium concentration, which impacts column breakthrough performance. Increased sodium levels can potentially reduce breakthrough performance significantly. Particle size distribution (PSD) and porosity impact column performance marginally.

Below, additional comments are listed to provide more insight into the specific modeling efforts and results observed during the course of this activity. The major accomplishments and conclusions are:

- A detailed thermodynamic isotherm model was employed to correlate available batch contact data. An approach to correlating the batch equilibrium data was used based on a simple algebraic isotherm model derived assuming average values for the various selectivity coefficients. A four-component (i.e., cesium, potassium, sodium, and hydrogen) cation exchange isotherm model was created. The adequacy of this approach is tested by comparison to the available database and through their use in column simulations/assessments.

- To achieve adequate batch contact "K_d" test data, sufficient contact time and agitation (i.e., mixing) is paramount. A limited set of batch contact tests and particle kinetics tests was performed. This limited database was used to establish key modeling parameter (i.e., isotherm and pore diffusivity) values where focus was made on the most recent production-scale 250 gallon batch of SuperLig® 644 resin. Very consistent data were achieved based primarily on the use of well defined protocols that were initially verified. Prior significant variability observed in batch equilibrium "K_d" test data was not present.

- Only "effective" single-component (cesium specific) column transport simulations were performed. Prior efforts have shown that for the cesium loading-phase only, the simpler "effective" single-component column model is adequate for design purposes. As explained in section 3.3, competing ions (i.e., sodium and potassium) break through much earlier than cesium. Multi-component modeling would have only a marginal improvement in breakthrough prediction accuracy.

- For the majority of modeling parameters required to perform an ion-exchange transport simulation, an existing methodology was employed that was updated as appropriate test data became available. With few additional alterations this methodology can also be applied to other ion-resin systems of interest (e.g., the Resorcinol-Formaldehyde [RF] system).

- In the order of estimated affinity, the four major cations competing for surface sites on SuperLig® 644 resin considered are: hydronium, cesium, potassium, and sodium. For the above cations SuperLig® 644 resin is most selective for H^+, then Cs^+, followed by K^+, and then Na^+. Based on stated pKa values for SuperLig® 644 resin, Cs capacity varies significantly in the pH range of 7 to 12. The sorption sites along the functional groups exhibit some variability for pH values above 12. Therefore, an observed OH dependence can be seen in batch equilibrium "K_d" test data for liquid solutions with pH values.

- A total cesium ion-exchange capacity for SuperLig® 644 resin (250 gallon batch) is pH dependent with a value of approximately 0.54 mmole/g at high OH concentration levels (i.e., a plateau value that drops off significantly for OH concentrations below 0.5 M).

- Model simulations were run for several experimental column tests to assess the predictability of the methodology. In the majority of cases, reasonable predictions were achieved for the cesium exit breakthrough curves. Both actual and simulant feed solutions have been assessed.

- Based on this methodology full-scale facility "best estimate" (i.e., nominal) simulations were run for three feed streams assuming a three-column carousel configuration. The exit cesium product criterion value varied for each feed stream considered. For all three feed streams considered, cesium removal performance significantly exceeded minimum design specifications. The calculations performed evaluated both fresh resin, as well as resin estimated to be chemically/radiologically degraded after approximately 10 operating cycles. The degradation factor used is intended to acount for both chemicaly and radioytically induced resin degradation.

- The three column carousel full-facility analyses performed assumed that the fresh polishing column had initially zero residual Cs loaded. The exit product criterion Prior sensitivity analyses to assess the potential impact of this assumption has demonstrated that as long as the residual Cs loading is below approximately 90% of the exit criterion, no significant reduction in breakthrough performance is observed.

- When a ^{137}Cs inventory limit is also imposed on the column loading, we find that the number of BVs to process the "Envelope B Operations" and "Subsequent Operations" feed streams become limited. An inventory limit of 75,000 Ci was assumed. Given this inventory limit VERSE predictions indicate that this limit is reached in ~43 BVs for the Envelope B Operations feed stream and ~338 BVs for the Subsequent Operations feed stream.

Tables 1-1 through 1-4 (i.e., fresh and degraded resin performance) provide a brief summary of the number of bed volumes that can be processed for the first 5 cycles for each of the three feed compositions considered and also the exit concentration ratio of the lead column at the end of each cycle. Both the number of BVs processed based on a cesium exit product criterion and a total cesium inventory limit were computed. The current design and operational strategy appear sufficient to achieve the desired decontamination factors (i.e., significant bed volumes of feed can be processed per operation cycle for all three feeds considered). The estimated cesium isotherms for each of the three feed compositions considered is shown in Figure 1-1. Figures 1-2 through 1-4 illustrate the cesium breakthrough performance for each feed stream considered. The total cesium exit criterion employed for "Hot Commissioning Operation" is 2.74×10^{-5} M, for "Envelope B Operations" is 2.83×10^{-4} M, and for "Subsequent Operations" is 5.00×10^{-5} M. The results shown are for a resin bed estimated to be chemically degraded due to approximately 10 operating cycles. Note that the exit concentration ratios being plotted in Figures 1-2 through 1-4 are the inlet concentration ratios for the lag column at the end of each cycle and the inlet concentration ratio for the subsequent-cycle lead column. Zero residual cesium is being assumed for each guard column upon the start of each new cycle. During operation of a cycle the guard column never experiences cesium concentration exceeding the exit criterion value being imposed on the lag column exit.

The cesium exit concentration from the lead, lag, and guard columns is provided in Tables 1-5 and 1-6 for both freash and 20% degraded resin beds. The results provided are for the carousel operation during the fifth cycle of operation. For the Hot Commissioning feed the lag column exit criterion is reached just prior to reaching 50% breakthrough in the lead column. For the Envelope B and Subsequent Operation feeds the lag column exit criterion is not reached prior to exceeding 50% breakthrough in the lead column. As such, both the concentration results at 50%

breakthrough and at the exit criterion are provided. Exit concentration ratios for the first five cycles are provided in Tables 1-7 through 1-9 for the three feeds considered. The results shown are based on degraded resin beds. These results are the exit concentration ratios at the point when the carousel operation occurs and the values listed for the lag column correspond to the product criterion values for each feed. Similar results are provided in Tables 1-10 through 1-12 where the concentration ratios values at 50% lead column breakthrough is listed. For a couple of cases, the lag column exit criterion was reached prior to reaching 50% breakthrough in the lead column.

1.4 Quality Requirements

The Liquid Chromatography code VERSE-LC (Whitley and Wang, 1998) was chosen to perform these column performance assessments. Version 7.80 of VERSE-LC was used for verification purposes where several test cases (i.e., see certification package for VERSE-LC Version 7.80 by Hamm et al., 2000a) were checked to ensure its implementation on the stated PC platform. Further benchmarking was made by assessment to several key particle kinetics and column tests. Column test benchmarking is considered to be the ultimate check of the accuracy of the methodology employed. Column test benchmarking results are provided in Chapter 9 where the cases considered demonstrated reasonably good predictive capability.

This work was conducted in accordance with the RPP-WTP QA requirements specified for work conducted by SRNL as identified in DOE IWO MOSRLE60. SRNL has provided matrices to WTP demonstrating compliance of the SRNL QA program with the requirements specified by WTP. Specific information regarding the compliance of the SRNL QA program with RW-0333P, Revision 10, NQA-1 1989, Part 1, Basic and Supplementary Requirements and NQA-2a 1990, Subpart 2.7 is contained in these matrices. This Task was conducted under the Task Plan for the ion exchange computer model upgrades (Hamm et al., 2002).

1.5 R&T Analysis Conditions

Original effort was to address full-scale facility performance for the 16 Phase 1 LAW feeds in their planned processing sequence. However, by the time required to perform the analyses presented within this report, no such feed stream definitions were available. WTP provided three unique feed stream compositions to be considered instead. Due to the continuing variability in resin behavior between each resin manufacturing scale (e.g., 1-gallon batch, 25-gallon batch, and 250-gallon batch) and poor experimental protocol consistency among labs, the acceptable database for SuperLig® 644 resin behavior was significantly reduced. This limited our ability to fully understand and quantify many of the key characteristics of SuperLig® 644 resin (e.g., limited algebraic isotherm models).

1.6 Simulant Use

Due to the lack of an adequate database for modeling purposes, a small subset of experiments was performed under the task plan. These experiments provide the basis for the majority of results discussed within this report. An AN-105 simulant was employed for these tests and no direct comparison to actual waste was intended.

1.7 Discrepancies and Follow-on Analyses

In the process of performing this work no significant discrepancies (i.e., full-scale facility performance not being able to meet or exceed design objectives) were observed. No specific follow-on analyses are planned at this time.

Table 1-1 Number of bed volumes required to reach lag column Cs breakthrough during three-column carousel operation for Hot Commissioning Operations, Envelope B Operations, and Subsequent Operations feeds. Assumes a 0% chemical degradation factor for all results listed (i.e., fresh resin).

Cycle Number	Hot Commissioning Operation Feed (BV)	Envelope B Operations Feed (BV)	Subsequent Operations Feed (BV)
1	371	693 [43] [a]	729 [337] [a]
2	240	359	468
3	249	359	482
4	255	359	491
5	259	360	496

[a] Number of bed volumes to reach ^{137}Cs inventory limit of 75k Ci.

Table 1-2 Lead column exit concentration ratio once lag column Cs breakthrough reached during three-column carousel operation for Hot Commissioning Operations, Envelope B Operations, and Subsequent Operations feeds. Assumes a 0% chemical degradation factor for all results listed (i.e., fresh resin).

Cycle Number	Hot Commissioning Operation Feed (%)	Envelope B Operations Feed (%)	Subsequent Operations Feed (%)
1	93	100	100
2	72	100	99
3	57	100	97
4	51	100	96
5	49	100	96

Table 1-3 Number of bed volumes required to reach lag column Cs breakthrough during three-column carousel operation for Hot Commissioning Operations, Envelope B Operations, and Subsequent Operations feeds. Assumes a 20% chemical degradation factor for all results listed (resin with an approximated 10 cycle exposure).

Cycle Number	Hot Commissioning Operation Feed (BV)	Envelope B Operations Feed (BV)	Subsequent Operations Feed (BV)
1	298	556 [43] [a]	584 [339] [a]

2	192	287	374
3	200	288	386
4	204	288	393
5	207	287	397

[a] Number of bed volumes to reach ^{137}Cs inventory limit of 75k Ci.

Table 1-4 Lead column exit concentration ratio once lag column Cs breakthrough reached during three-column carousel operation for Hot Commissioning Operations, Envelope B Operations, and Subsequent Operations feeds. Assumes a 20% chemical degradation factor for all results listed (resin with an approximated 10 cycle exposure).

Cycle Number	Hot Commissioning Operation Feed (%)	Envelope B Operations Feed (%)	Subsequent Operations Feed (%)
1	93	100	100
2	71	100	99
3	56	100	97
4	50	100	96
5	50	100	96

Table 1-5 Lead, lag, and guard column exit concentration ratios at certain lead column breakthrough points for the fifth cycle of operation during three-column carousel operation for Hot Commissioning Operations, Envelope B Operations, and Subsequent Operations feeds. Assumes a 0% chemical degradation factor for all results listed (i.e., fresh resin).

Cs Feed & Exit Crierion [M]	Lead Column Conc. Ratio (C/C_o)	Lag Column Conc. Ratio (C/C_o)	Guard Column Conc. Ratio (C/C_o)	Lag Column Conc. Ratio Criterion (C/C_o)
Hot Commissioning: Cs Feed = 2.74×10^{-5} M Cs Crit = 3.7×10^{-8} M	0.491 (criterion reached)	1.35×10^{-3}	4.24×10^{-8}	1.35×10^{-3}
Envelope B: Cs Feed = 2.83×10^{-4} M Cs Crit = 3.4×10^{-8} M	1.0	1.20×10^{-4}	~0.0	1.20×10^{-4}
Envelope B: Cs Feed = 2.83×10^{-4} M Cs Crit = 3.4×10^{-8} M	0.5	~0.0	~0.0	1.20×10^{-4}
Subsequent: Cs Feed = 5.0×10^{-5} M Cs Crit = 3.4×10^{-8} M	0.95 (criterion reached)	6.80×10^{-3}	3.47×10^{-9}	6.80×10^{-3}
Subsequent: Cs Feed = 2.74×10^{-5} Cs Crit = 5.0×10^{-8}	0.5	2.75×10^{-5}	2.78×10^{-11}	6.80×10^{-3}

Table 1-6 Lead, lag, and guard column exit concentration ratios at certain lead column breakthrough points for the fifth cycle of operation during three-column carousel operation for Hot Commissioning Operations, Envelope B Operations, and Subsequent Operations feeds. Assumes a 20% chemical degradation factor for all results listed (resin with an approximated 10 cycle exposure).

Cs Feed & Exit Crierion [M]	Lead Column Conc. Ratio (C/C_o)	Lag Column Conc. Ratio (C/C_o)	Guard Column Conc. Ratio (C/C_o)	Lag Column Conc. Ratio Criterion (C/C_o)
Hot Commissioning: Cs Feed = 2.74×10^{-5} M Cs Crit = 3.7×10^{-8} M	0.498 (criterion reached)	1.35×10^{-3}	7.96×10^{-8}	1.35×10^{-3}
Envelope B: Cs Feed = 2.83×10^{-4} M Cs Crit = 3.4×10^{-8} M	1.0	1.20×10^{-4}	~0.0	1.20×10^{-4}
Envelope B: Cs Feed = 2.83×10^{-4} M Cs Crit = 3.4×10^{-8} M	0.5	~0.0	~0.0	1.20×10^{-4}
Subsequent: Cs Feed = 5.0×10^{-5} M Cs Crit = 3.4×10^{-8} M	0.95 (criterion reached)	6.80×10^{-3}	3.347×10^{-9}	6.80×10^{-3}
Subsequent: Cs Feed = 2.74×10^{-5} Cs Crit = 5.0×10^{-8}	0.5	2.62×10^{-5}	2.55×10^{-11}	6.80×10^{-3}

Table 1-7 Lead, lag, and guard column exit concentration ratios at the end of each carousel cycle for Hot Commissioning Operations. Assumes a 20% chemical degradation factor for all results listed (resin with an approximated 10 cycle exposure).

Cycle Number	Lead Column Conc. Ratio (C/C_o)	Lag Column Conc. Ratio (C/C_o)	Guard Column Conc. Ratio (C/C_o)
1	0.92	1.35×10^{-3}	1.16×10^{-11}
2	0.70	1.35×10^{-3}	1.09×10^{-9}
3	0.55	1.35×10^{-3}	7.24×10^{-9}
4	0.48	1.35×10^{-3}	4.52×10^{-8}
5	0.50	1.35×10^{-3}	7.96×10^{-8}

Table 1-8 Lead, lag, and guard column exit concentration ratios at the end of each carousel cycle for Envelope B Operations. Assumes a 20% chemical degradation factor for all results listed (resin with an approximated 10 cycle exposure).

Cycle Number	Lead Column Conc. Ratio (C/C_o)	Lag Column Conc. Ratio (C/C_o)	Guard Column Conc. Ratio (C/C_o)
1	1.00	1.20×10^{-4}	~0.0
2	1.00	1.20×10^{-4}	~0.0

3	1.00	$1.20x10^{-4}$	~0.0
4	1.00	$1.20x10^{-4}$	~0.0
5	1.00	$1.20x10^{-4}$	~0.0

Table 1-9 Lead, lag, and guard column exit concentration ratios at the end of each carousel cycle for Subsequent Operations. Assumes a 20% chemical degradation factor for all results listed (resin with an approximated 10 cycle exposure).

Cycle Number	Lead Column Conc. Ratio (C/C_o)	Lag Column Conc. Ratio (C/C_o)	Guard Column Conc. Ratio (C/C_o)
1	1.00	$6.80x10^{-3}$	$8.23x10^{-14}$
2	0.99	$6.80x10^{-3}$	$1.94x10^{-11}$
3	0.97	$6.80x10^{-3}$	$2.94x10^{-10}$
4	0.96	$6.80x10^{-3}$	$5.50x10^{-10}$
5	0.95	$6.80x10^{-3}$	$3.347x10^{-9}$

Table 1-10 Lead, lag, and guard column exit concentration ratios at the end of each carousel cycle for Hot Commissioning Operations. Assumes a 20% chemical degradation factor for all results listed (resin with an approximated 10 cycle exposure).

Cycle Number	Lead Column Conc. Ratio (C/C_o)	Lag Column Conc. Ratio (C/C_o)	Guard Column Conc. Ratio (C/C_o)
1	0.50	$2.59x10^{-6}$	$3.97x10^{-17}$
2	0.50	$1.97x10^{-4}$	$4.38x10^{-11}$
3	0.50	$8.52x10^{-4}$	$6.76x10^{-9}$
4	0.496 (criterion reached)	$1.35x10^{-3}$	$4.14x10^{-8}$
5	0.498 (criterion reached)	$1.35x10^{-3}$	$7.96x10^{-8}$

Table 1-11 Lead, lag, and guard column exit concentration ratios at the end of each carousel cycle for Envelope B Operations. Assumes a 20% chemical degradation factor for all results listed (resin with an approximated 10 cycle exposure).

Cycle Number	Lead Column Conc. Ratio (C/C_o)	Lag Column Conc. Ratio (C/C_o)	Guard Column Conc. Ratio (C/C_o)
1	0.50	~0.0	~0.0
2	0.50	~0.0	~0.0
3	0.50	~0.0	~0.0
4	0.50	~0.0	~0.0
5	0.50	~0.0	~0.0

Table 1-12 Lead, lag, and guard column exit concentration ratios at the end of each carousel cycle for Subsequent Operations. Assumes a 20% chemical degradation factor for all results listed (resin with an approximated 10 cycle exposure).

Cycle Number	Lead Column Conc. Ratio (C/C_o)	Lag Column Conc. Ratio (C/C_o)	Guard Column Conc. Ratio (C/C_o)
1	0.50	9.87×10^{-9}	~0.0
2	0.50	1.47×10^{-6}	6.15×10^{-16}
3	0.50	7.70×10^{-6}	2.27×10^{-13}
4	0.50	1.73×10^{-5}	4.64×10^{-12}
5	0.50	2.62×10^{-5}	2.55×10^{-11}

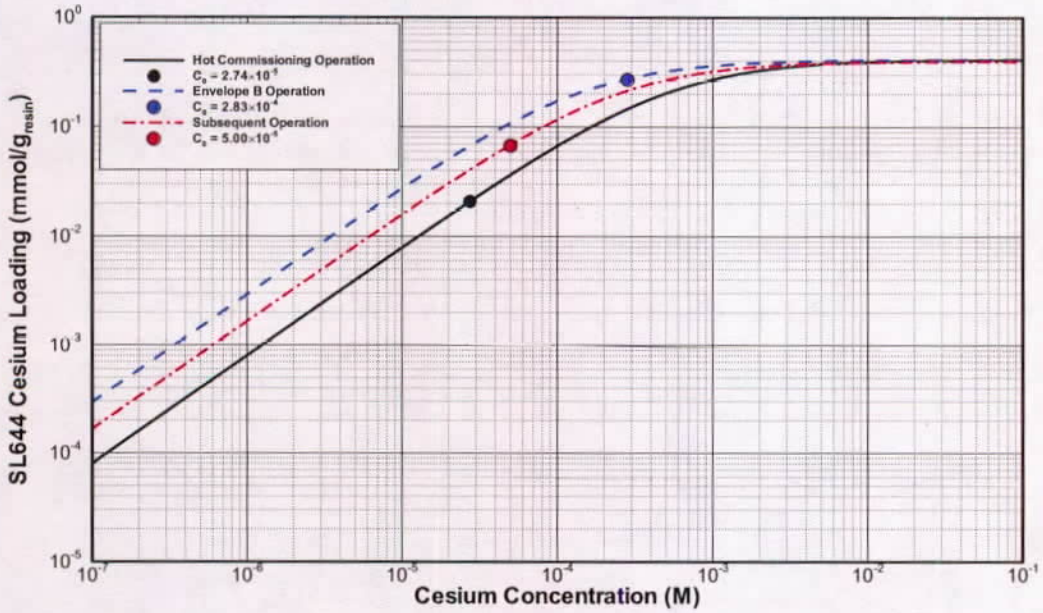

Figure 1-1. Cesium isotherm curves for the three feed compositions considered for column performance assessment (i.e., Hot Commissioning Operations, Envelope B Operations, and Subsequent Operations). A 20% degradation factor was assumed for all three isotherms shown and the solid circles indicate the cesium concentration value for each feed (concentrations in M units provided).

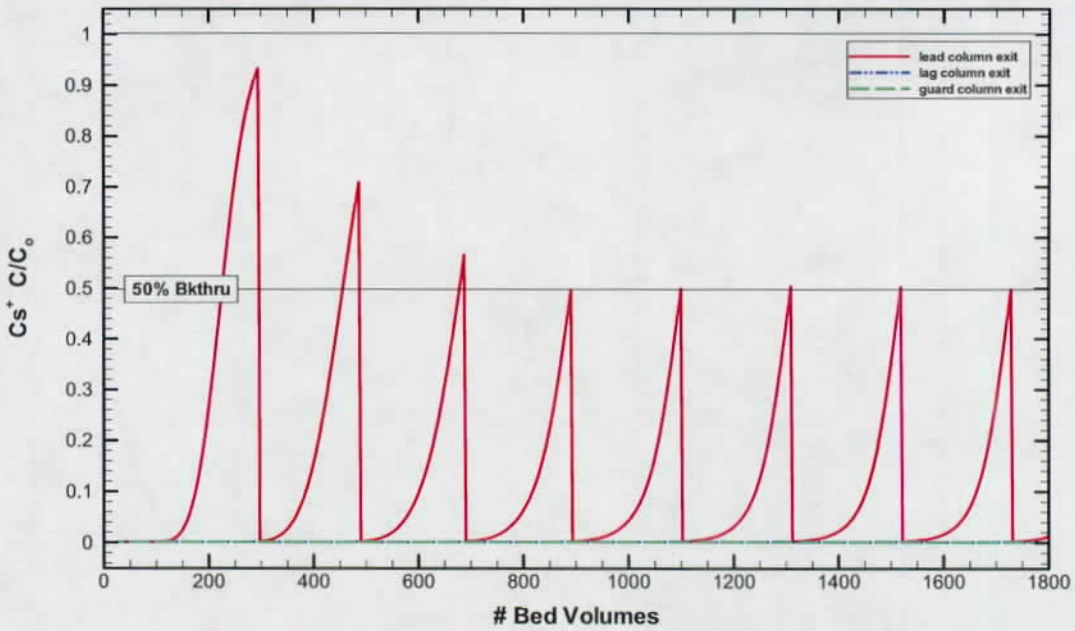

Figure 1-2. VERSE-LC Cesium removal predictions for a full-scale 3 column carousel under Hot Commissioning Operations feed. The figure shows lead, lag, and guard breakthrough behavior. The calculations assume a 20% degradation factor.

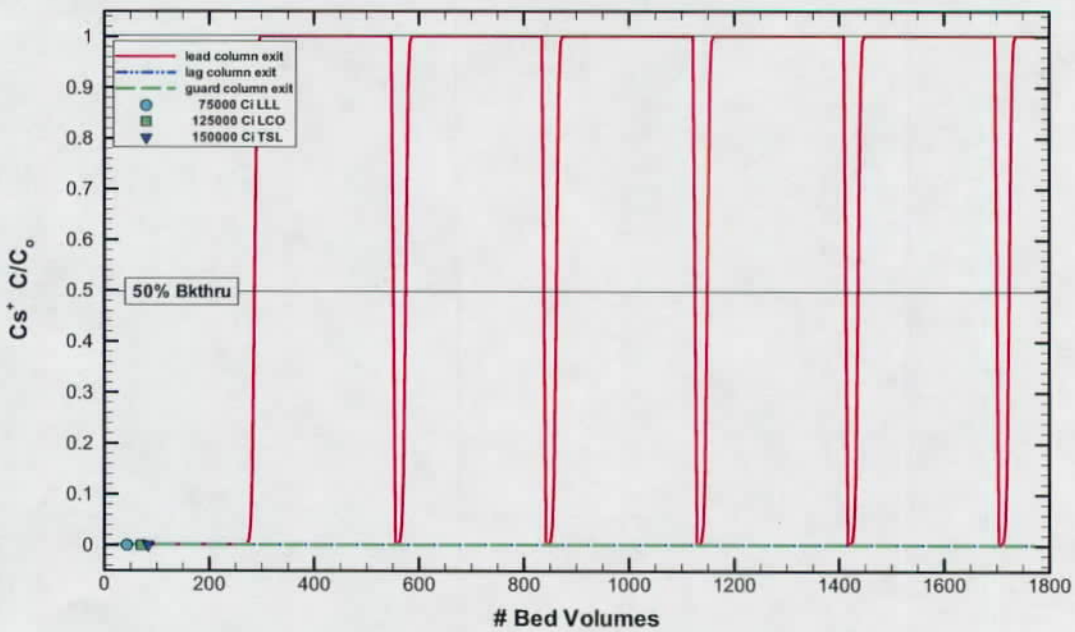

Figure 1-3. VERSE-LC Cesium removal predictions for a full-scale 3 column carousel under Envelope B Operations feed. The figure shows lead, lag, and guard breakthrough behavior. The calculations assume a 20% degradation factor.

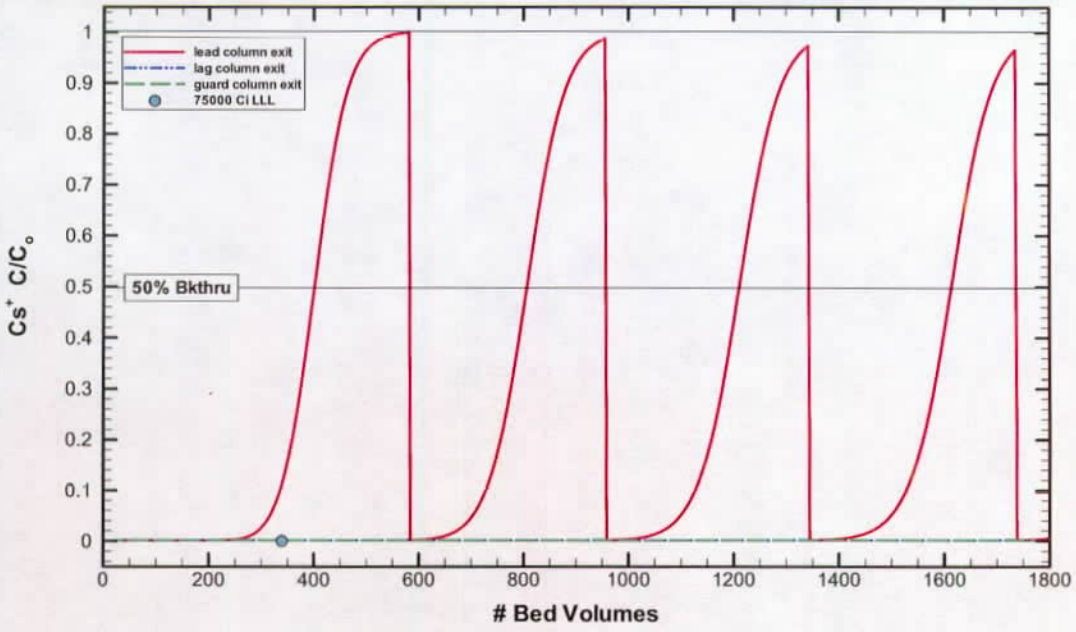

Figure 1-4. VERSE-LC Cesium removal predictions for a full-scale 3 column carousel under Subsequent Operations feed. The figure shows lead, lag, and guard breakthrough behavior. The calculations assume a 20% degradation factor.

2.0 Introduction and Background

A proposed facility is being designed for the immobilization of Hanford Site high level radioactive waste. One unit process in the facility is designed to remove radioactive cesium by ion-exchange from the strongly alkaline aqueous phase. A resin specifically designed with high selectivity of cesium under alkaline conditions is being investigated. This resin also is elutable under more acidic conditions. The proposed design of the facility consists of three packed columns placed in series (i.e., a lead column followed by a lag column then a guard column configuration). During operation, upon reaching a specified cesium concentration criterion at the exit of the guard column, a carousel operation is performed. The cesium-loaded lead column is processed (i.e., washed and eluted) and switched to the guard position in a subsequent cycle. The previous lag column is then placed in the lead position (without eluting), the previous guard column is then placed in the lag position, and the system is ready for use in the next cycle. For a well designed process, the loading and elution processes result in significant volume reductions in aqueous high level waste. Also, by design it is hoped that the loading step will exceed the process time required to elute and place one configuration back into operation. Note that the original carousel design for the cesium ion exchange system used only two columns in series (i.e., a lead lag configuration) and was then revised to include a single third column located after the lead and lag columns. The third column provides additional assurance that the target cesium concentration in the treated waste solution is not exceeded prior to meeting design objectives.

2.1 Ion Exchange Modeling

This ion-exchange system is one of many unit operations within a larger process flowsheet. Experimental efforts were performed to characterize the resin and the ion-exchange process in support of the overall design. Modeling the ion-exchange process in detail provides supporting key information needed in establishing the overall flowsheet. For example, cycle (time) average decontamination factors are required at the overall flowsheet level. Separate (off-line) detailed transient column modeling provides these average decontamination factors where the detail of the analysis is not restricted due to constraints imposed by the flowsheet runtime and storage requirements.

In addition, modeling:

- Reduces the overall number of experiments required;
- Provides guidance on experimental efforts and focuses attention on the critical parameters;
- Evaluates the adequacy and consistency of multiple data sets;
- Consolidates available information on a particular ion exchange system; and
- Establishes, then confirms, full-scale facility design and operational requirements.

2.2 Chosen Ion Exchange Material

IBC Advanced Technologies, Inc. (American Fork, UT) has developed a new class of sequestering ligand agents (referred to as SuperLig® in Izatt et al., 1993) that selectively removes various radionuclides (cesium, strontium, etc.) from high ionic-strength alkaline solutions based on molecular recognition technology and macrocyclic chemistry (covalent bonding). Earlier studies have demonstrated that one of these materials (SuperLig® 644) can remove cesium from simulated and actual Hanford Site alkaline waste even in the presence of excess quantities of sodium and potassium (Brown et al., 1995b; Brown et al., 1996; and Bray et al., 1995). The SuperLig® 644 resin can be eluted when the affinity for cesium adsorption drops significantly with lowering pH. The variation of cesium adsorption with respect to pH can be seen in Figure 3.6 of Bray et al. (1995). The visual appearance of SuperLig® 644 can vary between batches and swells upon exposure to liquid solutions of varying alkalinity (i.e., can more than double its size from dry to aqueous conditions). In general its shape is not spherical and its "mean" particle (i.e., diameter) sizes are measured through wet sieve analyses. In a dry "as received" state (i.e., unswollen state) sieve analyses have determined its size distribution to vary between approximately 63 microns (250 mesh) to 700 microns (45 mesh) with mean sizes of 240 to 420 microns. The particle size distribution could potentially be altered by having the vendor change their grinding procedures. The chemical and radiolytic stability of SuperLig® 644 material was investigated by Brown et al. (1995a). They found that SuperLig® 644 material is sensitive to oxidative and radiolytic degradation; however, they conclude that the material is sufficiently stable for cesium ion exchange removal processes in alkaline supernates up to a 10^8-10^9 rad cumulative exposure range. IBC stated the expected cesium capacity of SuperLig® 644 resin to be approximately 0.3333 $mmole_{Cs}/g$ (on a dried resin mass basis). The majority of analyses presented within report are based on a 20-40 mesh cut.

Based on limited analytical data of the eluate retrieved from elution cycles during various column tests, the following four cations appear to be species competing for active surface sites: Cesium [Cs^+], Potassium [K^+], Sodium [Na^+], and Hydronium [H_3O^+, sometimes referred to as H^+]. Our current estimate for the relative affinities of SuperLig® 644 resin for ion-exchange are $H^+ >> Cs^+ >> K^+ > Na^+$. Also, eluates from some actual waste samples contain chromium, although the valence condition of the chromium species has not been determined. Nickel and other trace metal cations also have been detected in the cesium eluate.

2.3 Report Overview

This report focuses on the cesium-loading phase of a complete cycle under multicycle conditions. An analysis methodology is developed where as much of the available and pertinent data associated with the production-scale batch is chosen (i.e., 250-gallon batch) on the Cesium-SuperLig® 644 system is incorporated. The methodology can easily be updated as new information becomes available (e.g., measured bed and particle porosities).

This document represents a final report on our current knowledge and capability to model the ion-exchange process for the Cesium-SuperLig® 644 system under Hanford Site feed conditions. The methodology, its justification, assessment, and application to the

proposed facility are discussed in the following sections. Supporting information has also been provided in several appendices.

Section 3 briefly discusses the transport model chosen for modeling column behavior. The governing equations and an appropriate simplification are presented. For the modeling efforts presented in this report the VERSE-LC code was chosen (Berninger et al., 1991) based on its availability and widespread (and accepted) use in this field and our earlier use of it during preliminary analysis efforts. Local equilibrium between the pore fluid and its neighboring surface sites is assumed where an equilibrium adsorption isotherm must be specified. The algebraic isotherm model used and the database employed in its creation are discussed in Section 4. A detailed thermodynamically based equilibrium model was developed and is also presented. Key column properties are addressed in Section 5 where the constraint between the porosities is highlighted. Particle size distribution and swelling effects for the SuperLig® 644 resin under Hanford Site feed conditions are addressed in Section 6. Pore diffusion and Brownian motion are discussed in Section 7 where an assessment to batch kinetics data is provided. The VERSE-LC code input and output files for the batch kinetics simulations are provided in Appendix C. In Section 8 the constitutive models for axial dispersion and film diffusion are presented. Headspace and short column impacts are also discussed where a correction factor is developed from limited literature data. Section 9 contains our laboratory-scale column assessments. Appendix D contains the VERSE-LC code input and output files for each laboratory-scale simulation. Based on the current design specifications for the full-scale facility, Section 10 presents full-scale column predictions for three proposed inlet feed stream compositions, along with a series of sensitivity analyses. The VERSE-LC code input and output files for the full-scale facility simulations are contained in Appendix D.

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3.0 Column Model Formulations

The modeling of ion exchange columns is typically broken up into two basic categories:

- An equilibrium model generally highly empirical in nature, and
- A column model based on one-dimensional solute transport.

In this section the equations for the multi-component and the simpler single-component ion exchange column models are addressed. Section 4 of this report addresses the equilibrium models considered. For details on VERSE-LC® and its application to modeling the Cesium-SuperLig 644 ion exchange system see Hamm et al. (2000a, VERSE-LC® verfication report), Hamm et al. (2000b, preliminary Cs removal performance using SuperLig® 644 report), Hamm et al. (2000c, preliminary Tc removal performance using SuperLig® 639 report), and Hamm et al. (2002b, Cs removal performance using CST report).

To take into account the various mechanisms for ion transport and adsorption as it travels down an ion exchange column, a porous particle solute transport formulation has experienced widespread use and acceptability. For this class of column models five basic aspects of the ion exchange column are addressed as highlighted in Figure 3-1. In order of their importance with respect to predicting exit breakthrough curves for the Cesium-SuperLig® 644 system, they are:

- **Bed Definition** (high impact) – column size, geometry and resin mass have a very direct impact on overall column performance, with particle geometry having a slightly less important impact (Shifts entire breakthrough curve with respect to number of column volumes required to reach a specified concentration level); The Bed Volume (Column Volume) is normally defined as the volume occupied by the resin bed during the regeneration cycle (normally 0.25 M NaOH solution), although the resin shrinks slightly in a 5 M [Na^+] salt solution. However, in this report bed volume (or column volume) refers to the conditions associated with the feed conditions during the loading cycle (generally ~5 M [Na^+]).
- **Adsorption Isotherms** (high impact) – resin affinities for the various competing ions of interest have a very direct impact on overall column performance (Shifts entire breakthrough curve with respect to number of column volumes required to reach a specified effluent concentration level and for non-linear isotherms alters breakthrough curve shape as well as its sensitivity with respect to inlet feed conditions);
- **Pore Diffusion** (moderate impact) – intra-particle mass transport by pore diffusion to available surface sites has a moderate impact on overall column performance, with particle geometry having a slightly less important impact (Alters the shape of exit breakthrough curves typically by a rotation about the ~50% relative concentration level with slight shifting);
- **Film Diffusion** (low impact) – liquid mass transport by film diffusion across the particle-to-bed boundary has a low impact on overall column performance (Alters the shape of exit

breakthrough curves typically by a rotation about the ~50% relative concentration level with slight shifting);

- **Axial Dispersion** (low impact) – mass transport along the column by axial dispersion has a low impact on overall column performance (Alters the shape of exit breakthrough curves typically by a rotation about the ~50% relative concentration level with slight shifting);

The above stated levels of impact are based on sensitivity studies and are relative values. Mechanisms such as surface migration or adsorption kinetics are not included in our column model since their impacts were considered to be negligible or already indirectly incorporated into the other features during our parameter estimation process. A simple graphical representation of the various transport mechanisms listed above and considered to be important for the Cesium-SuperLig® 644 system is shown in Figure 3-2.

3.1 The Multi-Component Model

For the Cesium-SuperLig® 644 resin system a porous particle multi-component ion exchange column model was considered. In this model we assume that the kinetics associated with local ion exchange at an active resin site are very fast (faster than the various liquid mass transfer mechanisms that transport ions to that site). Assuming radial effects to be negligible within the active region of the packed bed (i.e., a large column-to-particle diameter ratio), a one-dimensional species (ion) transport equation for the mobile phase (within the bed) becomes

$$\varepsilon_b \frac{\partial c_{bi}}{\partial t} + \varepsilon_b u \frac{\partial c_{bi}}{\partial z} = \varepsilon_b E_{bi} \frac{\partial^2 c_{bi}}{\partial z^2} - \left(\frac{3}{< R_p >}\right)(1-\varepsilon_b)k_f\left(c_{bi} - c_{pi}\Big|_{r=R_p}\right), \qquad (3\text{-}1a)$$

storage **advection** **axial dispersion** **liquid film diffusion (mass transfer)**

with boundary and initial conditions

$$z = 0, \qquad \varepsilon_b E_b \frac{\partial c_{bi}}{\partial z} = uL\left[c_{bi} - c_{bi}^{feed}(t)\right], \qquad (3\text{-}1b)$$

$$z = 1, \qquad \varepsilon_b E_b \frac{\partial c_{bi}}{\partial z} = 0, \qquad (3\text{-}1c)$$

$$t = 0, \qquad c_{bi} = c_{bi}(0,z). \qquad (3\text{-}1d)$$

where

ε_b	Bed porosity
ε_p	Particle porosity
u	Linear interstitial velocity, cm/min
c_{bi}	Species i conc. in bed fluid, M
z	Axial coordinate, cm

E_{bi}	Species i axial dispersivity, cm^2/min
$< R_p >$	Average particle radius, μm
k_f	Liquid film mass transfer coefficient, cm/min
c_{pi}	Species i conc. in pore fluid, M
r	Radial coordinate within avg. size particle, cm
t	Time

Assuming uniformly sized spherical particles with a homogeneous distribution of pores, a one-dimensional species transport equation for the pore phase (within an average sized particle of resin) becomes

$$\varepsilon_p \frac{\partial c_{pi}}{\partial t} + \left(1-\varepsilon_p\right)\overline{C}_T \sum_{j=1}^{N_s}\left[\left(\frac{\partial q_i}{\partial c_{pj}}\right)\frac{\partial c_{pj}}{\partial t}\right] = \varepsilon_p D_{pi}\frac{1}{r^2}\frac{\partial}{\partial r}\left[r^2\frac{\partial c_{pi}}{\partial r}\right], \qquad (3\text{-}2a)$$

storage **surface adsorption** **Fickian pore diffusion**

with boundary and initial conditions

$$r = 0, \qquad \varepsilon_p D_p \frac{\partial c_{bi}}{\partial r} = 0 \ , \qquad (3\text{-}2b)$$

$$r = <R_p>, \qquad \varepsilon_p D_p \frac{\partial c_{bi}}{\partial r} = k_f\left(c_{bi} - c_{pi}\right) , \qquad (3\text{-}2c)$$

$$t = 0, \qquad c_{pi} = c_{pi}(0, r) \ . \qquad (3\text{-}2d)$$

where

$\overline{C}_T$	Total ion-exchange capacity of resin, $mmole/g_{resin}$.
q_i	Species i fractional surface site loading.
D_{pi}	Species i pore diffusion coefficient, cm^2/min.

In Eq. (3-2) it is assumed that the pore diameters are large relative to the size of migrating ions of interest. Therefore, Fickian diffusion is acceptable and surface migration is considered to be small when compared to pore diffusion.

Assuming local equilibrium between the pore fluid and its neighboring surface sites, an equilibrium isotherm model for the ion exchange between the pore and solid phases can be generically expressed as:

$$q_i = F_i\left(\overline{C}_T, c_{p1}, c_{p2}, \cdots, c_{pN_s}\right), \quad i = 1, N_s, \qquad (3\text{-}3)$$

multi-component isotherm

where it has been assumed that surface loadings for the i^{th} species can be explicitly related to the liquid concentrations locally. The number of species required to model the behavior of the i^{th} species depends upon its dependence on other species through the functional form (i.e., F_i) of the isotherm model [Eq. (3-3)]. Specific application of Eq. (3-3) to the cesium-SuperLig® 644 resin system is discussed in Section 4. Initial and boundary conditions for Eqs. (3-1) and (3-2) must also be specified. For further details on these equations and their solution in VERSE-LC see Berninger et al. (1991). Helfferich and Carr (1993) provide an excellent review paper describing the behavior of non-linear waves in chromatography and also a brief listing of available algorithms (see their Table I.4). Their paper provides very clear insight into how the above equation set behaves for non-linear isotherms consistent with the system of interest discussed in this report.

For the modeling efforts presented in this report the VERSE-LC code was chosen (Berninger et al., 1991) based on its availability and widespread (and accepted) use in this field. Prior to applying VERSE-LC to the ion exchange modeling presented in this report a verification process was completed and the results of that effort are reported in Hamm et al. (2000a). The verification process provided us quality assurance that the installed PC Window95™ version of VERSE-LC (i.e., version 7.80) was capable of adequately solving the above mentioned equations and also helped us to better understand how to accurately use the VERSE-LC code (e.g., mesh refinement requirements and input/output options). For all column results presented in this report numerical errors associated with the results of VERSE-LC should be very small when compared to the uncertainties associated with various model input parameters (bed density, particle radius, pore diffusion, etc.). Adjustments can be made to VERSE-LC input to accomandate resin particles having nonspherical geometries. This is typically done by altering the average particle radius assumed and is ultimately validated through assessments to particle kineticas test data.

3.2 The Single-Component Model

Under certain situations the porous particle multi-component transport equations discussed in Section 3.1 can be adequately decoupled to a series of single-component transport equations. The reduction to single-component equations is:

- valid when the total ionic strength, C_T, is the same between the column's native and feed solutions; or
- a reasonable approximation when one ion absorbs significantly more onto the resin than others.

Making the same basic assumptions as in Section 3.1 the single-component equations can be derived. For each species a one-dimensional species (ion) transport equation for the mobile phase (within the bed) becomes

$$\varepsilon_b \frac{\partial c_b}{\partial t} + \varepsilon_b u \frac{\partial c_b}{\partial z} = \varepsilon_b E_b \frac{\partial^2 c_b}{\partial z^2} - \left(\frac{3}{< R_p >} \right) (1 - \varepsilon_b) k_f \left(c_b - c_p \Big|_{r=R_p} \right), \qquad (3\text{-}4)$$

storage **advection** **axial dispersion** **liquid film diffusion (mass transfer)**

where initial and boundary conditions are consistent with Eqs. (3-1b,c,d). A one-dimensional species transport equation for the pore phase (within a particle of resin) becomes

$$\varepsilon_p \frac{\partial c_p}{\partial t} + (1 - \varepsilon_p) \overline{C}_T \left(\frac{\partial q}{\partial c_p} \right) \frac{\partial c_p}{\partial t} = \varepsilon_p D_p \frac{1}{r^2} \frac{\partial}{\partial r} \left[r^2 \frac{\partial c_p}{\partial r} \right], \qquad (3\text{-}5)$$

storage **surface adsorption** **Fickian pore diffusion**

where initial and boundary conditions are consistent with Eqs. (3-2b,c,d).

The equilibrium isotherm model for species i for the ion exchange between the pore fluid and solid phases becomes:

$$q = \frac{c_p}{\beta + c_p}, \qquad (3\text{-}6)$$

single-component isotherm

where Eq. (3-6) is of the Langmuir form and β is a function of the feed conditions.

3.3 The Cesium-SuperLig® 644 System

Based on our current understanding, for the Cesium-SuperLig® 644 resin system the competition for cation exchange loading at the resin sites is primarily between cesium, potassium, and sodium. Prior to the loading phase the initial sodium and potassium levels in the resin pretreatment solution are approximately 0.25 M and 0 M, respectively. During the loading phase these concentration levels increase to approximately 5.0 M sodium and 0.0-to-1.0 M potassium. Therefore, a total ionic concentration wave will pass through the column. Based on available batch equilibrium studies estimates for the relative affinities for adsorption have been computed as discussed in Section 4 (i.e., the resin affinities are $Cs^+ >> K^+ > Na^+$).

Given the above information, early column performance (say the first 5 to 10 column volumes or so) generally requires the use of the multi-component formulations of Section 3.1. Long-term performance should be adequately handled using the simpler single-component formulations of Section 3.2. To check the validity of these statements, cesium exit breakthrough curves from several column simulations were compared where both the multi-component and single-component formulations were used. Very similar results were obtained. To illustrate the

differences in timing for the three ionic species, the exit breakthrough curves for each species is plotted in Figure 3-3 for a multi-component simulation of one of the experimental column tests (WK Exp. 2, King et al., 2000). As expected sodium breakthrough is the fastest, quickly followed by potassium, and then an order of magnitude later by cesium. When the single-component formulations are used, the cesium breakthrough curve is only slightly altered.

Since significant CPU savings are achieved when the single-component model is used and the differences are well within our current predictive capabilities, all column analyses presented in this report were performed using the single-component model.

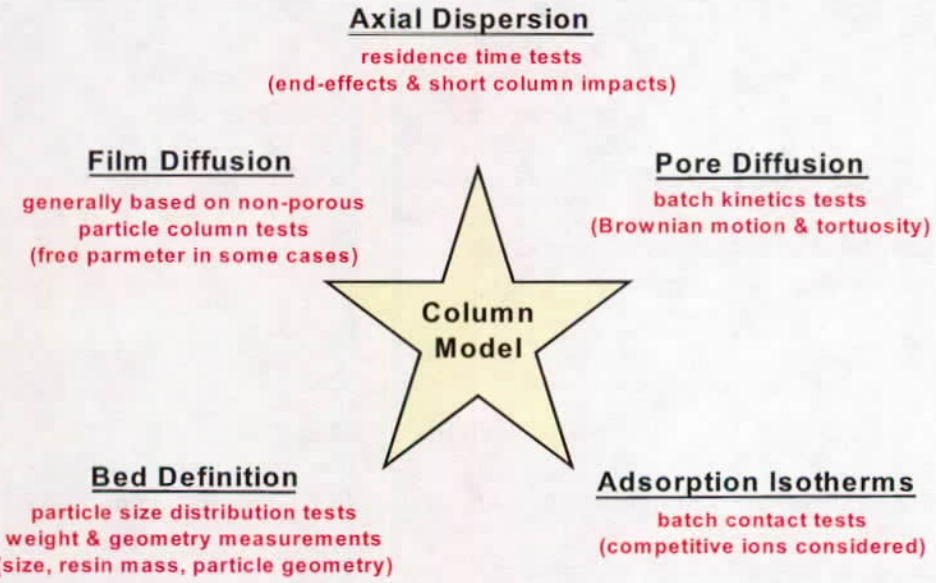

Figure 3-1. The basic building blocks of a porous particle ion exchange column model.

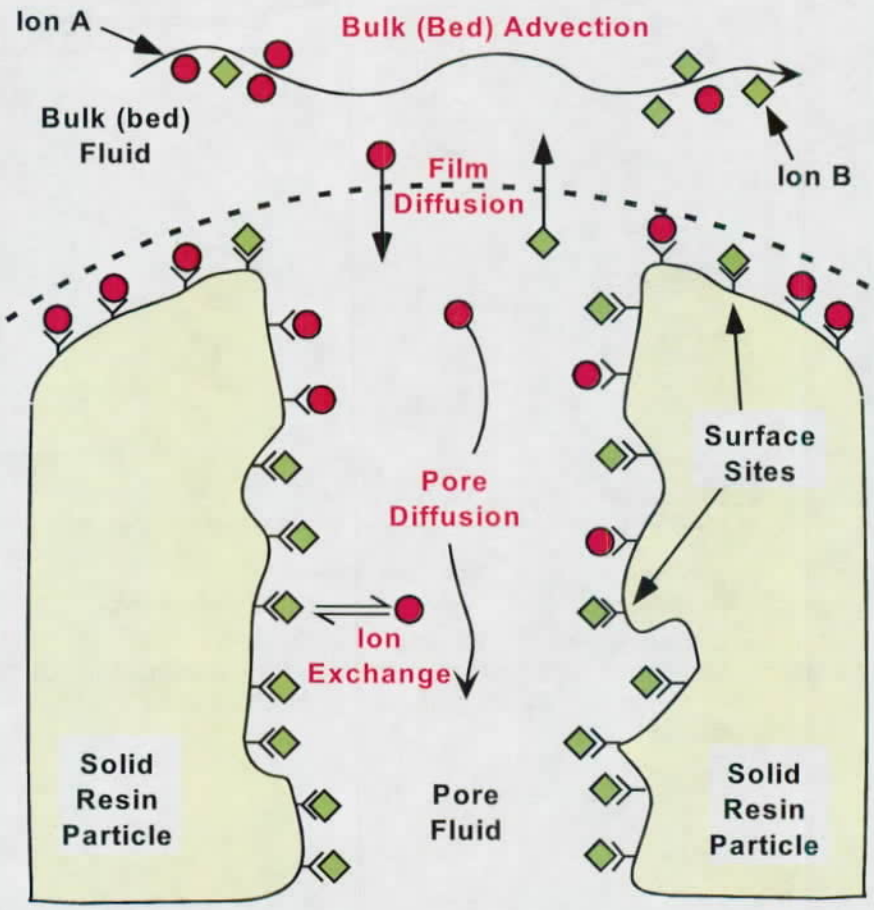

Figure 3-2. Graphical representation of the various mass transport mechanisms considered important for Cesium-SuperLig® 644 system ion exchange column modeling.

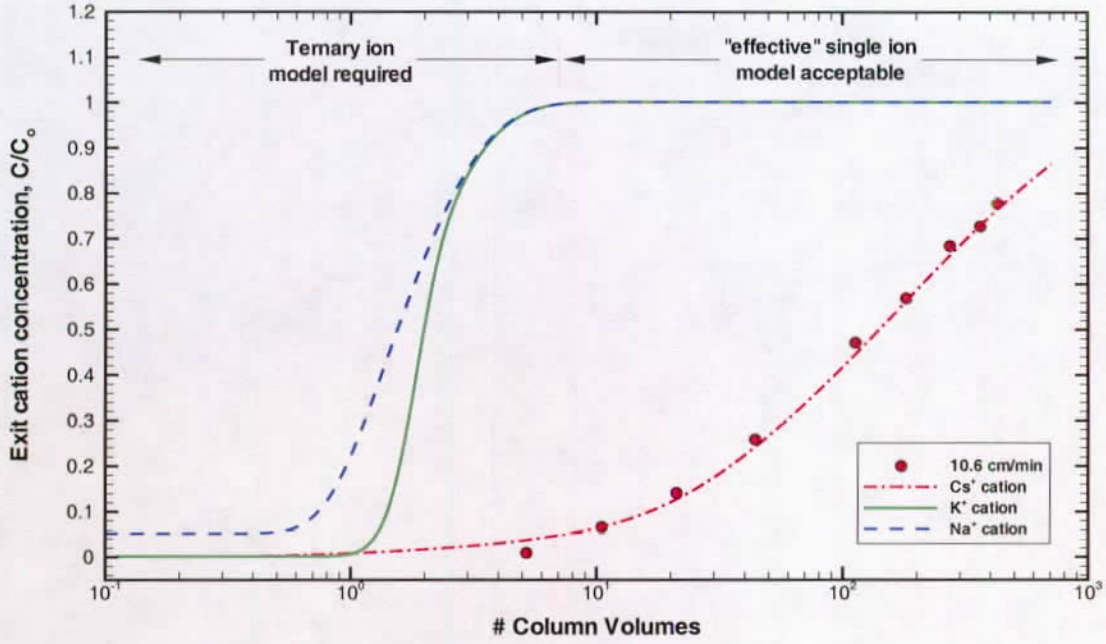

Figure 3-3. Estimated cesium, potassium, and sodium exit breakthrough curves for one column experiment based on the porous particle multi-component ion exchange column model (data from King et al., 2000).

4.0 Equilibrium Cesium Isotherms

In our column modeling efforts we assume that the rate of ion exchange (i.e., exchange of ions at a surface site) is very fast when compared to the rates of diffusion within the pore fluid and mass transfer across the liquid film at the outer boundaries of the particles. In other words, we assume that local equilibrium exists between the pore fluid and its neighboring surface sites. With this assumption an algebraic expression relating ionic (or species) concentrations between the pore fluid and the solid SuperLig® 644 resin (i.e., surface sites) can be established. No explicit attempt is made in this report to verify this assumption. In an indirect manner this assumption is either verified or incorporated into some of the model parameters. In addition, we assume that the cesium total ionic capacity (i.e., active sites for cesium per gram of SuperLig® 644 resin) is independent of total ionic strength or solution composition for each particular feed stream (i.e., unique values are estimated for each unique feed stream). The total cation exchange capacity of the SuperLig® 644 resin is hydroxide dependent.

In column sizing one of two possible design strategies are typically considered: (1) bounding analysis where "worst case" feed compositions are used or (2) global optimization where best estimate feed compositions for each individual batch are used. Each approach has its own advantages and disadvantages. For example, the bounding approach requires less analysis overall but it may be difficult to establish a reasonable bound that is not too excessive. Since the amount of waste to be processed, flowrate, and key feed compositions depend significantly on which envelope is being considered, the global optimization strategy is generally preferred. However, to use a global optimization strategy, "best estimate" cesium isotherms for each of the 16 batch feeds must be available. At the time of performing this work, no such set of 16 Phase 1 LAW feed streams was available. Instead, only three operating feed streams were provided (i.e., referred to as Hot Commissioning Operation, Envelope B Operation, and Subsequent Operation). Details describing these three feed streams are provided by Toth (2003). Isotherms for each of three feed streams were generated for both fresh resin and chemically degraded resin (i.e., approximated assuming 10 cycles of exposure). For our nominal feed stream (i.e., Hot Commissioning Operation) isotherms were also generated to assist in column performance sensitivity analyses.

In deriving these isotherms for use with each batch feed, a detailed thermodynamic model was used to generate isotherm data. The simulated isotherm data was then fit to the appropriate algebraic isotherm model consistent with VERSE-LC input needs. Based on these considerations a binary homovalent isotherm model was developed and is presented in this section. Overall the algebraic isotherm model meets all of our objectives for this effort. See Appendix A for further discussion of the detailed thermodynamic isotherm model that was used in support of the creation of the algebraic isotherms used. These isotherms are for the loading phase applications only. The isotherm model development discussed below follows very closely to the development efforts presented by Hamm et al. (2000b) for the Cesium-SuperLig® 644 ion-exchange system.

In the next subsection the "effective" cesium isotherm model is discussed based on an ion-exchange process and in the following subsection its specific application to the SuperLig® 644

ion-exchange system is discussed. All analyses performed, both isotherm and subsequent column transport modeling, assume the resin mass basis is in its sodium form.

4.1 The Isotherm Model

As demonstrated by Hamm et al. (2000b, Figure 3-3), for ion exchange competitors with affinities significantly less than the value for cesium, a single-component transport modeling approach is adequate for the cesium loading phase. To perform single-component transport simulations, an "effective" binary isotherm model in an algebraic form must be available for use in the VERSE-LC code. Based on our previous experience using VERSE-LC for modeling SuperLig® 644 and SuperLig® 639 resins (Hamm et al., 2000b and 2000c), the VERSE-LC Freundlich/Langmuir Hybrid isotherm model was chosen. As described by Hamm et al. (2000b, see Chapter 4), the cations cesium, potassium, sodium, and hydrogen form a 4-component homovalent system where the surface loading for cesium on the SuperLig® 644 material can be expressed as:

$$Q_{Cs} = \frac{\eta_{df}\overline{C}_T c_{Cs}}{c_{Cs} + [\tilde{K}_{21} c_K + \tilde{K}_{31} c_{Na} + \tilde{K}_{41} c_H + \cdots]} \Rightarrow \frac{\eta_{df}\overline{C}_T c_{Cs}}{c_{Cs} + \beta}, \qquad (4\text{-}1)$$

where

Q_{Cs} .....cesium solid loading, mmol/g
$\overline{C}_T$ .....total ion-exchange capacity of resin, mmol/g
η_{df} .....isotherm chemical degradation factor
c_i .....species i concentration in bed fluid, M
$\tilde{K}_{ji}$ .....selectivity coefficient between species j and i
β .....isotherm parameter constant, M

The beta parameter for cesium becomes dependent upon the other ionic competitors for SuperLig® 644 adsorption (i.e., K^+, Na^+, and H^+). The beta parameter contains the selectivity coefficients making it dependent upon temperature and liquid composition of all of the ionic species in solution. The larger the beta parameter the less favorable (lower loadings) an isotherm will be (have). The degradation factor (η_{df}) is unity when considering a fresh resin and becomes less than unity during chemical exposure (i.e., cycling). Given a degradation factor, Eq. (4-1) contains two free parameters (i.e., a total cesium capacity and a beta value) that need to be specified. For each particular feed stream, these two parameters are estimated by fitting Eq. (4-1) to data simulated using the detailed thermodynamic model as described in Appendix A.

4.2 Batch Feed Compositions

In order to generate the cesium loading isotherm databases using the detailed thermodynamic isotherm model (as described in detail in Appendix A), the feed compositions for the three candidate batch feeds had to be slightly altered to enforce a charge balance. The original feed compositions for each feed stream were supplied by Toth (2003). For each feed stream overall charge balancing was achieved by adjusting the anion concentrations for nitrite and nitrate (i.e.,

also maintaining the nitrite to nitrate ratio constant). The nominal feed composition for each feed stream is provided in Table 4-1 after achieving a charge balance.

Additional feed streams under off-nominal settings were also generated for sensitivity studies to determine competitor impacts on column performance. On an individual basis each competitor (i.e., potassium, sodium, and hydrogen [through varying hydroxide]) was varied by plus and minus 20% about their nominal value. Only sensitivity studies associated with the Hot Commissioning Operation feed stream were considered. The feed compositions for these three competitors are provided in Tables 4-2 to 4-4 for potassium, sodium, and hydrogen, respectively. The off-nominal feed compositions were achieved by varying each competitor along with the anions nitrite and nitrate to maintain charge balance (i.e., keeping the nitrite to nitrate ratio constant).

To address the impact of initial feed cesium concentration on column performance, the cesium feed concentration was also varied by plus and minus 20% about its nominal value for the Hot Commissioning Operation feed stream. These feed compositions are provided in Table 4-5. The off-nominal feed compositions were achieved by varying cesium along with the anions nitrite and nitrate to maintain charge balance (i.e., keeping the nitrite to nitrate ratio constant).

4.3 Simulant Compositions

AN-105 simulant was used by SRNL personnel (Appendix B) to conduct batch contact, particle kinetics and column testing. AZ-102 simulant was prepared by PNNL personnel to perform batch contact and column testing. Table 4-6 provides the compositions for a Base AN-105 and AZ-102 simulant at 5 M sodium. Trace ions that are not supported by the detailed thermodynamic isotherm model are excluded.

4.4 The Total Capacity and Beta Parameter Values

For each of the various feed compositions discussed above and presented in Tables 4-1 through 4-4, an isotherm database was generated using the detailed thermodynamic isotherm model as described in Appendix A. As discussed in Appendix A, this detailed isotherm model was established and benchmark using available batch contact experimental data. Appendix B discusses and provides the results form the batch contact experiments performed. For each unique feed (i.e., a total of nine), a nonlinear regression analyses was used to determine the total cesium exchange capacity and beta value, as defined in Eq. (4-1). The parameter estimation results of these regression analyses are provided in Table 4-7.

As shown in Table 4-7, the cesium exchange capacity varies based on feed hydroxide concentration. The algebraic isotherms for the three nominal feed streams are shown in Figures 4-1 through 4-3, where both fresh and chemically degraded resin isotherms are provided. The chemical degradation factor, as defined in Eq. (4-1), was set to 0.8 to approximate 10 cycles of column bed operation. The isotherm impact of competitor variations on the nominal Hot Commissioning Operation feed stream isotherm is shown in Figures 4-4 through 4-6 for potassium, sodium, and hydroxide, respectively. Figure 4-7 shows the AN-105 and AZ-102 simulant cesium isotherms.

4.5 Isotherm Model for VERSE-LC Application

In order to perform column transport simulations, the algebraic model given by Eq. (4-1) above must be converted into one of the available VERSE-LC isotherm modeling options. Based on our previous experience using VERSE-LC for modeling SuperLig® 644 and SuperLig® 639 resins (Hamm et al., 2000b and 2000c, respectively), the VERSE-LC Freundlich/Langmuir Hybrid isotherm model was chosen. See Hamm et al. (2000b, see Chapter 4) for further descriptions of the multi-component homovalent isotherm approach.

For a 4-component homovalent isotherm, the VERSE-LC Freundlich/Langmuir Hybrid model is expressed as:

$$\overline{C}_{pi} = \frac{a_i c_{pi}^{M_{ai}}}{\beta_i + b_1 c_{p1}^{M_{b1}} + b_2 c_{p2}^{M_{b2}} + b_3 c_{p3}^{M_{b3}} + b_4 c_{p4}^{M_{b4}}} \qquad \text{for} \quad i = 1,4, \tag{4-2}$$

where

$\overline{C}_{pi}$ .....species i solid surface concentration based on column volume, gmole/LCV or M

c_{pi} .....species i concentration in pore fluid, M

β_i, a_i, b_i .....Fruendlich/Langmuir Hybrid model coefficients for species i

M_{ai}, M_{bi} .....Freundlich/Langmuir Hybrid model exponents for species i

The model parameters (a_i, b_i, M_{ai}, M_{bi}, and β_i for i=1,4) can be determined from the parameter values associated with the 4-component homovalent model.

The Freundlich/Langmuir Hybrid model can also be used for an "effective" single-component case as well. Here the potassium, sodium, and hydrogen (actually hydroxide) concentrations throughout the column are assumed to be at their feed concentration levels. For an "effective" single-component total cesium isotherm, Eq. (4-2) under these conditions reduces to:

$$\overline{C}_{p1} = \frac{a_1 c_{p1}^{M_{a1}}}{[\beta_i + b_2 c_{p2}^{M_{b2}} + b_3 c_{p3}^{M_{b3}} + b_4 c_{p4}^{M_{b4}}] + b_1 c_{p1}^{M_{b1}}} \Rightarrow \frac{a_1 c_{p1}^{M_{a1}}}{\hat{\beta}_i + b_1 c_{p1}^{M_{b1}}}, \tag{4-3}$$

where

$\hat{\beta}_i$ .....Langmuir "effective" single isotherm model constant

The beta parameter for cesium becomes dependent upon the potassium, sodium, and hydrogen feed concentrations. The relationship between the two models expressed by Eqs. (4-2) and (4-3) (i.e., 4-component homovalent and "effective" single-component isotherm models, respectively) can be shown by the following relationships:

$$Q_{Cs^+} = \frac{\eta_{df}\overline{C}_T c_{pCs^+}}{c_{pCs^+} + \widetilde{K}_{21} c_{pK^+} + \widetilde{K}_{31} c_{pNa^+} + \widetilde{K}_{41} c_{pH^+}}, \quad (4\text{-}4a)$$

$$Q_{Cs^+} = \frac{\eta_{df}\overline{C}_T c_{pCs^+}}{c_{pCs^+} + \beta}, \quad (4\text{-}4b)$$

$$\beta = \widetilde{K}_{21} c_{pK^+} + \widetilde{K}_{31} c_{pNa^+} + \widetilde{K}_{41} c_{pH^+} \quad (4\text{-}4c)$$

It has been assumed that the binary selectivity coefficients are not composition dependent, but are true constants (i.e., note that the selectivity coefficients actually contain the true equilibrium constants and liquid/solid phase activity coefficients; see Appendix A for details). This assumption appears to be somewhat adequate when considering different feeds within the same envelope (i.e., generally only small variations are observed in selectivity coefficients within a given envelope), but should not be used between envelopes. The composite impact on cesium loading from the other cation competitors is summed up in the beta parameter as shown above in Eq. (4-4). The chemical degradation factor, η_{df}, is set to unity for fresh resin behavior and less than unity to account for chemical degradation effects.

The modeling parameter values for a cesium single-component isotherm are listed in Table 4-7 for two simulants and nine ion-exchange feed streams. The VERSE-LC a_1 parameter of Eq. (4-3) is computed by:

$$a_1 = \rho_b \eta_{df} \overline{C}_T \quad (4\text{-}5)$$

where

ρ_b .....bed density of active column, g/ml

Table 4-1. Waste compositions used to represent ion exchange performance during selected operating time periods (nominal values and charge balanced).

Ion Category	Species	Hot Commissioning Operation Projection (M)	Envelope B Operation Projection (M)	Subsequent Operation Projection (M)
Cations*	**Na^+**	4.57	4.13	4.6
	K^+	0.48	0.091	0.15
	Total Cs^+	2.74E-05	2.83E-04	5.0E-05
	$^{137}Cs^+$ (Ci/L)	0.072	1.18	0.14
	g $^{137}Cs^+$/g Total Cs^+	0.22	0.35	0.24
Anions	**SO_4^{2-}**	0.032	0.129	0.03

Ion Category	Species	Hot Commissioning Operation Projection (M)	Envelope B Operation Projection (M)	Subsequent Operation Projection (M)
	OH^- (free)	1.85	1.28	0.80
	NO_2^-	0.523	0.921	0.750
	NO_3^-	1.393	0.882	2.340
	CO_3^{2-}	0.61	0.44	0.40

Table 4-2. Hot Commissioning Operation waste composition with variation about nominal value in potassium concentration.

Ion Category	Species	Hot Commissioning Low K+ (M)	Hot Commissioning Nominal (M)	Hot Commissioning High K+ (M)
Cations*	Na^+	4.57	4.57	4.57
	K^+	0.384	0.48	0.576
	Total Cs^+	2.74E-05	2.74E-05	2.74E-05
	$^{137}Cs^+$ (Ci/L)	0.072	0.072	0.072
	g $^{137}Cs^+$/g Total Cs^+	0.22	0.22	0.22
Anions	SO_4^{2-}	0.032	0.032	0.032
	OH^- (free)	1.85	1.85	1.85
	NO_2^-	0.496	0.523	0.549
	NO_3^-	1.324	1.393	1.463
	CO_3^{2-}	0.61	0.61	0.61

Table 4-3. Hot Commissioning Operation waste composition with variation about nominal value in sodium concentration.

Ion Category	Species	Hot Commissioning Low Na+ (M)	Hot Commissioning Nominal (M)	Hot Commissioning High Na+ (M)
Cations*	Na^+	3.656	4.57	5.484
	K^+	0.48	0.48	0.48
	Total Cs^+	2.74E-05	2.74E-05	2.74E-05

Ion Category	Species	Hot Commissioning Low Na+ (M)	Hot Commissioning Nominal (M)	Hot Commissioning High Na+ (M)
	$^{137}Cs^{+}$ (Ci/L)	0.072	0.072	0.072
	g $^{137}Cs^{+}$/g Total Cs^{+}	0.22	0.22	0.22
Anions	SO_4^{2-}	0.032	0.032	0.032
	OH^{-} (free)	1.85	1.85	1.85
	NO_2^{-}	0.273	0.523	0.772
	NO_3^{-}	0.729	1.393	2.058
	CO_3^{2-}	0.61	0.61	0.61

Table 4-4. Hot Commissioning Operation waste composition with variation about nominal value in hydroxide concentration.

Ion Category	Species	Hot Commissioning Low OH– (M)	Hot Commissioning Nominal (M)	Hot Commissioning High OH– (M)
Cations*	Na^{+}	4.57	4.57	4.57
	K^{+}	0.48	0.48	0.48
	Total Cs^{+}	2.74E-05	2.74E-05	2.74E-05
	$^{137}Cs^{+}$ (Ci/L)	0.072	0.072	0.072
	g $^{137}Cs^{+}$/g Total Cs^{+}	0.22	0.22	0.22
Anions	SO_4^{2-}	0.032	0.032	0.032
	OH^{-} (free)	1.48	1.85	2.22
	NO_2^{-}	0.623	0.523	0.422
	NO_3^{-}	1.663	1.393	1.124
	CO_3^{2-}	0.61	0.61	0.61

Table 4-5. Hot Commissioning Operation waste composition with variation about nominal feed value in cesium concentration.

Ion Category	Species	Hot Commissioning Low Cs+ (M)	Hot Commissioning Nominal (M)	Hot Commissioning High Cs+ (M)

Ion Category	Species	Hot Commissioning Low Cs+ (M)	Hot Commissioning Nominal (M)	Hot Commissioning High Cs+ (M)
Cations*	Na^+	4.57	4.57	4.57
	K^+	0.48	0.48	0.48
	Total Cs^+	2.192E-05	2.74E-05	3.288E-05
	$^{137}Cs^+$ (Ci/L)	0.0576	0.072	0.0864
	g $^{137}Cs^+$/g Total Cs^+	0.22	0.22	0.22
Anions	SO_4^{2-}	0.032	0.032	0.032
	OH^- (free)	1.85	1.85	1.85
	NO_2^-	0.523	0.523	0.523
	NO_3^-	1.393	1.393	1.393
	CO_3^{2-}	0.61	0.61	0.61

Table 4-6. Waste compositions used to represent AN-105 and AZ-102 simulants at 5 M Na^+.

Ion Category	Species	AN-105 Simulant (M)	AZ-102 Simulant (M)
Cations*	Na^+	5.000	5.000
	K^+	0.089	0.146
	Cs^+	variable	variable
Anions	$Al(OH)_4^-$	0.502	0.050
	$C_2O_4^{2-}$	0.003	0.058
	$C_2H_3O_2^-$	0.022	0.020
	Cl^-	0.120	0.000
	CHO_2^-	0.030	0.184
	CO_3^{2-}	0.098	0.876
	F^-	0.000	0.096
	NO_2^-	1.127	1.190

Ion Category	Species	AN-105 Simulant (M)	AZ-102 Simulant (M)
	NO_3^-	1.290	0.753
	OH^- (free)	1.789	0.334
	PO_4^{2-}	0.000	0.010
	SO_4^{2-}	0.004	0.310

Table 4-7. Two-parameter fit of algebraic isotherm parameters (Na-form mass basis).

Simulant or IX Feed	Composition Variability	C_T (mmol/g_{resin})	β (M)
AN-105 Simulant	5 M Na^+	0.5154	1.5758E-04
AZ-102 Simulant	5 M Na^+	0.4431	2.3835E-04
Hot Commissioning Operation	Nominal	0.5160	5.1474E-04
Envelope B Operation	Nominal	0.5078	1.4192E-04
Subsequent Operation	Nominal	0.4926	2.4279E-04
Hot Commissioning Operation	$[K^+]$ + 20 %	0.5160	6.0329E-04
Hot Commissioning Operation	$[K^+]$ – 20 %	0.5160	4.2670E-04
Hot Commissioning Operation	$[Na^+]$ + 20 %	0.5160	5.6334E-04
Hot Commissioning Operation	$[Na^+]$ – 20 %	0.5160	4.8191E-04
Hot Commissioning Operation	$[OH^-]$ + 20 %	0.5191	4.9934E-04
Hot Commissioning Operation	$[OH^-]$ – 20 %	0.5114	5.3147E-04

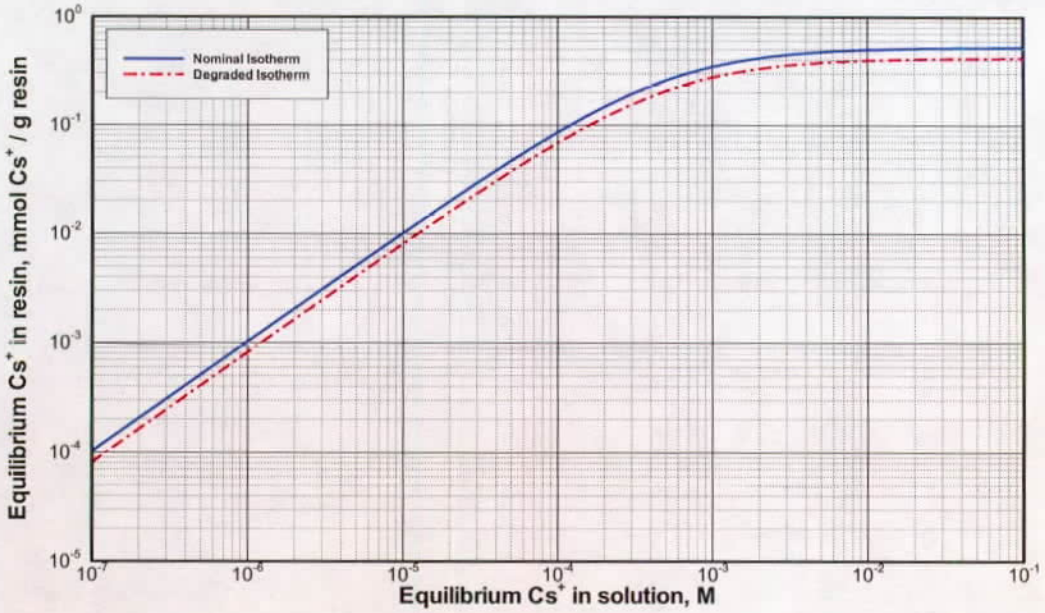

Figure 4-1. Hot Commissioning Operation Cs^+ isotherms for SuperLig® 644 resin (Na-form mass basis).

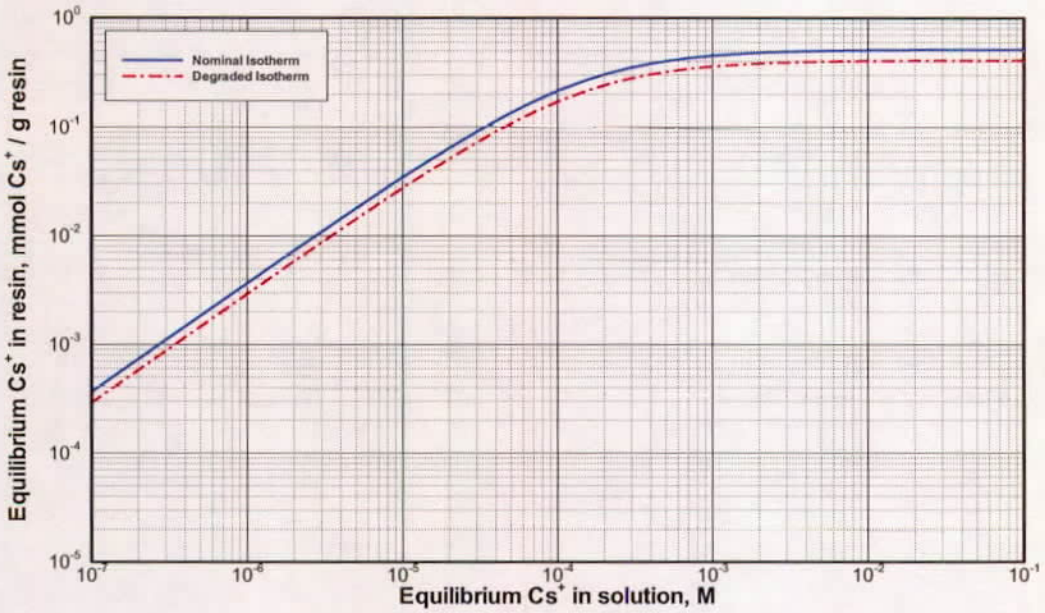

Figure 4-2. Envelope B Operation Cs^+ isotherms for SuperLig® 644 resin (Na-form mass basis).

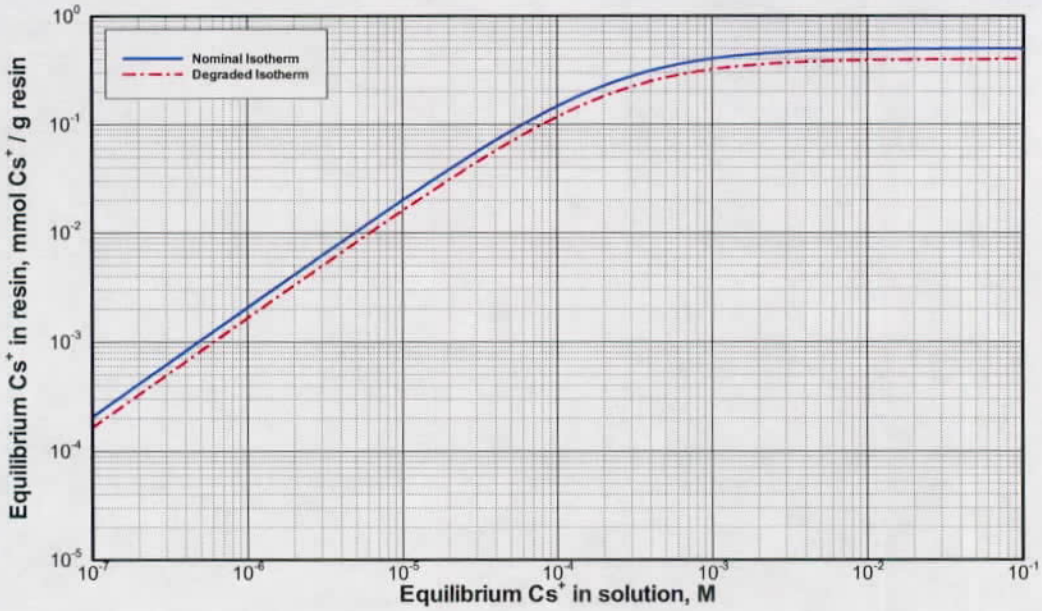

Figure 4-3. Subsequent Operation Cs^+ isotherms for SuperLig® 644 resin (Na-form mass basis).

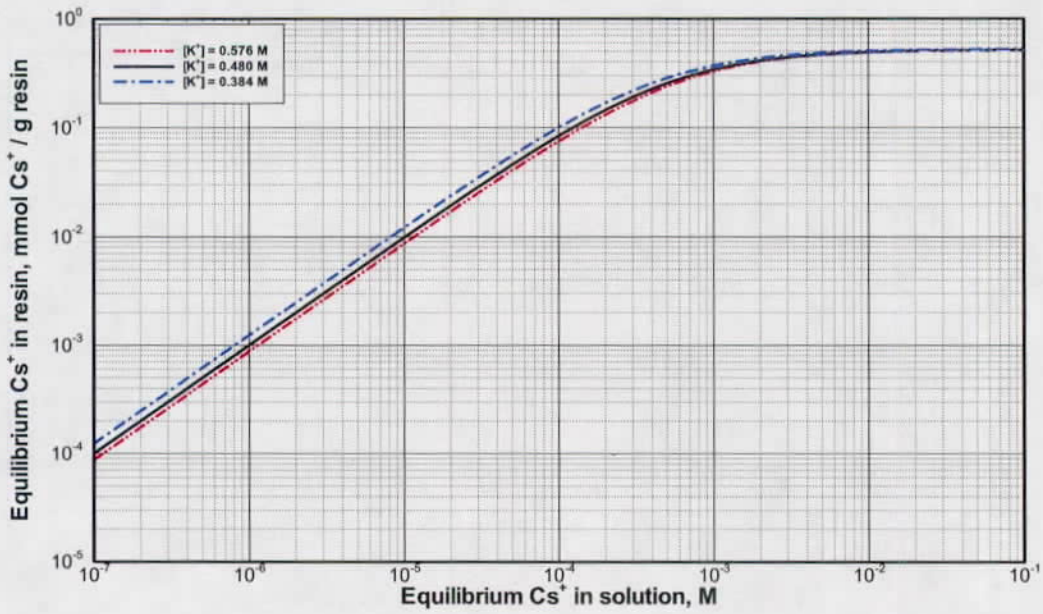

Figure 4-4. Hot Commissioning Operation Cs^+ isotherm sensitivity to K^+ initial concentration for SuperLig® 644 resin (Na-form mass basis).

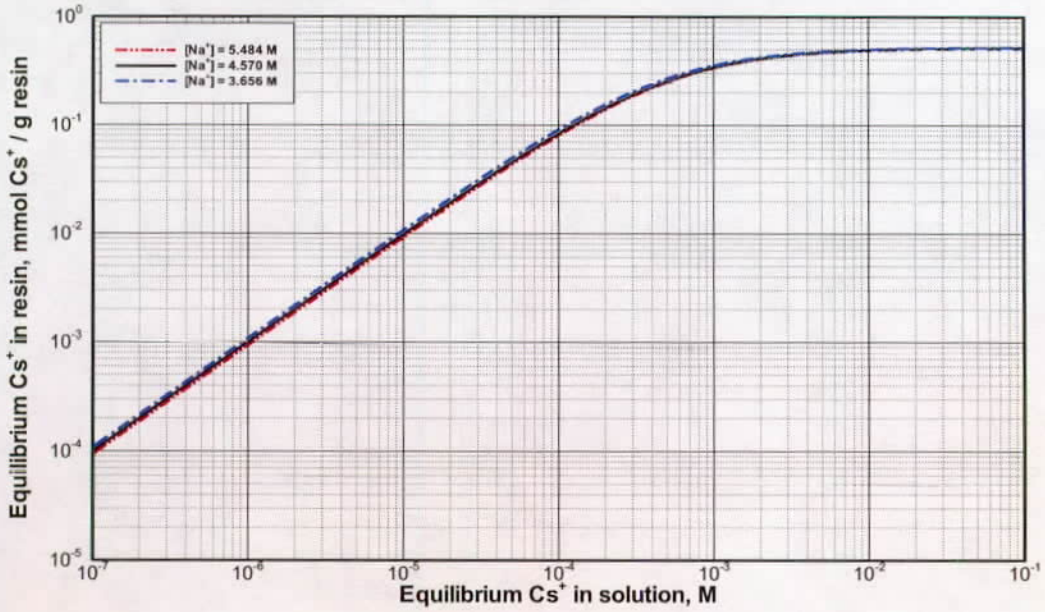

Figure 4-5. Hot Commissioning Operation Cs^+ isotherm sensitivity to Na^+ initial concentration for SuperLig® 644 resin (Na-form mass basis).

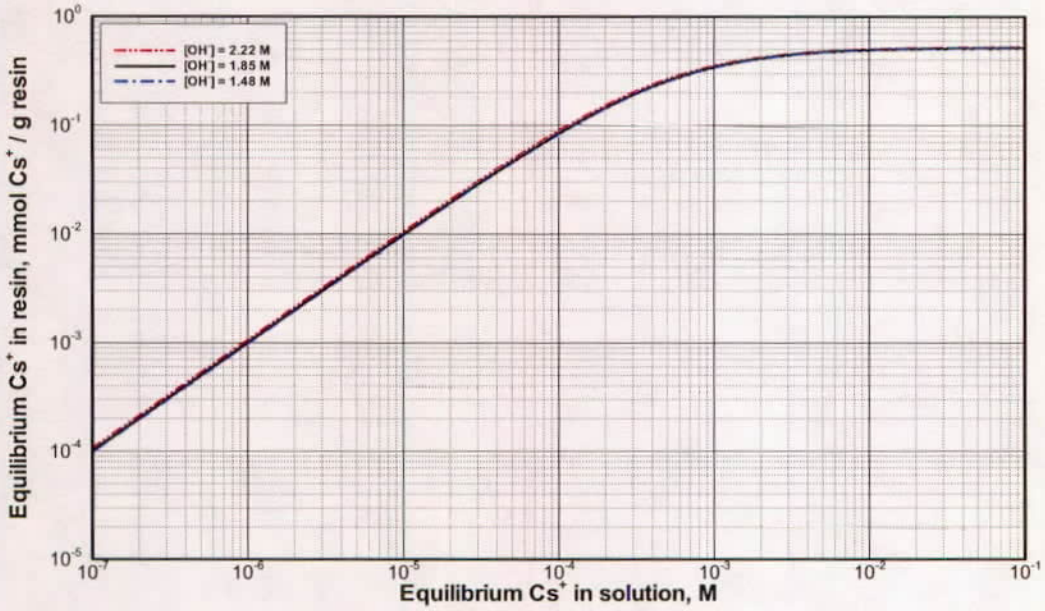

Figure 4-6. Hot Commissioning Operation Cs^+ isotherm sensitivity to OH^- initial concentration for SuperLig® 644 resin (Na-form mass basis).

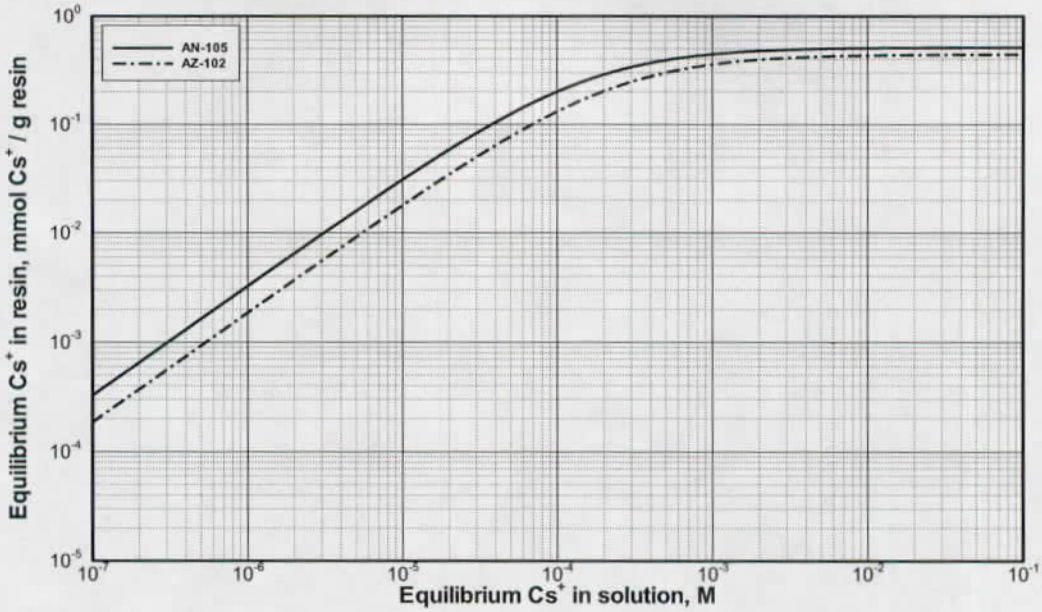

Figure 4-7. AN-105 and AZ-102 simulant Cs^+ isotherms for SuperLig® 644 resin (Na-form mass basis).

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5.0 Column Properties

Certain material properties (such as, resin density and total ionic capacity) are unique to the ion-exchange material and vary only between batches. On the other hand, composite properties associated with an ion-exchange column (such as, bed density and porosities) are inherently column specific. Even when different columns are made from the same batch of resin, column properties can vary. During operational cycles where a significant variation in total ionic strength of the feed occurs, the active bed size of a column can change as much as 100% (see King et al., 2000). The discussion that follows focuses on the column properties required to perform column transport simulations during the loading phase of a column cycle. Column properties were determined from experiments using -20 to +30 mesh samples from the 250 gallon batch of SuperLig® 644.

For additional details on column properties required to perform a VERSE-LC column performance analysis see Hamm et al. (2000b, preliminary Cs removal performance using SuperLig® 644 report), Hamm et al. (2000c, preliminary Tc removal performance using SuperLig® 639 report), and Hamm et al. (2002b, Cs removal performance using CST report)

5.1 Basic Constraint Functions

Based on geometrical considerations not all densities and porosities are independent. The following two expressions place constraints on the densities and porosities:

$$\varepsilon_t = \varepsilon_b + (1-\varepsilon_b)\varepsilon_p, \tag{5-1}$$

and

$$\rho_b = \rho_s(1-\varepsilon_t) = \rho_s(1-\varepsilon_b)(1-\varepsilon_p), \tag{5-2}$$

where

ε_t .....total porosity of active column, [-]
ε_b .....bed porosity of active column, [-]
ε_p .....pore porosity of resin particles, [-]
ρ_b .....bed density of active column, g/ml
ρ_s .....solid (particle) density of resin, g/ml

For the five variables listed above only three are independent. The various porosities used in Eq. (5-1) are defined as:

$$\varepsilon_b = \frac{V_{void} - V_{pore}}{V_{bed}}; \quad \varepsilon_p = \frac{V_{pore}}{V_{part}}; \quad \varepsilon_t = \frac{V_{void}}{V_{bed}} = \frac{V_{bed} - V_{sld}}{V_{bed}} \tag{5-3}$$

where

V_{bed} .....total volume of active (bed) column, ml

V_{void} .....total volume of voids within active column, ml

V_{pore} .....total volume of pores within particles, ml

V_{part} .....total volume of particles within active column, ml

V_{sld} .....total volume of solid resin within active column, ml

5.2 Densities

The particle ("skeletal") density of SuperLig® 644 has been determined in sodium and hydrogen form using pycnometer techniques in Appendix B. Results are provided in Tables 5-1 and B-12. For the column modeling presented in this report the average particle density of 1.451 g/ml listed in Table 5-1 for Na-form SuperLig® 644 in AN-105 simulant was employed.

The actual amount of resin present within a column is a parameter of prime importance with respect to column performance (i.e., exit breakthrough curves). For the column studies assessed within this report an estimate of column bed density was derived from the drainable void study in Appendix B. The dry resin mass and bed volume were measured for the SuperLig® 644 in Na-form. The column bed density was computed as

$$\rho_b = \frac{m_{resin}}{V_{bed}} = \frac{26.82\,g}{89.84\,ml} = 0.2985\,g/ml \qquad (5\text{-}4)$$

The bed density computed by Eq. (5-4) represents our nominal value. For application to specific column tests sometimes adjustments were made if column volume changes occurred and were reported.

5.3 Porosities

The drainable void volume of a SuperLig® 644 resin bed packed in a prototypical manner was determined by a liquid drainage technique in Appendix B. The drainable void fraction for a ninety-milliliter nominal sample of SuperLig® 644 was found to be

$$\varepsilon_b = \frac{V_{void} - V_{pore}}{V_{bed}} = \frac{34.44\,ml}{89.84\,ml} = 0.38 \pm 1\% \qquad (5\text{-}5)$$

The bed porosity computed by Eq. (5-5) represents our nominal value. The average measured porosity for dense packing of mono-sized hard spheres is 0.363 as reported by German (1989). Greater packing fractions (or smaller bed porosities) can be achieved when multi-sized spheres are employed. Given the non-uniform shapes of the granular SuperLig® 644 resin particles, no specific lower limit can be uniquely specified.

Based on Eq. (5-2) the pore porosity of the resin particles is known once the particle density, bed density and bed porosity are specified. Using the values presented in the above subsection the pore porosity of the resin particles becomes:

$$\varepsilon_p = 1 - \rho_b/\rho_s(1-\varepsilon_b) = 1 - 0.2985/1.451(1-0.38) = 0.6682 \quad (5\text{-}6)$$

The pore porosity computed by Eq. (5-6) represents our nominal value.

Table 5-1. Particle densities for -20 to +30 mesh samples of SuperLig® 644 resin.

Liquid	Resin Form	Particle Density (g/ml)
DI H_2O	Na^+	1.489
AN-105 simulant	Na^+	1.451
DI H_2O	H^+	1.343
0.5M HNO_3	H^+	1.308

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6.0 Particle Size Distributions

The particle size distribution of granular SuperLig® 644 resin samples were characterized in sodium form. Wet sieve analysis was used to characterize the particle size distribution of granular 1-Gallon, 25-Gallon and 250-Gallon Batches of SuperLig® 644 resin. Microtrac® analysis is presented in Appendix B for various particle sieve cuts for the 250-Gallon Batch of SuperLig® 644. Section 6.1 discusses the wet sieve analyses for the 1-Gallon and 25-Gallon Batches of SuperLig® 644. Section 6.2 presents the wet sieve analysis for the 250-Gallon Batch of SuperLig® 644. Sections 6.3 and 6.4 discuss the fit of the wet sieve data to the Rosin-Rammler equation and the calculation of spherically-equivalent particle diameters, respectively.

For details on particle size distribution properties required to perform a VERSE-LC column performance analysis see Hamm et al. (2000b, preliminary Cs removal performance using SuperLig® 644 report), Hamm et al. (2000c, preliminary Tc removal performance using SuperLig® 639 report), and Hamm et al. (2002b, Cs removal performance using CST report).

6.1 Wet Sieving Analyses for the 1-Gallon Batch and 25-Gallon Batches of SuperLig® 644 Resin.

Wet sieve analyses were performed for the 1-Gallon and 25-Gallon Batches (1, 2 and 3) of SuperLig® 644 by Serkiz et al. (2004). The SuperLig® 644 resin samples were wet sieved with mesh sizes 10, 16, 20, 30, 40, 50, 60, 80, and 100 to provide a more resolved size distribution for each sample. The 10, 16 and 20 mesh trays were not used for the 1-Gallon Batch of SuperLig® 644 samples. The results are summarized in Tables 6-1 to 6-4 for the 1-Gallon Batch, 25-Gallon Batch 1, 25-Gallon Batch 2 and 25-Gallon Batch 3 of SuperLig® 644, respectively. The results are displayed as percentage by weight passing the sieve. The Serkiz results are given as weight percent retained on wet sieve tray.

6.2 Wet Sieving Analysis for the 250 Gallon Batch of SuperLig® 644 Resin.

Wet sieve analyses were performed for the 250-Gallon Batch of SuperLig® 644 by King. The resin sample was wet sieved with mesh sizes 18, 20, 30, 40, 50, 70 and 100. The results are summarized in Table 6-5 for the 250-Gallon Batch of SuperLig® 644.

6.3 Rosin-Rammler Fit of Wet Sieve Data for SuperLig® 644 Resin.

The Rosin-Rammler equation (Latham et al., 2002) is one of the most commonly used theoretical equations used to fit the observed cumulative distribution of particle sizes for crushed minerals and blastpiles. The Rosin-Rammler cumulative distribution function was applied to the wet sieve particle size analysis data for SuperLig® 644. Table 6-6 summarizes the Rosin-Rammler cumulative and probability distribution functions.

A non-linear least square optimization of the cost function computed from normalized residuals of the wet sieve data and the Rosin-Rammler equation was performed. The Rosin-Rammler

characteristic size and the uniformity coefficient for each batch of SuperLig® 644 are shown in Table 6-7.

Figures 6-1 to 6-5 show plots of the wet sieve data and the Rosin-Rammler CDF for the 1-Gallon Batch, 25-Gallon Batch 1, 25-Gallon Batch 2, 25-Gallon Batch 3 and 250-Gallon Batch of SuperLig® 644, respectively.

6.4 Calculation of Average Spherically-Equivalent Particle Diameters

Once we have established the cumulative distribution function, we can compute the pdf of the particle size distribution on a weight or number basis. The Powder Technology Handbook (Gotoh, 1997) provides nine distinct definitions of mean or average particle diameters. Table 6-8 provides the definition and corresponding integral representation of the diameters in terms of the number basis pdf. The range of integration is over the particle size or sieve size interval of interest.

Spherically-equivalent particle diameters were computed for SuperLig® 644 samples using the definitions in Table 6-8. Tables 6-9 to 6-13 provide the particle diameter calculations in microns for the 1-Gallon Batch, 25-Gallon Batch 1, 25-Gallon Batch 2, 25-Gallon Batch 3 and 250-Gallon Batch of SuperLig® 644, respectively. Table 6-13 provides the particle diameter statistics for the as-received 250-Gallon Batch resin, -20+70 mesh, as well as four other mesh ranges utilized in particle kinetics and column studies in this report.

Table 6-1. Wet sieve particle size analysis data for granular 1-Gallon Batch of SuperLig® 644.

ASTM Sieve Size	Sieve Opening (microns)	Primary Wt % Passing Sieve	Replicate Wt % Passing Sieve
30	600	96.81	99.41
40	425	38.16	36.95
50	300	14.11	12.79
60	250	2.18	1.21
80	180	0.17	0.08
100	150	0.00	0.00

Table 6-2. Wet sieve particle size analysis data for granular 25-Gallon Batch 1 of SuperLig® 644.

ASTM Sieve Size	Sieve Opening (microns)	Primary Wt % Passing Sieve	Replicate Wt % Passing Sieve
10	2000	100.00	100.00
16	1180	99.94	99.85

ASTM Sieve Size	Sieve Opening (microns)	Primary Wt % Passing Sieve	Replicate Wt % Passing Sieve
20	850	96.56	95.06
30	600	58.02	58.10
40	425	27.61	28.75
50	300	10.93	12.07
60	250	1.68	1.70
80	180	0.17	0.13
100	150	0.00	0.00

Table 6-3. Wet sieve particle size analysis data for granular 25-Gallon Batch 2 of SuperLig® 644.

ASTM Sieve Size	Sieve Opening (microns)	Primary Wt % Passing Sieve	Replicate Wt % Passing Sieve
10	2000	99.98	99.97
16	1180	99.69	99.73
20	850	95.94	95.84
30	600	58.28	62.94
40	425	27.62	31.26
50	300	12.67	14.58
60	250	2.82	3.25
80	180	0.31	0.37
100	150	0.00	0.00

Table 6-4. Wet sieve particle size analysis data for granular 25-Gallon Batch 3 of SuperLig® 644.

ASTM Sieve Size	Sieve Opening (microns)	Primary Wt % Passing Sieve	Replicate Wt % Passing Sieve
10	2000	99.82	99.94
16	1180	97.85	99.68

ASTM Sieve Size	Sieve Opening (microns)	Primary Wt % Passing Sieve	Replicate Wt % Passing Sieve
20	850	92.88	95.73
30	600	55.81	62.11
40	425	30.56	31.94
50	300	13.49	13.46
60	250	2.46	2.82
80	180	0.23	0.20
100	150	0.00	0.00

Table 6-5. Wet sieve particle size analysis data for granular 250-Gallon Batch of SuperLig® 644.

ASTM Sieve Size	Sieve Opening (microns)	Wt % Passing Sieve
18	1000	99.90
20	850	99.14
30	600	52.90
40	425	22.94
50	300	4.97
70	212	0.31
100	150	0.00

Table 6-6. Rosin-Rammler cumulative and probability distribution functions.

Function	Basis	Equation
cdf	weight	$W(x) = 1 - \exp\{-(x/x_c)^{m_{rr}}\}$
pdf	weight	$w(x) = \frac{dW(x)}{dx} = \left(\frac{m_{rr}}{x_c}\right)\left(\frac{x}{x_c}\right)^{m_{rr}-1} \exp\{-(x/x_c)^{m_{rr}}\}$
pdf	number	$n(x) = w(x)/f(x)\sigma(x)x^3$

where

cdf .....cumulative distribution function

pdf .....probability distribution function

W(x) .....fraction by weight finer than a given sieve size or particle diameter

x .....sieve size or particle diameter

x_c .....Rosin-Rammler characteristic size, taken to be 63.2% passing size

m_{rr} .....Rosin-Rammler uniformity coefficient

f(x) .....particle volume shape factor ($\pi/6$ for a sphere)

$\sigma(x)$ .....particle density (assumed constant)

Table 6-7. Rosin-Rammler estimated parameters for SuperLig® 644 samples.

Batch	Sample	x_c	m_{rr}
1 Gallon	1	484.4	4.99
1 Gallon	2	482.0	5.54
25 Gallon B1	1	615.3	3.31
25 Gallon B1	2	616.6	3.17
25 Gallon B2	1	615.4	3.20
25 Gallon B2	2	594.7	3.07
25 Gallon B3	1	627.0	2.93
25 Gallon B3	2	597.0	3.08
250 Gallon	1	632.4	3.85

Table 6-8. Definitions of various average or mean particle diameters.

Definition of Diameter	Equation
Number mean diameter, D_1	$\int n(x)xdx \Big/ \int n(x)dx$
Length mean diameter, D_2	$\int n(x)x^2dx \Big/ \int n(x)xdx$
Surface mean, Sauter mean or mean volume-surface diameter, D_3	$\int n(x)x^3dx \Big/ \int n(x)x^2dx$
Volume or mass mean diameter, D_4	$\int n(x)x^4dx \Big/ \int n(x)x^3dx$

Definition of Diameter	Equation
Diameter of average surface, D_s	$\left(\int n(x)x^2dx \Big/ \int n(x)dx\right)^{1/2}$
Diameter of average volume, D_v	$\left(\int n(x)x^3dx \Big/ \int n(x)dx\right)^{1/3}$
Harmonic mean diameter, D_h	$\int n(x)dx \Big/ \int n(x)/x\,dx$
Number median diameter or geometric mean diameter, NMD	$\exp\left(\int n(x)\ln x dx \Big/ \int n(x)dx\right)$
Volume or mass median diameter, MMD	$\exp\left(\int n(x)x^3\ln x dx \Big/ \int n(x)x^3dx\right)$

Table 6-9. Spherically-equivalent particle diameters for 1-Gallon Batch of SuperLig® 644.

Diameter Definition	Sample 1 (microns)	Sample 2 (microns)
D_1	348.60	363.56
D_2	382.01	393.31
D_3	410.82	418.39
D_4	434.72	439.14
D_s	364.92	378.14
D_v	379.62	391.11
D_h	312.54	329.98
NMD	330.91	347.40
MMD	423.61	429.47

Table 6-10. Spherically-equivalent particle diameters for 25-Gallon Batch 1 of SuperLig® 644.

Diameter Definition	Sample 1 (microns)	Sample 2 (microns)
D_1	344.64	336.71

Diameter Definition	Sample 1 (microns)	Sample 2 (microns)
D_2	415.78	408.85
D_3	489.11	485.50
D_4	556.17	557.00
D_s	378.54	371.03
D_v	412.30	405.82
D_h	285.80	279.03
NMD	312.99	305.38
MMD	524.47	523.06

Table 6-11. Spherically-equivalent particle diameters for 25-Gallon Batch 2 of SuperLig® 644.

Diameter Definition	Sample 1 (microns)	Sample 2 (microns)
D_1	338.02	324.24
D_2	409.79	392.40
D_3	485.59	466.76
D_4	556.02	537.74
D_s	372.18	356.70
D_v	406.69	390.15
D_h	280.23	270.85
NMD	306.69	295.09
MMD	522.61	503.83

Table 6-12. Spherically-equivalent particle diameters for 25-Gallon Batch 3 of SuperLig® 644.

Diameter Definition	Sample 1 (microns)	Sample 2 (microns)
D_1	326.07	325.41
D_2	400.99	394.00
D_3	484.97	468.67
D_4	566.13	539.77
D_s	361.59	358.07
D_v	398.77	391.68
D_h	269.57	271.60
NMD	294.85	296.04
MMD	527.33	505.83

Table 6-13. Spherically-equivalent particle diameters for 250-Gallon Batch of SuperLig® 644.

Mesh Size Range									
-20 to +25		-20 to +30		-25 to +30		-20 to +40		-20 to +70	
diam	value	diam	value	diam	value	diam	value	diam	value
D_1	762.67	D_1	682.99	D_1	648.10	D_1	558.20	D_1	419.12
D_2	764.53	D_2	688.98	D_2	649.60	D_2	575.64	D_2	469.32
D_3	766.42	D_3	694.64	D_3	651.11	D_3	594.25	D_3	518.41
D_4	768.36	D_4	700.82	D_4	652.62	D_4	613.51	D_4	562.56
D_s	763.60	D_s	685.83	D_s	648.85	D_s	566.85	D_s	443.51
D_v	764.54	D_v	688.75	D_v	649.60	D_v	575.84	D_v	467.19
D_h	760.85	D_h	677.60	D_h	646.63	D_h	542.28	D_h	372.87

NMD	761.75	NMD	680.25	NMD	647.36	NMD	549.98	NMD	395.16
MMD	767.39	MMD	697.70	MMD	651.86	MMD	603.85	MMD	541.66

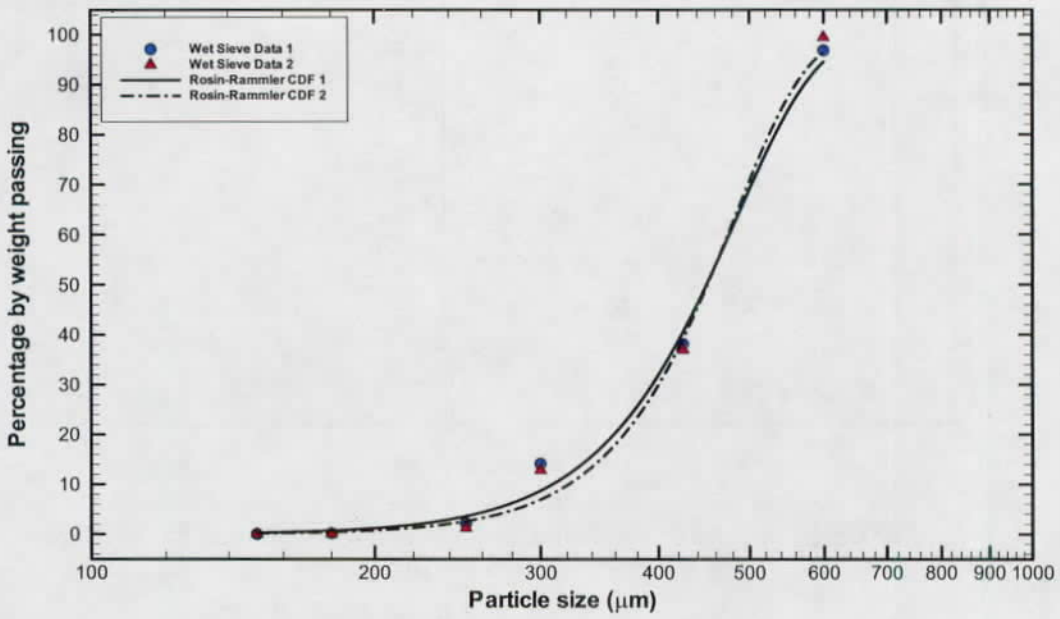

Figure 6-1. Wet sieve data and Rosin-Rammler cumulative distribution for 1-Gallon Batch of SuperLig® 644.

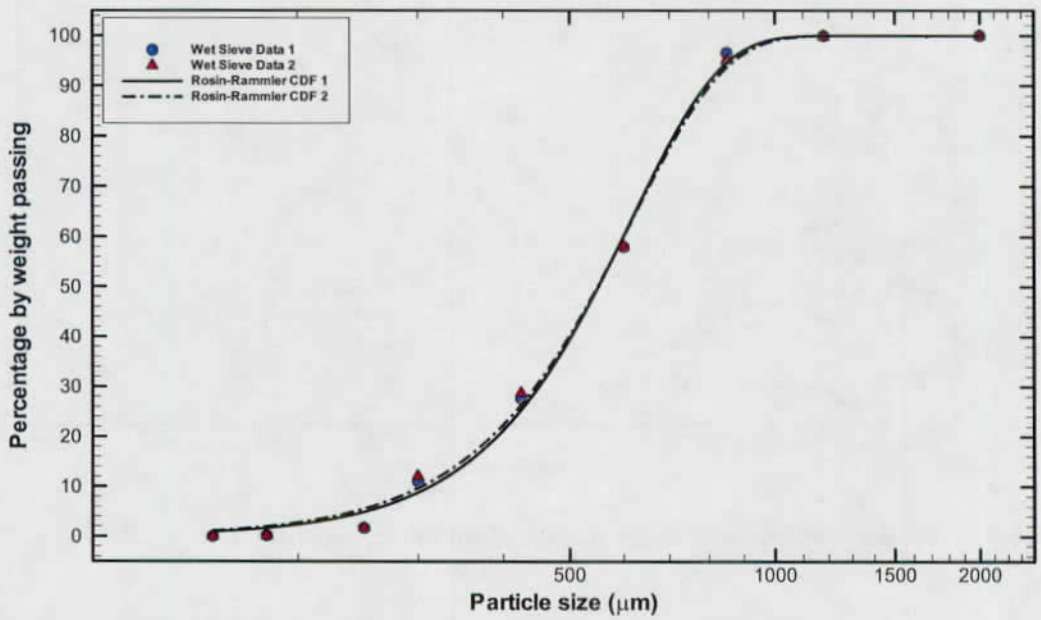

Figure 6-2. Wet sieve data and Rosin-Rammler cumulative distribution for 25-Gallon Batch 1 of SuperLig® 644.

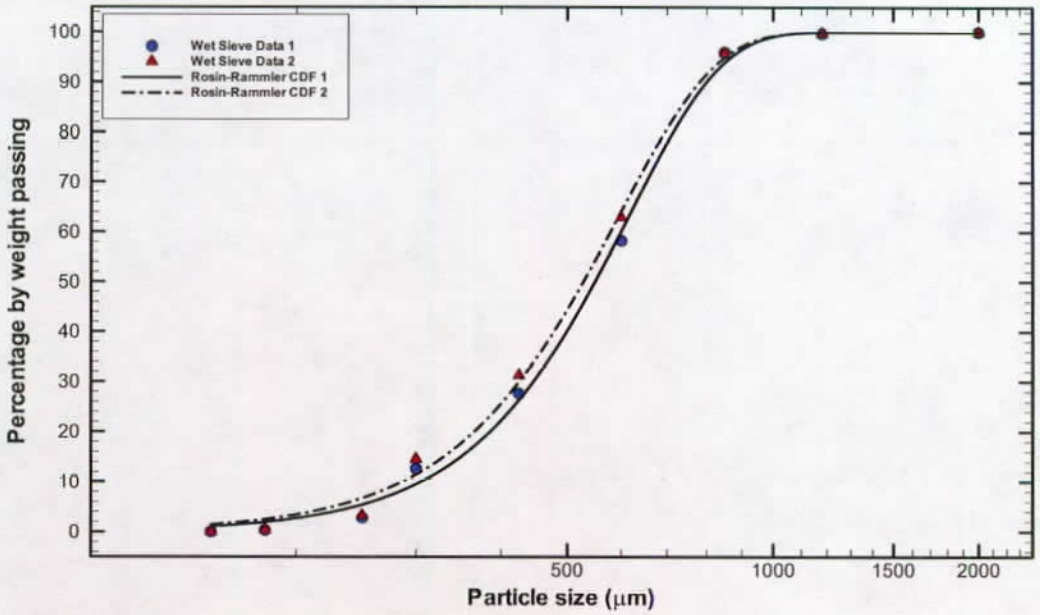

Figure 6-3. Wet sieve data and Rosin-Rammler cumulative distribution for 25-Gallon Batch 2 of SuperLig® 644.

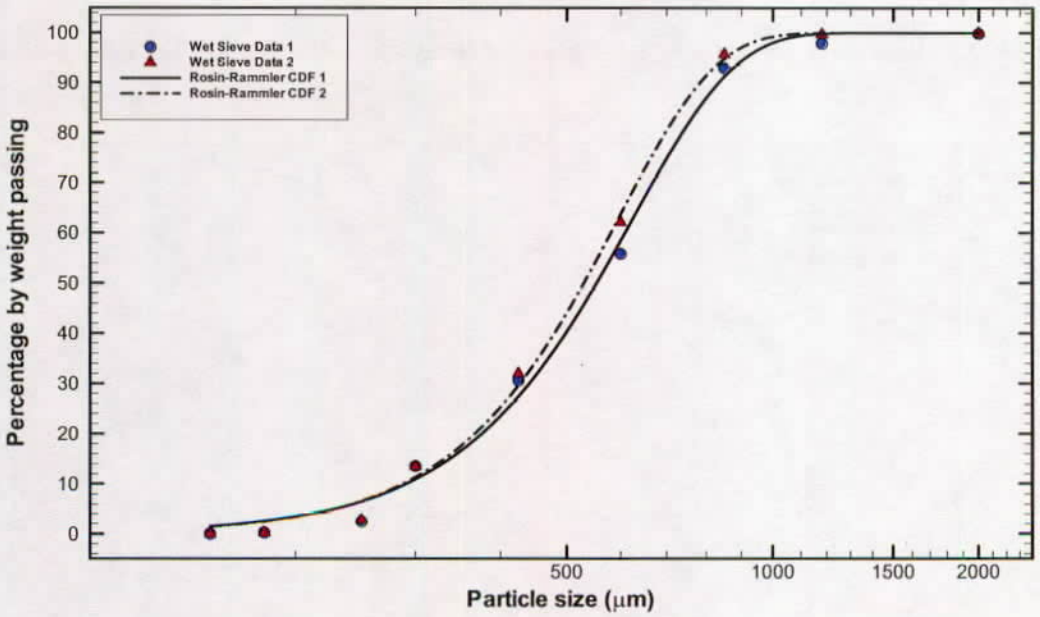

Figure 6-4. Wet sieve data and Rosin-Rammler cumulative distribution for 25-Gallon Batch 3 of SuperLig® 644.

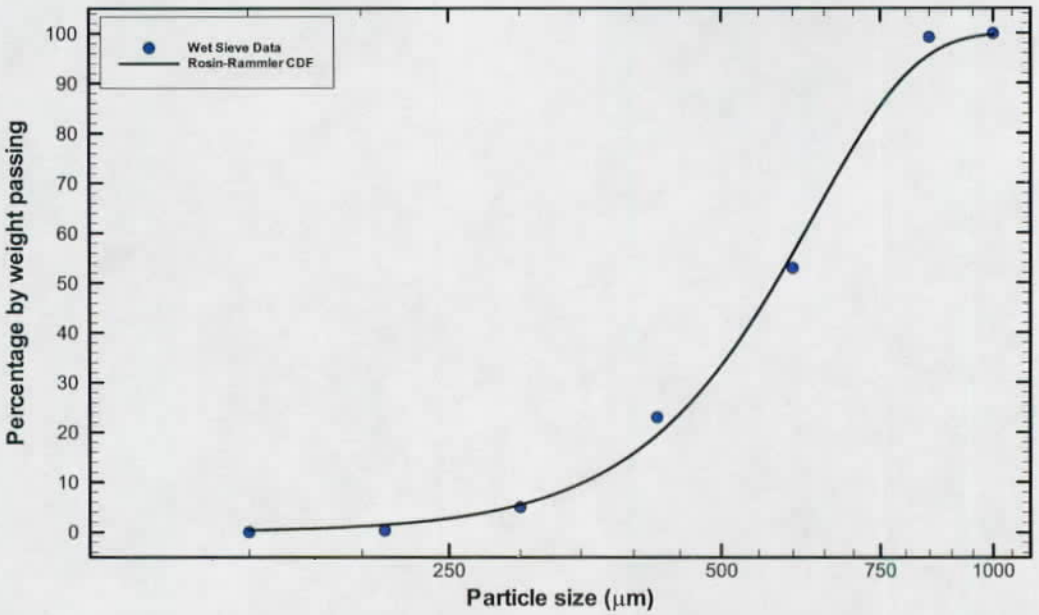

Figure 6-5. Wet sieve data and Rosin-Rammler cumulative distribution for 250-Gallon Batch of SuperLig® 644.

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7.0 Pore Diffusion

A series of VERSE-LC simulations were performed to identify the values of the pore diffusivity and effective particle radius from experimental data. Once the values for these parameters were established, the consistency of the model was tested by comparing its predictions with data from other experiments. All tests discussed in this section were performed using the SRNL kinetics rig at 25°C and are discussed in Appendix B. Sample VERSE-LC input and output files are listed in Appendix C.

7.1 Bulk Diffusivity of Cs^+ in Simulants and LAW IX Feeds

The bulk or free-stream diffusivity of Cs^+ in various simulants and LAW IX feeds typical of Envelope A, B and C operation were computed using OLI Systems, Inc. Stream Analyzer Version 1.3 (Build 1.3.0.23). The OLI Stream Analyzer contains a comprehensive model for calculating self-diffusion coefficients in multicomponent aqueous electrolyte systems. The model combines contributions of long-range (Coulombic) and short-range interactions. The long-range interaction contribution is obtained from the dielectric continuum-based mean-spherical approximation (MSA) theory for the unrestricted primitive model. The short-range interactions are represented using the hard-sphere model. In the combined model, aqueous species are characterized by effective radii, which depend on the ionic environment. For multicomponent systems, a mixing rule has been developed. The effects of complexation are taken into account by combining the diffusivity model with thermodynamic speciation calculations. The model accurately reproduces self-diffusivities of ions and neutral species in aqueous solutions ranging from infinitely dilute to concentrated (up to ca. 30 mol/kg H_2O). Also, the model makes it possible to predict diffusivities in multicomponent solutions using data for single-solute systems. The OLI Stream Analyzer results are shown in Table 7-1. The ratio column in the table refers to the ratio of the diffusivity calculated from the Hot Commissioning sensitivity study in the "Composition Variability" column to the nominal value. The Hot Commissioning Operation feed with sodium variation shows the greatest impact on the diffusivity from the nominal case. The Hot Commissioning Operation feed with sodium concentration increased by 20% has a diffusivity which is a factor of 20 smaller than the value for the nominal case. This observation warrants further investigation theoretically and experimentally (particle kinetics testing at 6 M Na^+ simulants).

7.2 Particle Kinetics Parameters

The rate of cesium uptake controls the transient behavior of the column. As the rate of cesium uptake by the resin is increased, the breakthrough curve becomes sharper (steeper) and utilization of the resin is increased. Thus, a proper evaluation of the parameters that control the rate of cesium uptake is essential for modeling column performance. For SuperLig® 644 resin, we assume that the rate of chemical adsorption (i.e. exchange of ions at a surface site) is very fast when compared to the rates of diffusion within the pore fluid and mass transfer across the liquid film at the outer boundary of the particles. Hence, within the resin particles, the rate of cesium uptake is dominated by intra-particle diffusion. Diffusion within the particles is governed by the pore diffusivity, particle porosity, and the shape and size of the particles.

Externally, the rate of cesium transport from the inter-particle fluid to the particle surface depends upon the film mass transfer coefficient. Due to their influence on the rate of cesium uptake and, thus, the transient behavior of the column, the particle porosity, pore diffusivity, particle geometry and the film mass transfer coefficient are referred to as kinetics parameters.

7.3 Effective Particle Radius and Pore Diffusivity

In VERSE-LC the film mass transfer coefficient is calculated from a correlation developed by Wilson and Geankoplis (1966). The particle porosity is available from data in Section 5. Therefore, of the kinetics parameters, the pore diffusivity and the variables affecting the shape and size of the resin particles remain to be determined. Within VERSE-LC, the model for intra-particle diffusion assumes that the particles are spheres of uniform radius. The granular SuperLig® 644 particles, however, have a distribution of particle sizes and are irregular in shape. To apply the VERSE-LC model to the SuperLig® 644 resin it is therefore necessary to determine an effective "radius", which accounts for the geometry and size distributions, and an effective pore diffusivity. Due to the complexity of the particle geometry, coupled with the scarcity of data for the particle shape, an empirical approach was adopted. In this approach, the effective particle radius or pore diffusion length is expressed as

$$r_{eff} = \phi \frac{< d_p >}{2} \tag{7-1}$$

where

r_{eff} .....effective particle radius or pore diffusion length, microns

ϕ .....particle shape factor

$< d_p >$ .....average spherically-equivalent particle diameter, microns

Since particle size controls particle diffusion as $1/r^2$ in spheres, we chose the number median diameter as the spherically-equivalent particle diameter. The number median diameter provides a metric that is weighted more toward the smaller particles in the distribution. The smaller particles in the distribution control the particle kinetics. The particle shape factor is used to arrive at the effective pore diffusion length for the irregular, non-spherically shaped resin particles. The number median diameter has been used successfully in the Kozeny-Carman equation to fit water permeability data for five mesh sieve cuts of 250-Gallon Batch of SuperLig® 644 (Fowley et al., 2004).

Specific information on the actual pore sizes are not available, however, IBC vendor information suggests that the pore sizes are large relative to the size of the migrating ions of interest and that pore diffusion coefficients should not be significantly lower than their bulk or free stream values. However, some level of reduction is expected resulting from bends along the pore paths that are generally accounted for by a particle tortuosity factor defined as

$$D_p = \frac{D_\infty}{\tau} \tag{7-2}$$

where

D_p .....pore diffusivity of Cs^+ in the particle pore, cm^2/min

D_∞ .....bulk diffusivity of Cs^+ in the free stream, cm^2/min

τ .....particle tortuosity factor

7.4 SRNL Particle Kinetics Testing

The SRNL particle kinetics rig is a closed loop differential column with temperature control. The recirculation device contained 120 ml of simulant and produced a bed flowrate of 30 ml/min. The high bed flowrate made film mass transfer resistance negligible relative to that for diffusion in the pores of the particle. In this way, the effect of the film mass transfer coefficient was eliminated and the data showed only the effect of ϕ and τ.

Four experiments were conducted using three mesh cuts of SuperLig® 644 from the 250-Gallon Batch contacted with the base AN-105 simulant at 25°C. In Experiments 1 (primary) and 2 (duplicate), a -20 to + 30 mesh cut of SuperLig® 644 resin from the 250-Gallon Batch was contacted with the base AN-105 simulant at 25°C. Experiment 3 was performed with a -20 to +25 mesh cut. Experiment 4 was performed with a -25 to +30 mesh cut. The phase ratio for these experiments ranged from 354 ml/mg (Experiments 1 and 2) to 388 ml/mg (Experiments 3 and 4).

7.5 Parameter Estimation

The particle shape factor and tortuosity factor were estimated using trial-and-error by comparison of VERSE-LC models for Experiments 1 (primary) and 2 (duplicate) in Table B-7 to data derived from the SRNL particle kinetics rig in Table B-9. A series of VERSE-LC calculations were executed using tortuosity factors of 2, 3 and 4 with particle diameters ranging 100%, 80%, 70% and 60% of the number median diameter of 680.3 μm in Table 6-13 for the -20 to +30 mesh cut. Prior to execution of the runs, the total capacity of the resin, $\rho_b C_T$, in mmol/ml was adjusted to match the equilibrium cesium loading observed in the experiments. The AN-105 isotherm parameters (C_T and β) for the -20 to +30 mesh cut of SuperLig® 644 resin from the 250-Gallon Batch are specified in Table 4-7.

Figures 7-1 through 7-3 show a comparison of the transient aqueous cesium concentration for Experiments 1 and 2 to the VERSE-LC simulation for various particle radii with tortuosity factors set to 2, 3 and 4, respectively. The VERSE-LC simulation represents the transient cesium concentration exiting the CSTR upstream of the differential column. There are three combinations of particle shape factor and tortuosity factor that provide a good fit to data from Experiments 1 and 2; Figure 7-1 ($\phi = 0.8$, $\tau = 2$), Figure 7-2 ($\phi = 0.7$, $\tau = 3$), and Figure 7-3 ($\phi = 0.6$, $\tau = 4$). The midpoint values of the two parameters were arbitrarily chosen from Figure 7-2. Therefore, particle kinetics and column breakthrough assessment will be made using the following particle shape factor and tortuosity factor.

$$\phi = 0.7 \text{ and } \tau = 3 \qquad (7\text{-}3)$$

Figure 7-4 shows the cesium solid loading computed from the transient cesium concentration in Figure 7-2 using the parameter settings from Eq. (7-3).

7.6 SRNL Particle Kinetics Rig Assessment

To evaluate the accuracy of the parameters, ϕ and τ, developed for the effective particle radius and pore diffusivity, predictions made by VERSE-LC were compared with additional data from the SRNL particle kinetics rig. These comparisons are shown in Figures 7-5 through 7-8.

The VERSE-LC model was compared with SRNL particle kinetics rig data from Experiment 3 of Table B-7, which utilized the -20 to +25 mesh cut of SuperLig 644 from the 250-Gallon Batch. In the model $< d_p >$ was assigned a value of 533.2 μm, which is 70% of the number median diameter for the -20 to +25 mesh range in Table 6-13. Although the data were obtained for -20 to +25 mesh range, the model used the AN-105 cesium isotherm for the -20 to +30 mesh range given by Table 4-7 at 25°C. Prior to execution of the runs, the total capacity of the resin, $\rho_b C_T$, in mmol/ml was adjusted to match the equilibrium cesium loading observed in the experiment. The capacity of the resin is believed to vary with particle size distribution (more capacity with larger particles). For a given batch of resin, this has not been quantified experimentally. From Figures 7-5 and 7-6, it can be seen that the model is in reasonable agreement with the data.

The VERSE-LC model was compared with SRNL particle kinetics rig data from Experiment 4 of Table B-7, which utilized the -25 to +30 mesh cut of SuperLig 644 from the 250-Gallon Batch. In the model $< d_p >$ was assigned a value of 453.2 μm, which is 70% of the number median diameter for the -25 to +30 mesh range in Table 6-13. Although the data were obtained for -25 to +30 mesh range, the model used the AN-105 cesium isotherm for the -20 to +30 mesh range given by Table 4-7 at 25°C. Prior to execution of the runs, the total capacity of the resin, $\rho_b C_T$, in mmol/ml was adjusted to match the equilibrium cesium loading observed in the experiment. From Figures 7-7 and 7-8, it can be seen that the model is in reasonable agreement with the data.

Table 7-1. OLI diffusivities of Cs+ in simulants and LAW IX feeds at 25°C.

Feed or Simulant	Composition Variability	Diffusivity (m^2/s)	Diffusivity (cm^2/min)	Ratio
AN-105 Simulant	5 M Na^+	2.6328E-10	1.5797E-04	-
AZ-102 Simulant	5 M Na^+	1.8996E-10	1.1398E-04	-
Hot Commissioning Operation	Nominal	5.6046E-10	3.3628E-04	-
Envelope B Operation	Nominal	8.7046E-10	5.2228E-04	-
Subsequent Operation	Nominal	6.4681E-10	3.8809E-04	-
Hot Commissioning Operation	$[K^+]$ + 20%	4.8857E-10	2.9314E-04	0.87
Hot Commissioning Operation	$[K^+]$ – 20%	6.2890E-10	3.7734E-04	1.12

Feed or Simulant	Composition Variability	Diffusivity (m^2/s)	Diffusivity (cm^2/min)	Ratio
Hot Commissioning Operation	$[Na^+]$ + 20%	2.6241E-11	1.5745E-05	0.05
Hot Commissioning Operation	$[Na^+]$ – 20%	1.0540E-09	6.3240E-04	1.88
Hot Commissioning Operation	$[OH^-]$ + 20%	6.1161E-10	3.6697E-04	1.09
Hot Commissioning Operation	$[OH^-]$ – 20%	5.1332E-10	3.0799E-04	0.92

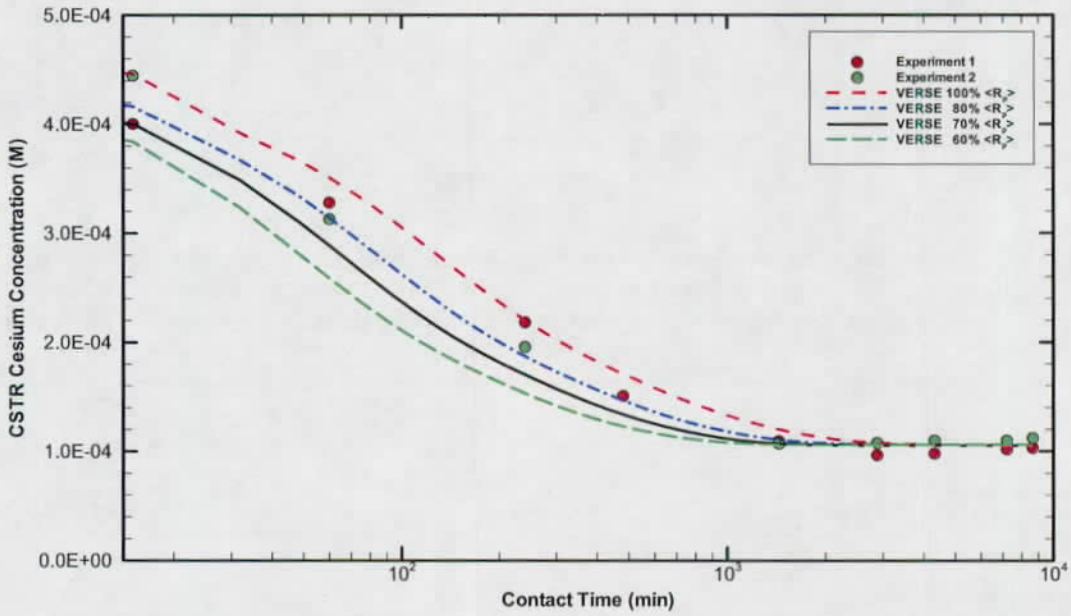

Figure 7-1. Transient aqueous cesium concentration during SRNL kinetics rig operation with 250-Gallon Batch of SuperLig® 644 -20+30 mesh for various particle radii. Cesium pore diffusivity set to 50% of bulk diffusivity in AN-105 simulant.

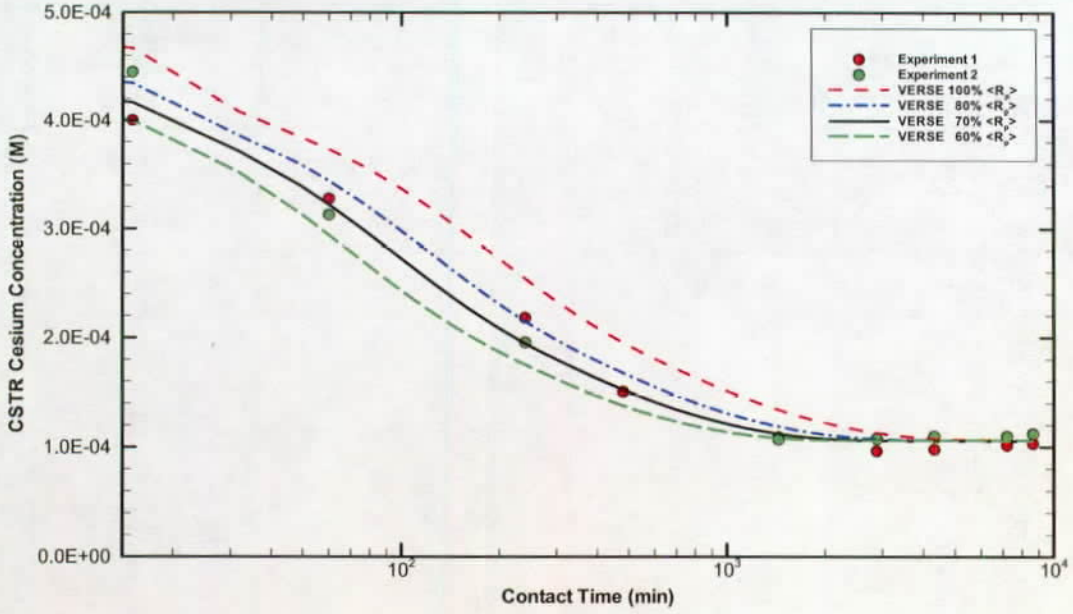

Figure 7-2. Transient aqueous cesium concentration during SRNL kinetics rig operation with 250-Gallon Batch of SuperLig® 644 -20+30 mesh for various particle radii. Cesium pore diffusivity set to 33% of bulk diffusivity in AN-105 simulant.

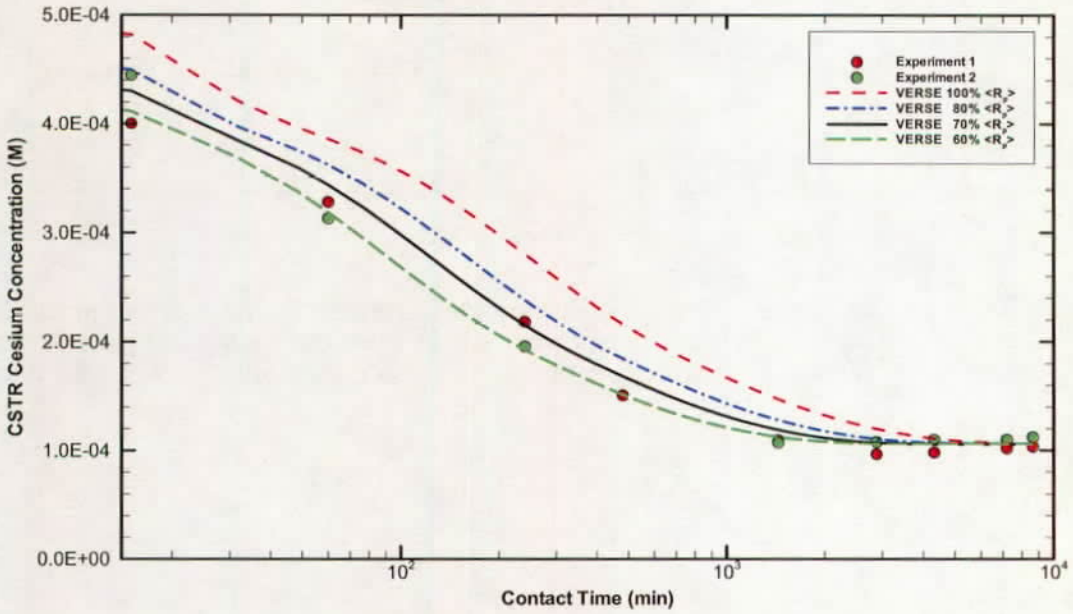

Figure 7-3. Transient aqueous cesium concentration during SRNL kinetics rig operation with 250-Gallon Batch of SuperLig® 644 -20+30 mesh for various particle radii. Cesium pore diffusivity set to 25% of bulk diffusivity in AN-105 simulant.

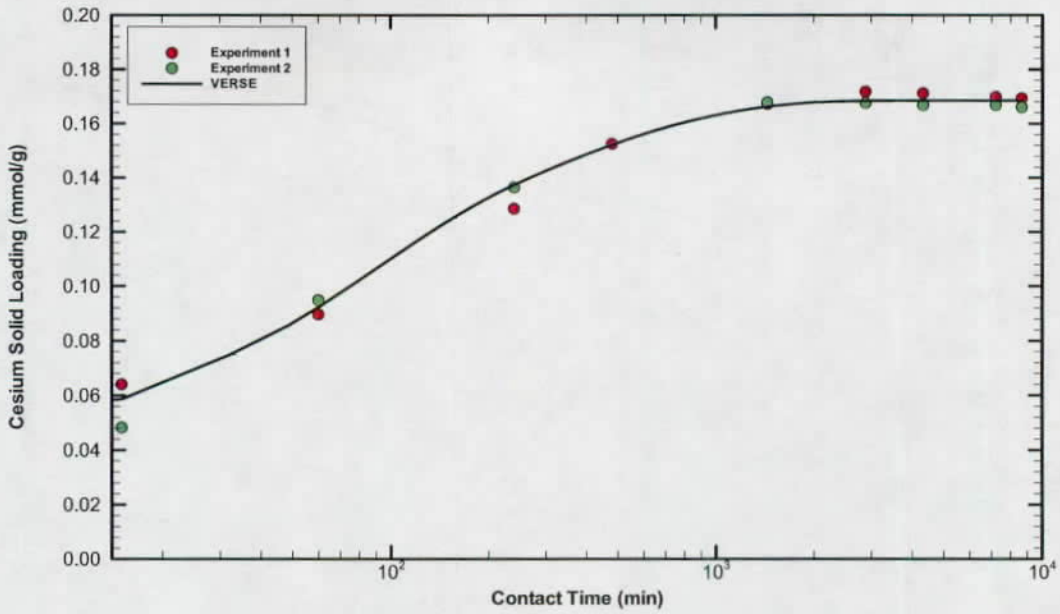

Figure 7-4. Transient cesium solid loading during SRNL kinetics rig operation with 250-Gallon Batch of SuperLig® 644 -20+30 mesh. Parameter settings set to $\phi = 0.7$ and $\tau = 3$.

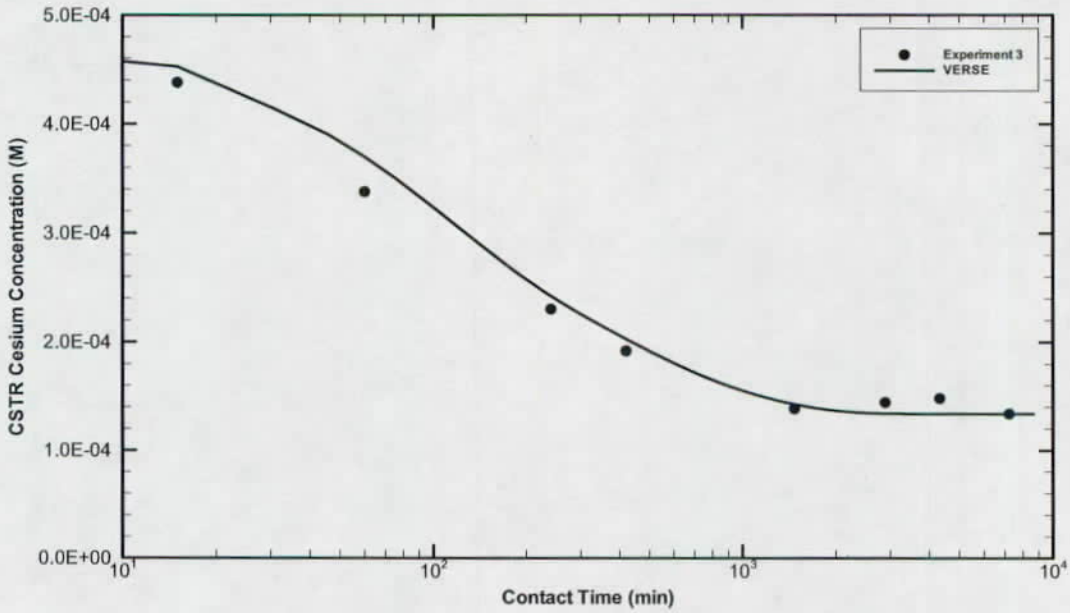

Figure 7-5. Transient aqueous cesium concentration during SRNL kinetics rig operation with 250-Gallon Batch of SuperLig® 644 -20+25 mesh. Cesium pore diffusivity set to 25% of bulk diffusivity in AN-105 simulant.

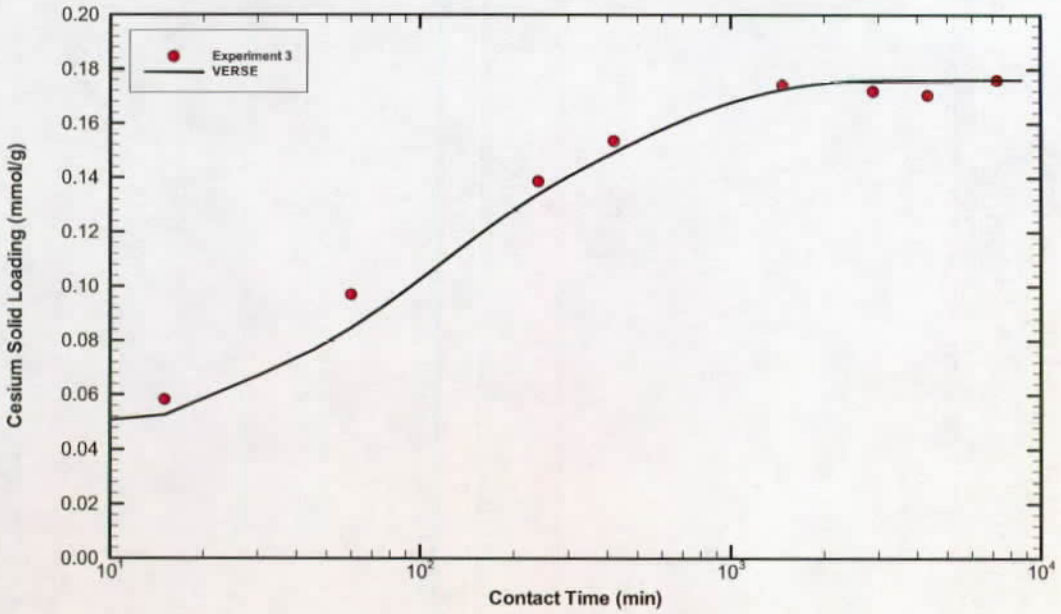

Figure 7-6. Transient cesium solid loading during SRNL kinetics rig operation with 250-Gallon Batch of SuperLig® 644 -20+25 mesh. Cesium pore diffusivity set to 33% of bulk diffusivity in AN-105 simulant.

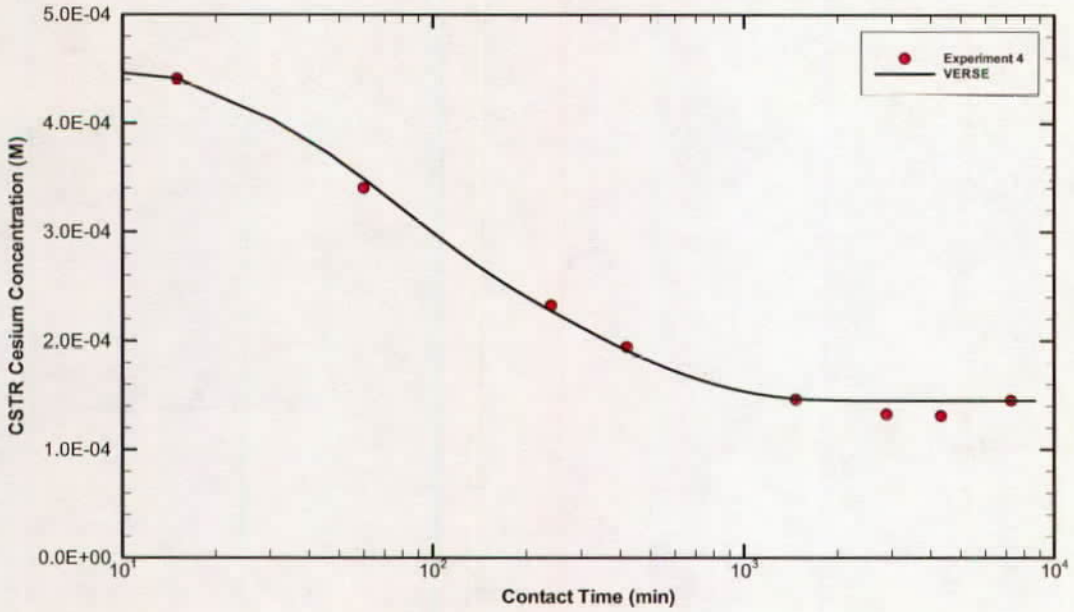

Figure 7-7. Transient aqueous cesium concentration during SRNL kinetics rig operation with 250-Gallon Batch of SuperLig® 644 -25+30 mesh. Cesium pore diffusivity set to 33% of bulk diffusivity in AN-105 simulant.

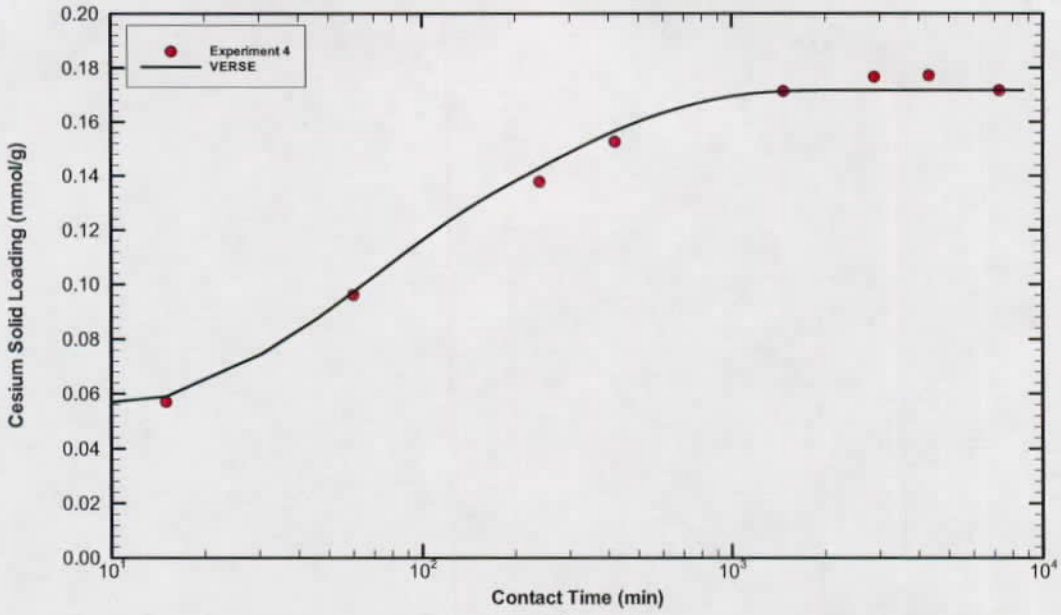

Figure 7-8. Transient cesium solid loading during SRNL kinetics rig operation with 250-Gallon Batch of SuperLig® 644 -25+30 mesh. Cesium pore diffusivity set to 33% of bulk diffusivity in AN-105 simulant.

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8.0 Axial Dispersion and Film Diffusion

For details on axial dispersion and film diffusion correlation values required to perform a VERSE-LC column performance analysis see Hamm et al. (2000b, preliminary Cs removal performance using SuperLig® 644 report), Hamm et al. (2000c, preliminary Tc removal performance using SuperLig® 639 report), and Hamm et al. (2002b, Cs removal performance using CST report).

In this section we present the correlations used to define: (1) axial dispersion along the bed length and (2) mass transfer across the liquid film separating the bed fluid from its neighboring particle pore fluid.

8.1 Film Diffusion

For the laboratory-scale column tests and proposed full-scale facility, with the SuperLig® 644 resin particle size distributions, the Reynolds number range is approximately 0.1 to 1.0. With respect to published literature this is a very low Reynolds number range. Numerous mass transfer correlations exist as discussed by Foo and Rice (1975, see their Figure 2). One of the correlations compared in Foo and Rice (1975) is one developed by Wilson and Geankoplis (1966) based on low Reynolds number data. Large variations between correlations can be seen; however, our sensitivity to the film coefficient is low as shown in the section discussing sensitivities. Since VERSE-LC has the Wilson and Geankoplis (1966) correlation as an option and this correlation falls somewhat within the spread of available low Reynolds number data we have chosen it for all the column simulations in this report. For each ion species considered, the Wilson and Geankoplis (1966) correlation is expressed as:

$$J \equiv \left[\frac{k_{fi}}{u\varepsilon_b}\right] Sc_i^{2/3} = \frac{1.09}{\varepsilon_b} Re^{-2/3}, \qquad (8\text{-}1)$$

where the Reynolds number is defined as

$$Re \equiv \frac{2R_p \rho_w u \varepsilon_b}{\mu_w},$$

and the Schmidt number for each species is defined as

$$Sc_i \equiv \frac{\mu_w}{\rho_w D_i^{\infty}}.$$

A standard deviation of approximately 25% is reported for Eq. (8-1) by Wilson and Geankoplis (1966), while from comparison to the various correlations presented by Foo and Rice (1975) a standard deviation of 100% to 200% is observed.

8.2 Axial Dispersion

Axial dispersion in packed columns is the result of mechanical dispersion added onto molecular diffusion. For practical flowrates mechanical dispersion dominates. For well-packed columns of sufficient diameter such that wall effects (i.e., channeling) are minimal a variety of correlations exist for long column performance. A brief discussion of minimum column sizing is presented in Brooks (1994).

In the low Reynolds number range of interest the Chung and Wen (1968) correlation is applicable for sufficiently large columns (i.e., large diameter and length) and is expressed as:

$$E_b = \frac{2R_p u \varepsilon_b}{0.2 + 0.011 \mathrm{Re}^{0.48}}, \qquad (8\text{-}2)$$

where the standard deviation of this correlation based on all available data points was reported to be 46%. Equation (8-2) applies for only sufficiently large columns and correction factors must be considered for columns with small diameters and/or short active bed lengths.

8.2.1 Radial Flow Maldistribution

Flow maldistribution is caused by packing irregularities. As such the bed porosity varies over the cross-section of a column and increases as the outer wall is approached (even for well-packed columns). "Channeling" near the wall becomes more serious for smaller column diameters and larger particle sizes. As a "rule of thumb" Helfferich (1962) states that this effect becomes significant when the bed diameter is less than thirty times the particle diameter.

The experimental and mathematical basis for this rule of thumb stems from the work of Schwartz and Smith (1953) and Morales et al. (1951). Their experimental efforts were for uniform packing of either spheres or cylinders using air-flow rates in the range of 145 to 547 cm/min. Over the range of their database they concluded that:

- The radial velocity profile (normalized) is independent of total flowrate and
- The divergence of the radial velocity profile from uniform behavior is less than 20% for column diameter to particle diameter ratios greater than 30.

A measure of the degree of non-uniformity in the radial velocity profiles can be made by looking at the ratio of peak-to-average velocity. Based on the limited database of Schwartz and Smith (1953) this peak-to-average velocity ratio is plotted versus column-to-particle diameter ratio in Figure 8-1. As illustrated in Figure 8-1 velocity ratios greater than 100% can occur for column-to-particle diameter ratios less than 10 and beyond ~50 the impact is negligible. Also shown in Figure 8-1 is a least squares fit of the data in the power law form:

$$\frac{u_{peak}}{u_{CL}} = \begin{cases} 4.3786\left(\dfrac{D}{2<R_p>}\right)^{-0.372935} & \text{for } \dfrac{D}{2<R_p>} < 52.44 \\ 1.0 & \text{for } \dfrac{D}{2<R_p>} \geq 52.44 \end{cases} . \quad (8\text{-}3)$$

Note that Eq. (8-3) is based on packed beds with uniformly shaped cylinders and air-flow rates in the range of 145 to 547 cm/min. This correlation may be suspect for conditions of non-uniformly shaped particles with liquid flows in the range of 0.5 to 12 cm/min as applies to the various column tests considered in this report.

Dorweiler and Fahien (1959) performed similar experiments that agreed with Schwartz and Smith (1953) and went to flowrates as low as 30 cm/min. In a later study by Fahien and Smith (1955) significant radial effects were observed for column-to-particle diameters less than 20.

The impact associated with non-uniform radial velocity profiles manifests itself in spreading out the exit breakthrough curves in a manner similar to increased axial dispersion. In the simulations performed in this report no explicit account was made for this apparent increase in axial dispersion.

When shrinkage of the resin results due to the feed conditions further channeling (sometimes referred to here as fingering) can occur. Byrne and Lapidus (1955) discuss this briefly in their technical note. For the SuperLig 644 resin shrinkage occurs upon increased ionic strength of the feed; however, the total ionic strength variations only occur during the first 5 to 10 column volumes.

8.2.2 Headspace and Short Column Impacts

Liles and Geankoplis (1960) conducted experiments to ascertain the impact short column lengths and void headspaces have on axial dispersion in packed bed columns. When end effects were eliminated they concluded that no effects of length on axial dispersion were observed. However, in the presence of end effects such as void headspaces significant effects of length can result. A summary of their data is presented in Figure 8-2 illustrating that the impact can become significant for columns under ~20 cm. Also shown in Figure 8-2 is a least squares fit of the data in the power law form:

$$\frac{E_b(L)}{E_b(L \to \infty)} = 1.0 + 61.4988L^{-1.20799} , \quad (8\text{-}4)$$

where column length is in units of cm. In the simulations performed in this report explicit account was made for this apparent increase in axial dispersion based on the power law fit shown in Figure 8-2 and given by Eq. (8-4).

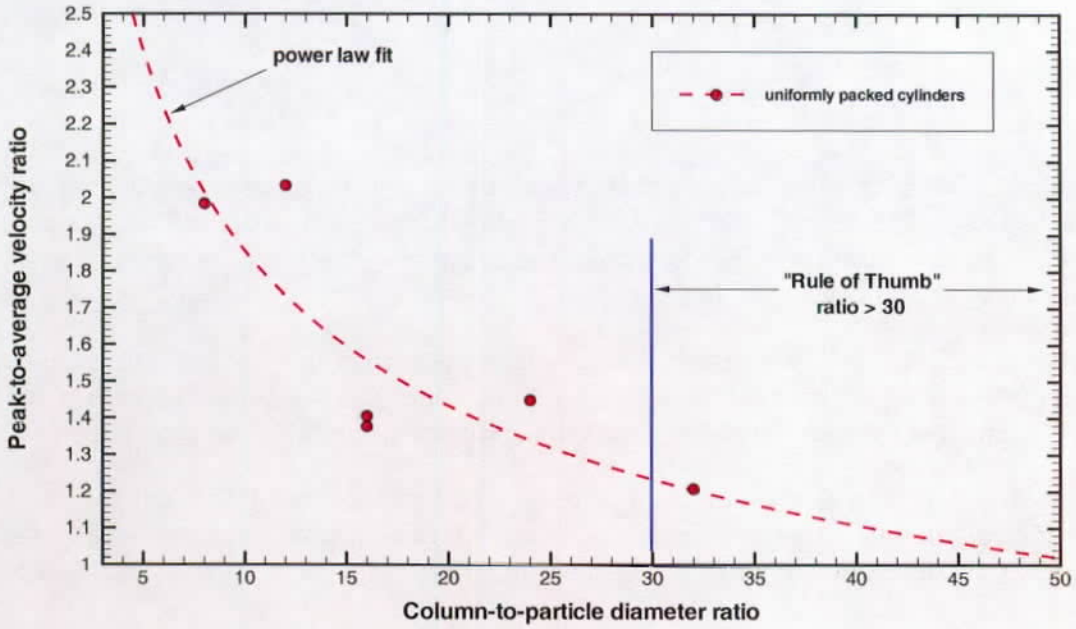

Figure 8-1. Estimated impact of column-to-particle diameter ratios on radial velocity profile based on the limited data by Schwartz and Smith (1953).

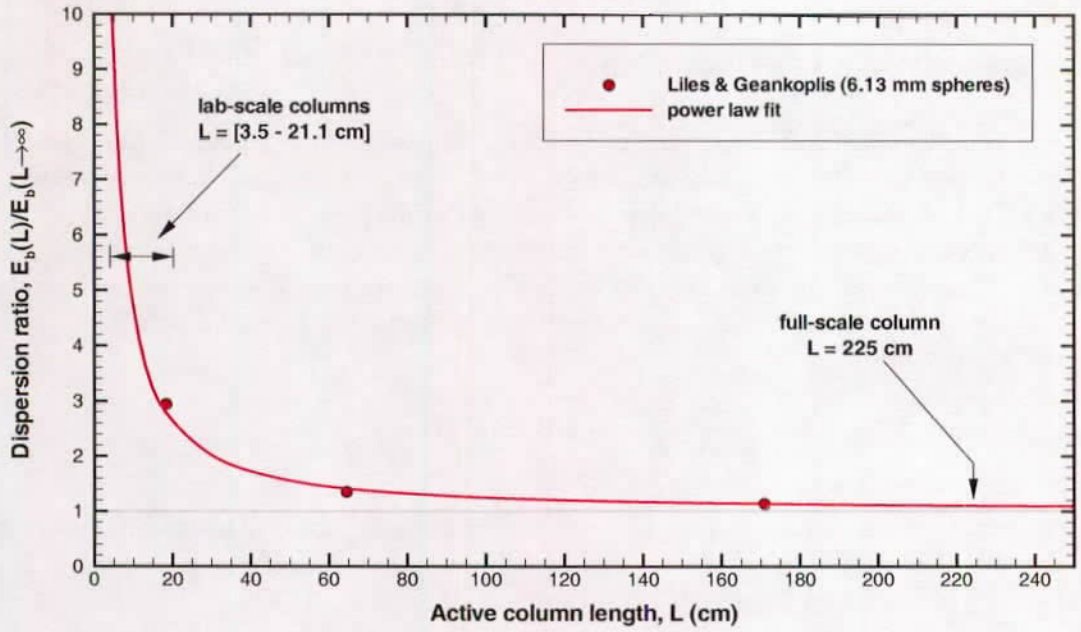

Figure 8-2. Estimation of the impact from end effects and short columns on axial dispersion based on the limited data by Liles and Geankoplis (1960).

9.0 Laboratory-Scale Column Assessments

Several laboratory-scale column experiments have been performed to measure the cesium removal capability of the SuperLig® 644 resin for feed conditions typical for a range of Hanford waste types (AN-105 and AZ-102).

VERSE-LC was used to model three column experiments where cesium breakthrough curves were experimentally measured for the 250-Gallon Batch (Serkiz et al., 2004) and 25-Gallon Batch 1 (Fiskum et al., 2004) of SuperLig® 644. The SRNL loading column test utilized a -20 to +30 mesh cut of SuperLig® 644 from the 250-Gallon Batch in AN-105 simulant. The PNNL loading column tests were performing using a -20 to +70 and a -20 to +30 mesh cut of SuperLig® 644 from the 25-Gallon Batch 1 in AZ-102 simulant. Figures 9-1 through 9-3 show comparisons of these model calculations to experimental data. The VERSE-LC input and output files for each of the simulations are listed in Appendix C.

9.1 SRNL Column Data

The SRNL ion exchange column apparatus consisted of a glass column with an internal diameter of 2.67 cm and water cooled to 25 ± 1°C. A sample from the 250-Gallon Batch of SuperLig® 644 was wet sieved to the -20 to +30 mesh range and pretreated prior to loading into the column. The mass of damp Na-form resin put in the column was 66.2 grams which produced a resin height of 17.2 cm. An F-Factor of 0.4225 was computed based on the average of quadruplicate measurements. The reported pre-column run dry mass of resin in Na-form was 28.0 grams. A column flowrate of AN-105 simulant was established at 3.43 ml/min (2.14 BV/hr) with an inlet cesium concentration of 77.5 μg/ml (5.8275E-4 M). The onset of breakthrough was 140 BVs. At the time of run termination of 260 BVs, 94.3% breakthrough had been attained.

The VERSE-LC model was compared with the SRNL column data from Table 4-36 of Serkiz et al. (2004), which utilized the -20 to +30 mesh cut of SuperLig® 644 from the 250-Gallon Batch. In the model $< d_p >$ was assigned a value of 476.2 μm, which is 70% of the number median diameter for the -20 to +30 mesh range in Table 6-13. The AN-105 cesium isotherm parameters for the -20 to +30 mesh range are given in Table 4-7 at 25°C. The bulk diffusivity of Cs^+ in AN-105 simulant is given in Table 7-1 at 25°C. The tortuosity factor of 3, given in Section 7, was used to compute the pore diffusivity. Bed and particle porosity are given in Section 5. The bed density was computed from the dry mass of Na-form resin and the bed volume. From Figure 9-1 it can be seen that the model is in reasonable agreement with the data.

9.2 PNNL Column Data

In addition to comparisons with SRNL data, the VERSE-LC model was also compared to PNNL column data, as shown in Figures 9-2 and 9-3. The PNNL tests were designated as Column 1 and Column 9. A description of the tests is reported in Fiskum et al. (2004). The Column 1 test utilized SuperLig® 644 resin from the 25-Gallon Batch 1, which was sieved to -20 to +70 mesh and contacted with AZ-102 simulant. In the Column 9 test, SuperLig® 644 resin from the 250-Gallon Batch was sieved to -20 to +30 mesh and contacted with AZ-102 simulant.

Each ion exchange column was 10 cm tall with an inside diameter of 2.0 cm. The fluid level above the resin bed was maintained at nominally the 9.5 ml height. Depending on whether the resin was expanded or contracted, fluid volume above the resin bed varied from nominally 9 ml to 17 ml. The dry mass of resin was computed using an F-factor for damp resin in H-form.

9.2.1 Column 1 Data

Column 1 tested the -20 to +70 mesh range of SuperLig® 644 from the 25-Gallon Batch 1 with 48.7 μg/ml cesium in the AZ-102 simulant. The mass of dry H-form resin added to the column was 4.07 grams which expanded in AZ-102 simulant to produce an initial resin height of 5.6 cm and a resin volume of 17.6 ml. By the end of the Cycle 1 loading, the resin height had decreased to 5.1 cm with a resin volume of 16.0 ml. In the PNNL report, 16.34 ml/BV was used to compute BVs processed which corresponds to a resin height of 5.20 cm. A column flowrate of AZ-102 simulant was established at an average value of 0.42 ml/min (1.54 BV/hr) with an inlet cesium concentration of 48.7 μg/ml (3.66E-4 M). Cycle 1 cesium breakthrough did not occur until 180 BVs, 50% breakthrough was at approximately 240 BVs.

The VERSE-LC model was compared with the PNNL Column 1, Cycle 1 load data from Table C.1 of Fiskum et al. (2004), which utilized the -20 to +70 mesh cut of SuperLig® 644 from the 25-Gallon Batch 1. In the model $< d_p >$ was assigned a value of 216.4 μm, which is 70% of the number median diameter (Average of Sample 1 and 2) in Table 6-10. Although the data were obtained for -20 to +70 mesh range, the model used the AZ-102 cesium isotherm parameters for the -20 to +30 mesh range given in Table 4-7 at 25°C. The bulk diffusivity of Cs^+ in AZ-102 simulant is given in Table 7-1 at 25°C. The tortuosity factor of 3 given in Section 7 was used to compute the pore diffusivity. Bed and particle porosity are given in Section 5. The I-factor for converting from a dry H-form resin mass to a dry Na-form resin mass was established as 1.10 based on information from Toth (2004). The bed density was estimated from the computed dry-Na resin mass of 4.477 grams and a bed volume of 16.34 ml. The total ionic capacity of the resin, C_T, in Table 7-1 was increased by 15% to match the breakthrough point of the experimental data. From Figure 9-2 it can be seen that the model is in reasonable agreement with the data. The VERSE-LC cesium breakthrough curve is steeper than the data which translates to better particle kinetics in the model.

9.2.2 Column 9 Data

Column 9 tested the -20 to +30 mesh range of SuperLig® 644 from the 250-Gallon Batch with 48.7 μg/ml cesium in the AZ-102 simulant. The mass of dry H-form resin added to the column was 4.649 grams which expanded in AZ-102 simulant to produce a resin height of 6.2 cm and a resin volume of 19.5 ml. In the PNNL report, 20.4 ml/BV was used to compute BVs processed which corresponds to a resin height of 6.50 cm in 1 M NaOH. A column flowrate of AZ-102 simulant was established at an average value of 0.58 ml/min (1.79 BV/hr) with an inlet cesium concentration of 48.7 μg/ml (3.66E-4 M). Cycle 1 cesium breakthrough did not occur until 133 BVs , 50% breakthrough was at approximately 195 BVs.

The VERSE-LC model was compared with the PNNL Column 9, Cycle 1 load data from Table C.9 of Fiskum et al. (2004), which utilized the -20 to +30 mesh cut of SuperLig® 644 from the

250-Gallon Batch. In the model $< d_p >$ was assigned a value of 476.2 μm, which is 70% of the number median diameter in Table 6-13. The AZ-102 cesium isotherm parameters for the -20 to +30 mesh range are given in Table 4-7 at 25°C. The bulk diffusivity of Cs^+ in AZ-102 simulant is given in Table 7-1 at 25°C. The tortuosity factor of 3 given by Section 7 was used to compute the pore diffusivity. Bed and particle porosity are given in Section 5. The I-factor for converting from a dry H-form resin mass to a dry Na-form resin mass was established as 1.10 based on information from Toth (2004). The bed density was estimated from the computed dry-Na resin mass of 5.113 grams and a bed volume of 19.5 ml. From Figure 9-3, it can be seen that the model has premature cesium breakthrough with respect to the data. The 50% breakthrough point computed by the model is consistent with the data. The solid and dash-dot curves represent the cesium breakthrough using the OLI Stream Analyzer calculation of Cs^+ bulk diffusivity in AZ-102 and AN-105 simulant, respectively. The bulk diffusivity of Cs^+ in AN-105 simulant is 39% larger than the value in AZ-102 simulant (Table 7-1). The sodium concentration is nominally 5 M in both simulants. The sensitivity of the bulk diffusivity to other compositional differences (Table 4-6) between the two simulants is not well understood. The computation of bulk diffusivities by the OLI Stream Analyzer warrants further investigation and benchmarking.

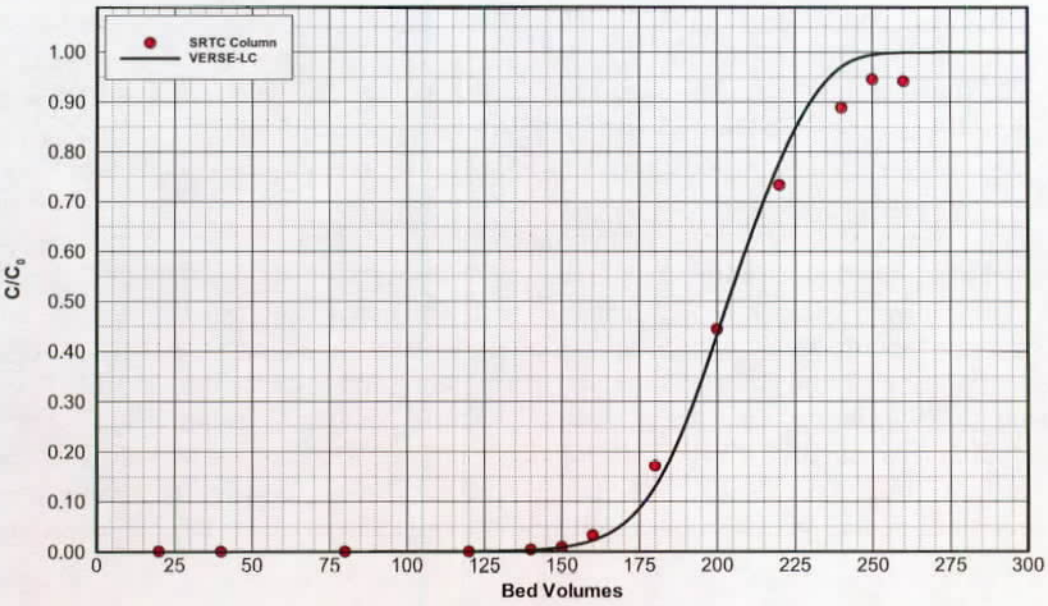

Figure 9-1. Comparison of VERSE-LC cesium breakthrough with data from the SRNL Column test. A -20 to +30 mesh cut of SuperLig® 644 from the 250-Gallon Batch was tested with AN-105 simulant.

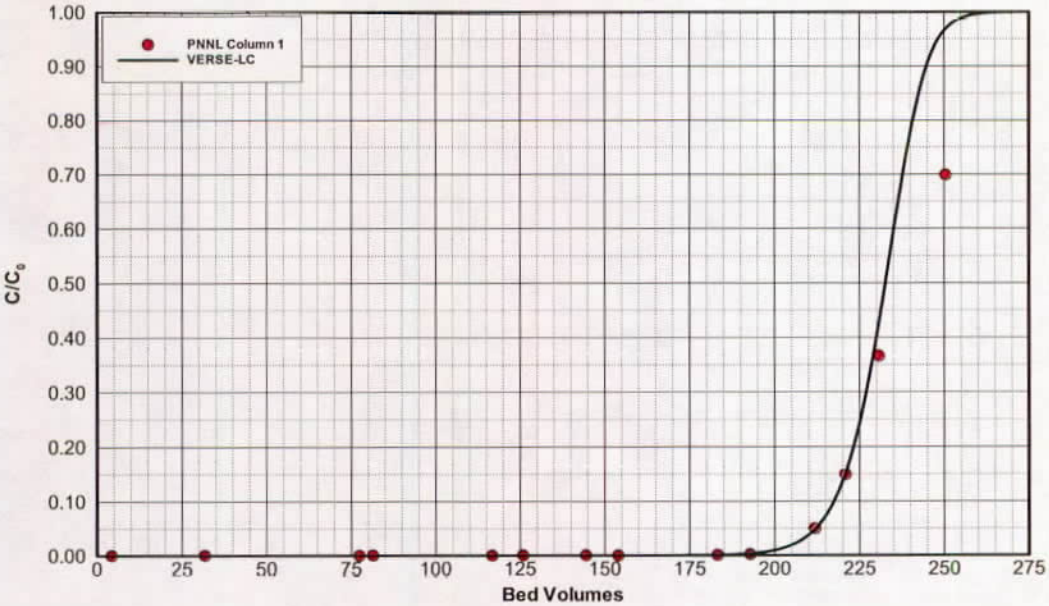

Figure 9-2. Comparison of VERSE-LC cesium breakthrough with data from the PNNL Column 1, Cycle 1 test. A -20 to +70 mesh cut of SuperLig® 644 from the 25-Gallon Batch 1 was tested with AZ-102 simulant.

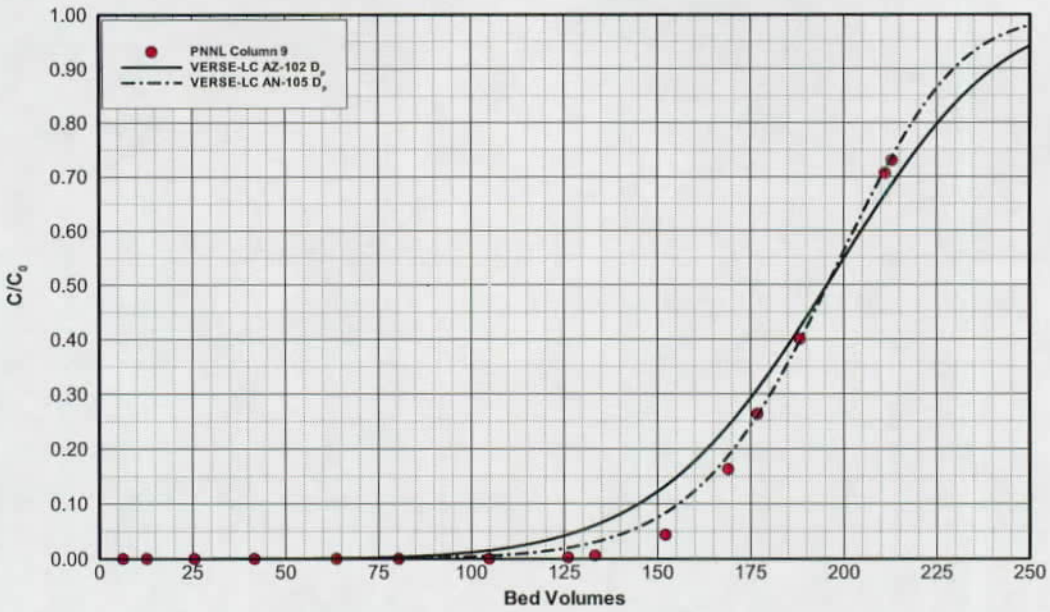

Figure 9-3. Comparison of VERSE-LC cesium breakthrough with data from the PNNL Column 9, Cycle 1 test. A -20 to +30 mesh cut of SuperLig® 644 from the 250-Gallon Batch was tested with AZ-102 simulant.

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10.0 Full-Scale Column Predictions

A series of VERSE-LC simulations were performed to predict the cesium removal performance of a full-scale facility consisting of a three-column carousel configuration. Each resin bed contained within a single column was 48 inches in diameter and 53 inches high. A total bed volume of 415 gallons of resin was assumed. The dimensions and operating parameters of the columns were specified by WTP. Nominal operations for "Nominal Hot Commissioning", "Envelope B Operations" and "Subsequent Operations" were investigated. In addition, sensitivity studies were made for the Nominal Hot Commissioning Operation feeds. The impact of degradation (due to resin usage; handled through reduction in the total Cs sorption capacity and referred to as a degradation factor) was examined for each of the three nominal feed cases. Facility carouseling operations were performed based on exit cesium product criteria as supplied by Toth (2003). For the carousel analyses no safety limit on the total amount of ^{137}Cs inventory within a given column was imposed.

The computed number of bed volumes to reach cesium product criterion at the exit of the lag column is provided in Tables 10-1 through 10-3 for column operation under nominal parameter settings. Results for both fresh resin and estimated chemically degraded resin after 10 operating cycles are provided. Similar bed volume results are provided in Tables 10-4 and 10-5 for the various sensitivity simulations performed for the Hot Commissioning Operation feed where the nominal isotherm used represents the 10 cycle degraded resin bed. A basic star pattern approach to the sensitivity runs was employed. See Appendix D for the nominal input and output results for the three nominal feed stream case runs.

When a ^{137}Cs inventory limit is also imposed on the column loading, we find that the number of BVs to process the "Envelope B Operations" and "Subsequent Operations" feed streams become limited. A LAW feed loading limit of 75,000 Ci was provided by Toth (2003). Given this inventory limit VERSE predictions indicate that this limit is reached in 43 BVs for the Envelope B Operations feed stream and 338 BVs for the Subsequent Operations feed stream. Table 10-6 summarizes the number of bed volumes required to reach the LAW loading limit (LLL), Limiting Condition for Operation (LCO)limit and Technical Safety Limit (TSL) of 75000, 125000 and 150000 Ci, respectively. Appendix E describes the method used to calculate total Cs inventories.

Figures 10-1 and 10-2 show the cesium breakthrough predictions for a full-scale 3 column carousel under Hot Commissioning Operations feed assuming fresh and chemically degraded resin, respectively.

Figures 10-3 and 10-4 show the cesium breakthrough predictions for a full-scale 3 column carousel under Envelope B Operations feed assuming fresh and chemically degraded resin, respectively.

Figures 10-5 and 10-6 show the cesium breakthrough predictions for a full-scale 3 column carousel under Subsequent Operations feed assuming fresh and chemically degraded resin, respectively.

Figure 10-7 shows the cesium breakthrough prediction for the lead column under Hot Commissioning Operations feed. The impact on breakthrough with variation in potassium concentration is shown for the first cycle. The order of breakthrough is from high to low potassium concentration.

Figure 10-8 shows the cesium breakthrough prediction for the lead column under Hot Commissioning Operations feed. The impact on breakthrough with variation in sodium concentration is shown for the first cycle. The order of breakthrough is from high to low sodium concentration. The premature breakthrough at high sodium concentration is due to a highly reduced cesium pore diffusivity. This impact has not been quantified experimentally.

Figure 10-9 shows the cesium breakthrough prediction for the lead column under Hot Commissioning Operations feed. The impact on breakthrough with variation in hydroxide concentration is shown for the first cycle. The order of breakthrough is from low to high hydroxide concentration. The apparent cesium capacity is a function of pH

Figure 10-10 shows the cesium breakthrough prediction for the lead column under Hot Commissioning Operations feed. The impact on breakthrough with variation in cesium concentration is shown for the first cycle. The order of breakthrough is from high to low cesium concentration.

Figure 10-11 shows the cesium breakthrough prediction for the lead column under Hot Commissioning Operations feed. The impact on breakthrough with variation in liquid flowrate is shown for the first cycle. The order of breakthrough is from high to low liquid flowrate.

Figure 10-12 shows the cesium breakthrough prediction for the lead column under Hot Commissioning Operations feed. The impact on breakthrough with variation in pore diffusivity is shown for the first cycle. The order of breakthrough is from low to high pore diffusivity.

Figure 10-13 shows the cesium breakthrough prediction for the lead column under Hot Commissioning Operations feed. The impact on breakthrough with variation in particle radius is shown for the first cycle. The order of breakthrough is from high to low particle radius.

Figure 10-14 shows the cesium breakthrough prediction for the lead column under Hot Commissioning Operations feed. The impact on breakthrough with variation in bed denity is shown for the first cycle. The order of breakthrough is from low to high bed density. Lower bed density implies less ion exchange sites which leads to earlier breakthrough.

Table 10-1. Number of bed volumes required to reach lag column Cs breakthrough during three-column carousel operation for Nominal Hot Commissioning Operations. Both degraded and fresh resin bed results are provided.

Percent Degradation (%)	Cycle Number	Lead Column Exit Concentration Ratio (%)	Number of bed volumes required to reach lag column exit criterion (BV)
0	1	93	371

Percent Degradation (%)	Cycle Number	Lead Column Exit Concentration Ratio (%)	Number of bed volumes required to reach lag column exit criterion (BV)
0	2	72	240
0	3	57	249
0	4	51	255
0	5	49	259
20	1	93	298
20	2	71	192
20	3	56	200
20	4	50	204
20	5	50	207

Table 10-2. Number of bed volumes required to reach lag column Cs breakthrough during three-column carousel operation for Nominal Envelope B Operations. Both degraded and fresh resin bed results are provided.

Percent Degradation (%)	Cycle Number	Lead Column Exit Concentration Ratio (%)	Number of bed volumes required to reach lag column exit criterion (BV)
0	1	100	693
0	2	100	359
0	3	100	359
0	4	100	359
0	5	100	360
20	1	100	556
20	2	100	287
20	3	100	288
20	4	100	288
20	5	100	287

Table 10-3. Number of bed volumes required to reach lag column Cs breakthrough during three-column carousel operation for Nominal Subsequent Operations. Both degraded and fresh resin bed results are provided.

Percent Degradation (%)	Cycle Number	Lead Column Exit Concentration Ratio (%)	Number of bed volumes required to reach lag column exit criterion (BV)
0	1	100	729
0	2	99	468
0	3	97	482
0	4	96	491
0	5	96	496
20	1	100	584
20	2	99	374
20	3	97	386
20	4	96	393
20	5	96	397

Table 10-4. Number of bed volumes required to reach lag column Cs breakthrough during three-column carousel operation for Nominal Hot Commissioning Operations 20% degradation factor applied. Parameter sensitivity results provided for isotherm competitors.

Cycle Number	Nominal (20% degraded)	Cs (+20%)	Cs (-20%)	Na (+20%)	Na (-20%)	K (+20%)	K (-20%)	OH (+20%)	OH (-20%)
1	298	294	301	49	361	246	367	315	280
2	192	191	194	45	218	162	234	201	183
3	200	198	201	45	224	169	242	208	190
4	204	203	205	45	228	173	247	213	195
5	207	206	208	46	229	176	251	216	198
6	210	208	211	46	232	177	254	219	199
7	210	209	212	46	233	177	255	219	200

Table 10-5 Number of bed volumes required to reach lag column Cs breakthrough during three-column carousel operation for Nominal Hot Commissioning Operations 20% degradation factor applied. Parameter sensitivity results provided for VERSE input variables.

Cycle Number	Nominal (20% degraded)	Flow (22 gpm)	Flow (5 gpm)	D_p (+20%)	D_p (-20%)	R_p (+20%)	R_p (-20%)	ρ_b (+20%)	ρ_b (-20%)
1	298	268	362	310	281	269	328	356	239
2	192	183	211	196	187	183	202	231	154
3	200	192	215	203	195	192	207	239	160
4	204	197	218	207	200	197	211	245	164
5	207	199	220	210	203	199	214	248	167
6	210	200	-	212	204	199	216	251	168
7	210	199	-	214	205	200	217	252	168

Table 10-6. Bed volumes required to reach ^{137}Cs loading limits.

LAW Feed Operations	Isotherm	LLL 75000 Ci	LCO 125000 Ci	TSL 150000 cI
Hot Commissioning	Nominal	na	na	na
Hot Commissioning	Degraded	na	na	na
Envelope B	Nominal	43	70	84
Envelope B	Degraded	43	70	84
Subsequent	Nominal	337	na	na
Subsequent	Degraded	339	na	na

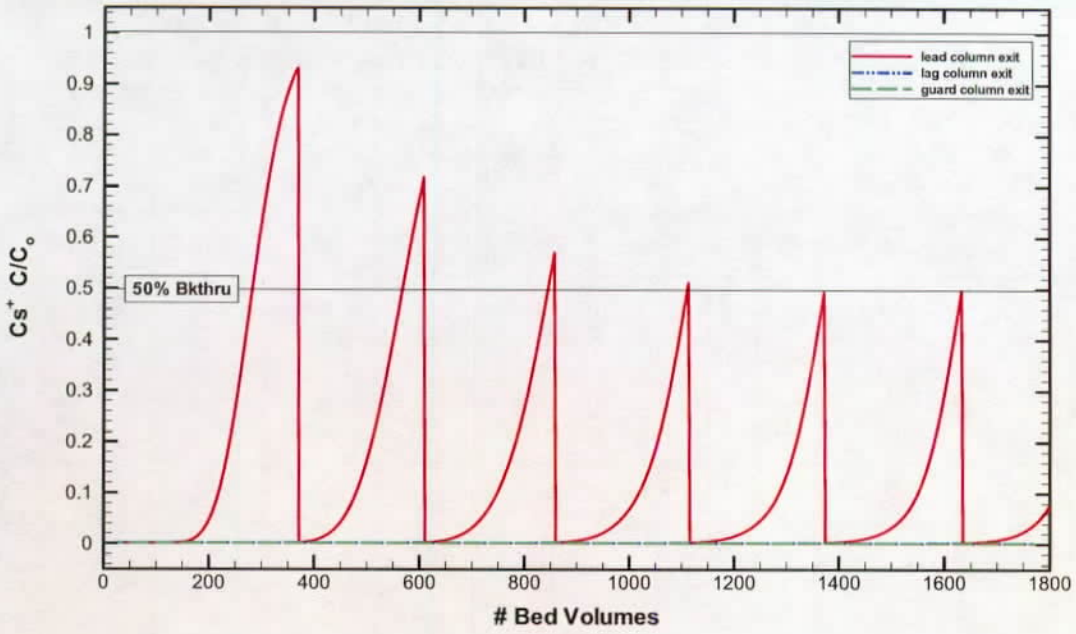

Figure 10-1. VERSE-LC cesium breakthrough predictions for a full-scale 3 column carousel under Hot Commissioning Operations feed. The calculations assume fresh SuperLig® 644 resin.

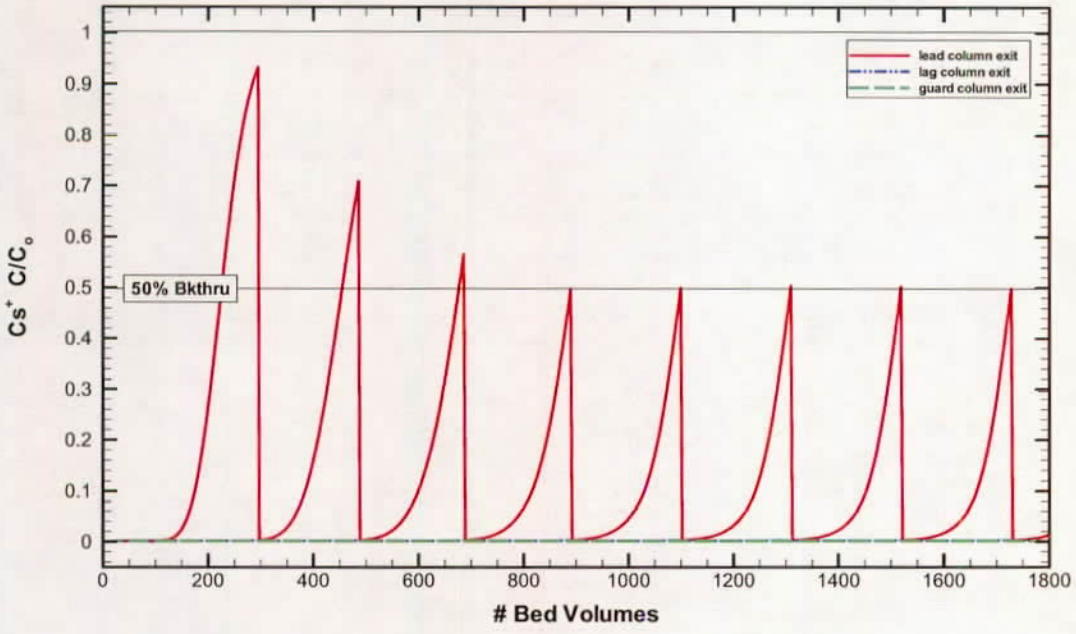

Figure 10-2. VERSE-LC cesium breakthrough predictions for a full-scale 3 column carousel under Hot Commissioning Operations feed. The calculations assume chemically degraded SuperLig® 644 resin.

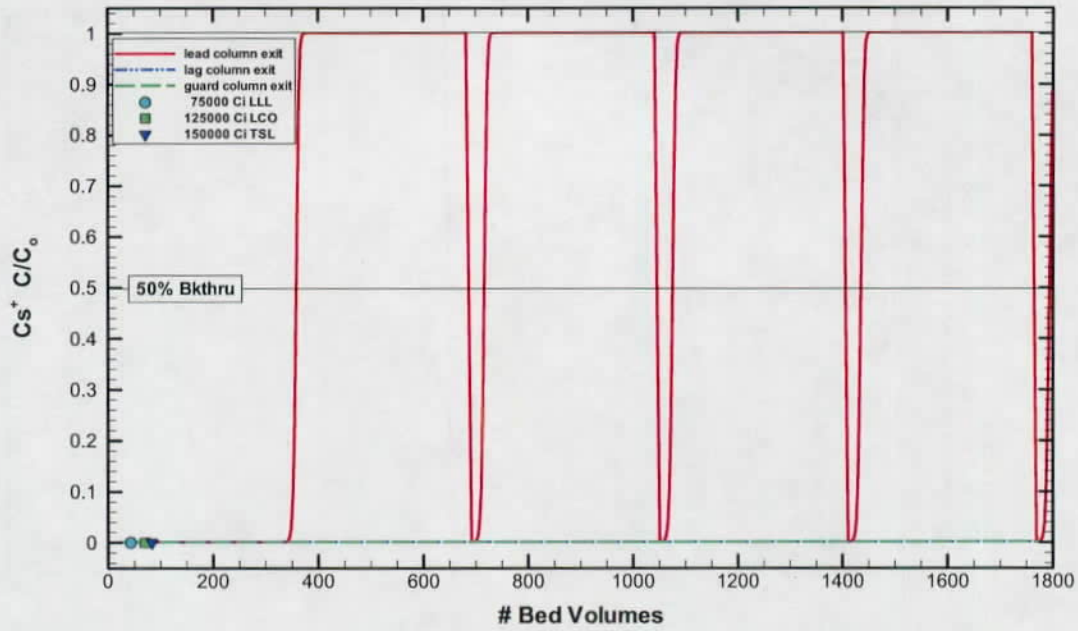

Figure 10-3. VERSE-LC cesium breakthrough predictions for a full-scale 3 column carousel under Envelope B Operations feed. The calculations assume fresh SuperLig® 644 resin.

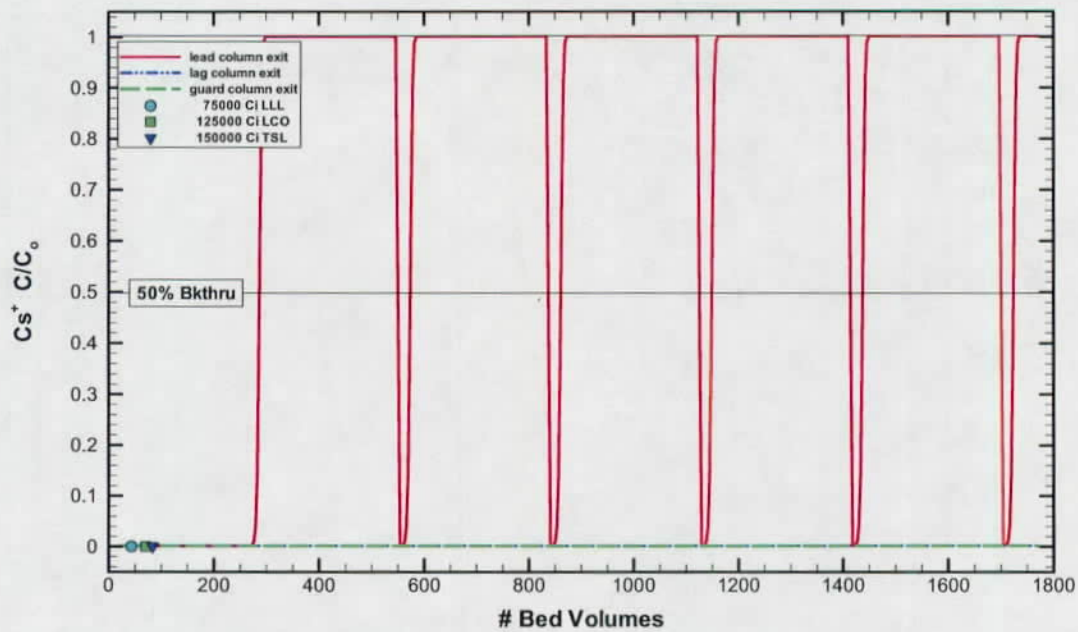

Figure 10-4. VERSE-LC cesium breakthrough predictions for a full-scale 3 column carousel under Envelope B Operations feed. The calculations assume chemically degraded SuperLig® 644 resin.

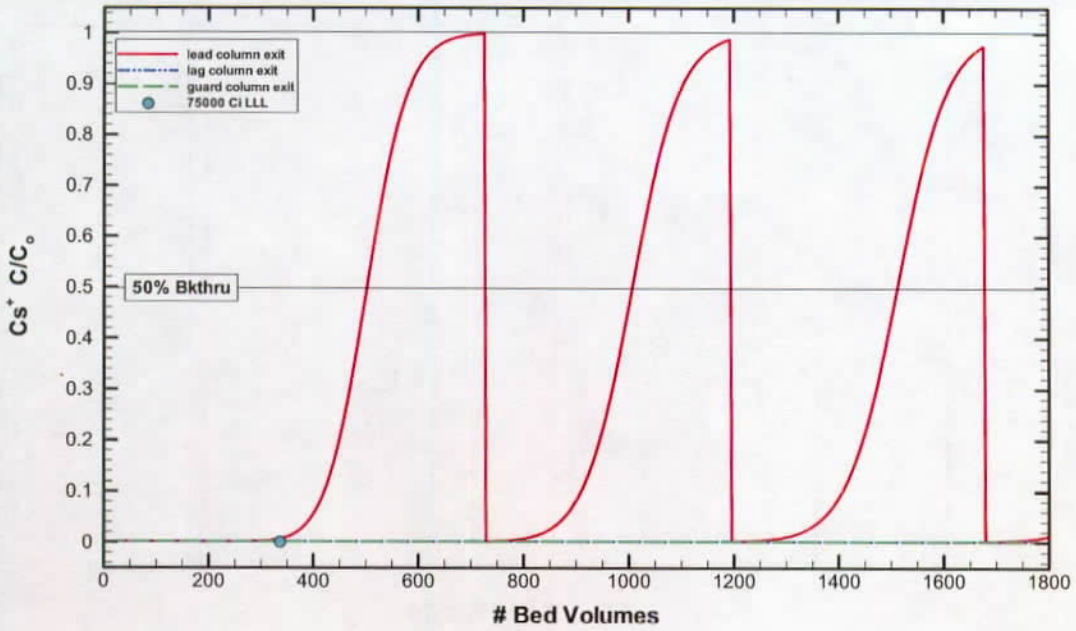

Figure 10-5. VERSE-LC cesium breakthrough predictions for a full-scale 3 column carousel under Subsequent Operations feed. The calculations assume fresh SuperLig® 644 resin.

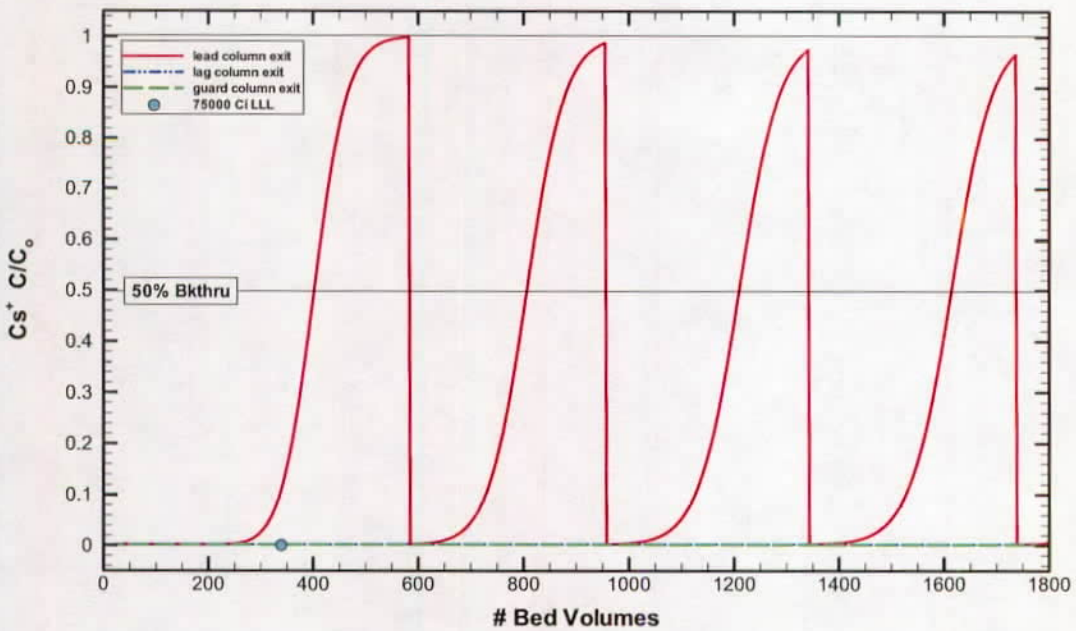

Figure 10-6. VERSE-LC cesium breakthrough predictions for a full-scale 3 column carousel under Subsequent Operations feed. The calculations assume chemically degraded SuperLig® 644 resin.

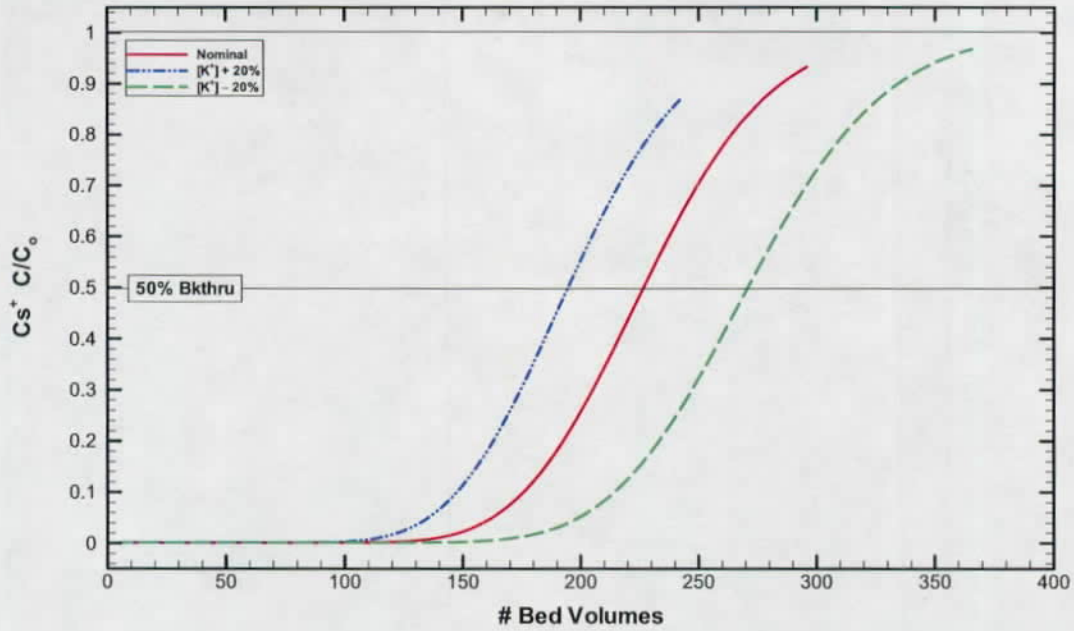

Figure 10-7. VERSE-LC cesium breakthrough prediction for the lead column under Hot Commissioning Operations feed. The impact on breakthrough with variation in potassium concentration is shown for the first cycle.

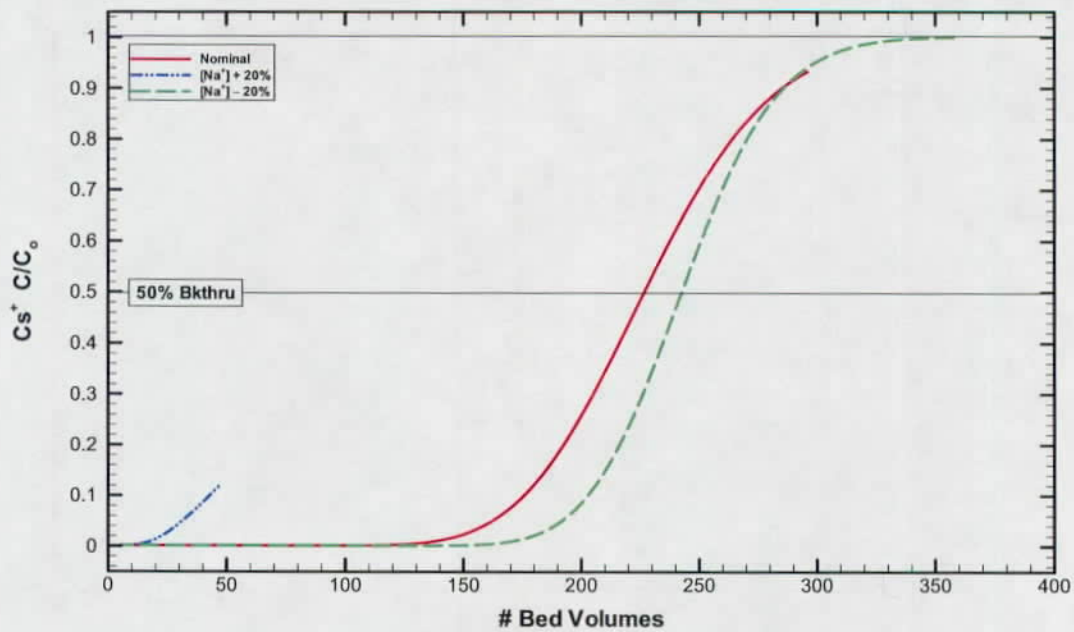

Figure 10-8. VERSE-LC cesium breakthrough prediction for the lead column under Hot Commissioning Operations feed. The impact on breakthrough with variation in sodium concentration is shown for the first cycle.

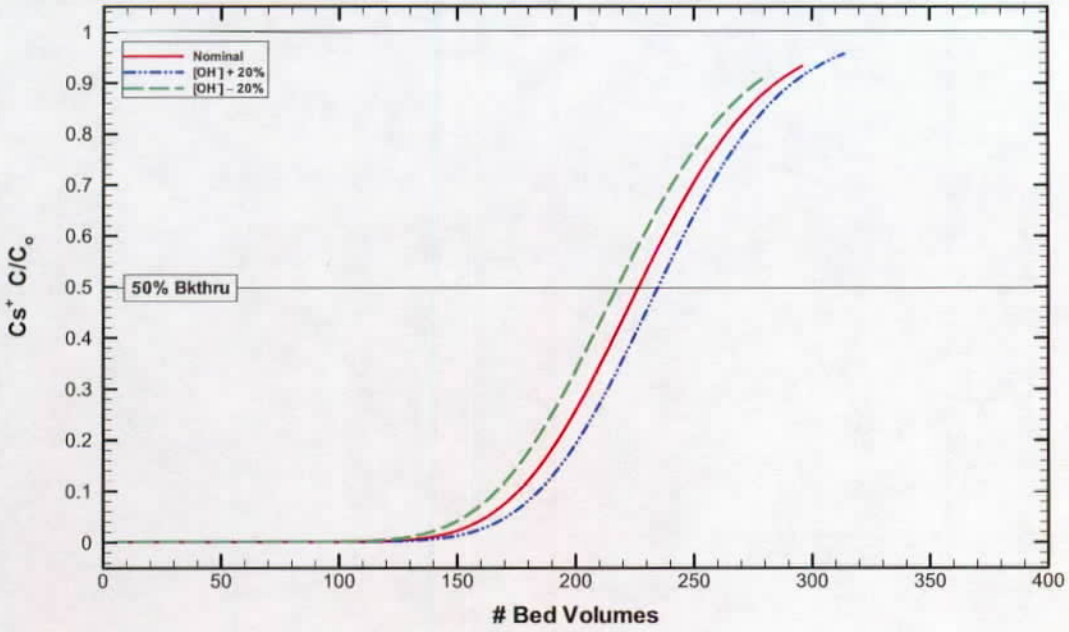

Figure 10-9. VERSE-LC cesium breakthrough prediction for the lead column under Hot Commissioning Operations feed. The impact on breakthrough with variation in hydroxide concentration is shown for the first cycle.

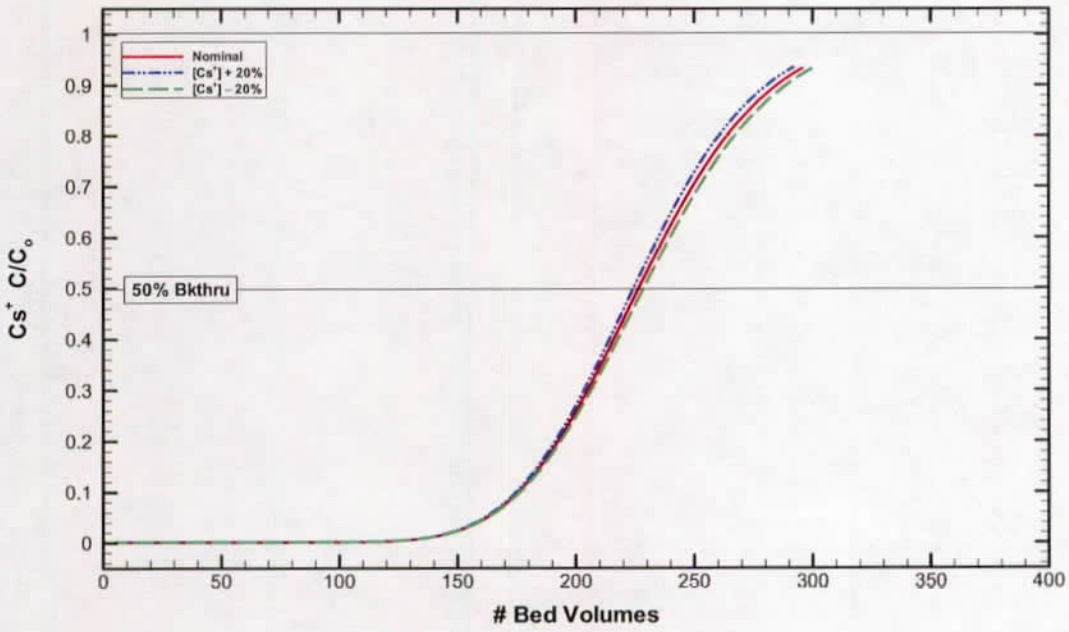

Figure 10-10. VERSE-LC cesium breakthrough prediction for the lead column under Hot Commissioning Operations feed. The impact on breakthrough with variation in cesium concentration is shown for the first cycle.

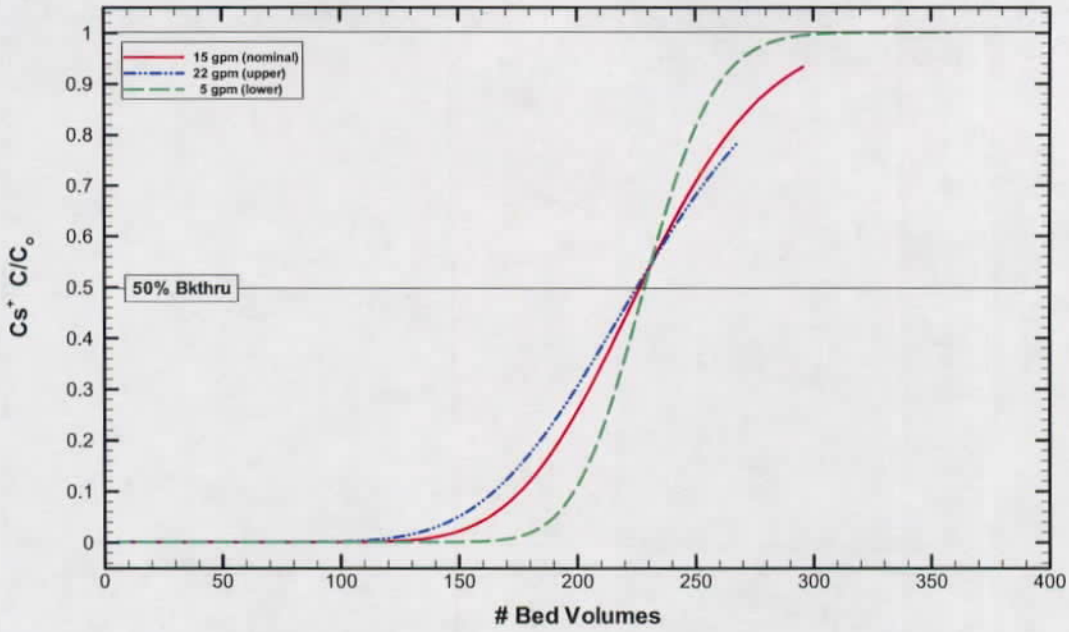

Figure 10-11. VERSE-LC cesium breakthrough prediction for the lead column under Hot Commissioning Operations feed. The impact on breakthrough with variation in liquid flowrate is shown for the first cycle.

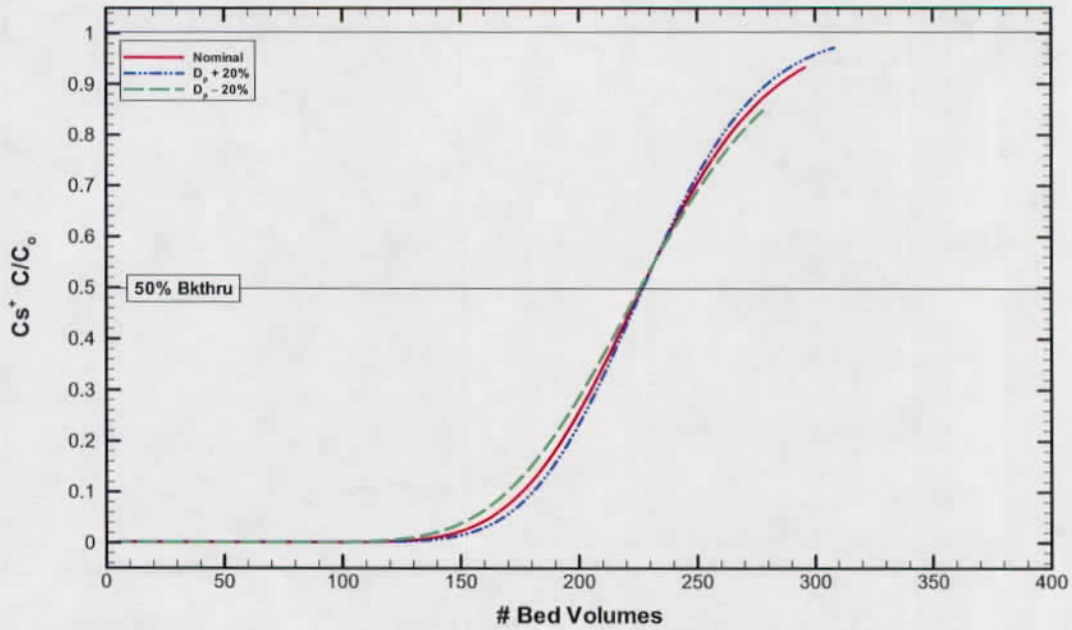

Figure 10-12. VERSE-LC cesium breakthrough prediction for the lead column under Hot Commissioning Operations feed. The impact on breakthrough with variation in pore diffusivity is shown for the first cycle.

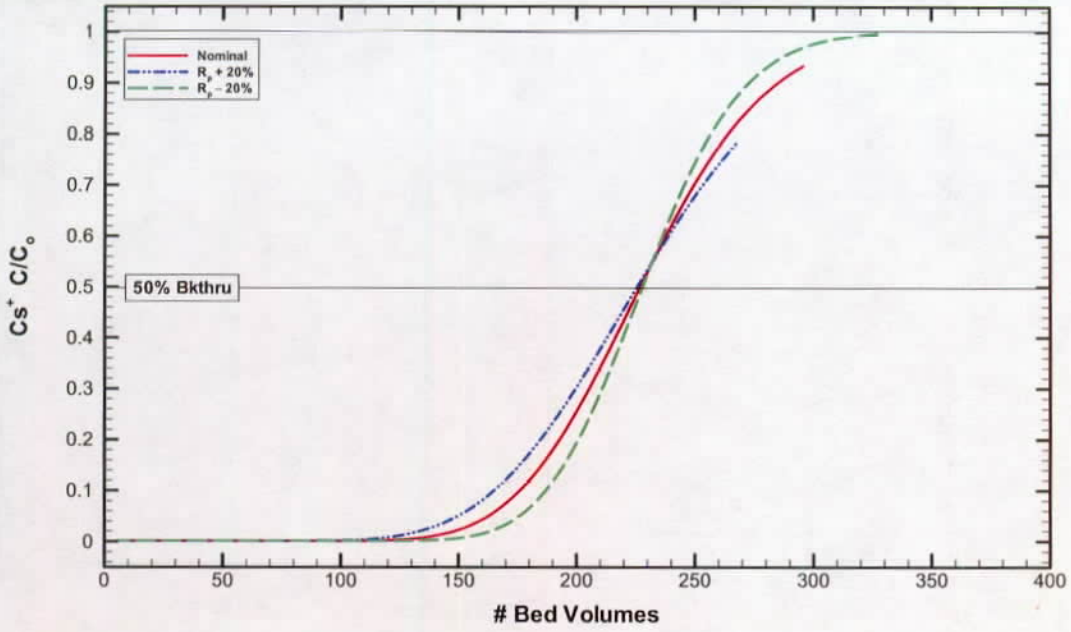

Figure 10-13. VERSE-LC cesium breakthrough prediction for the lead column under Hot Commissioning Operations feed. The impact on breakthrough with variation in particle radius is shown for the first cycle.

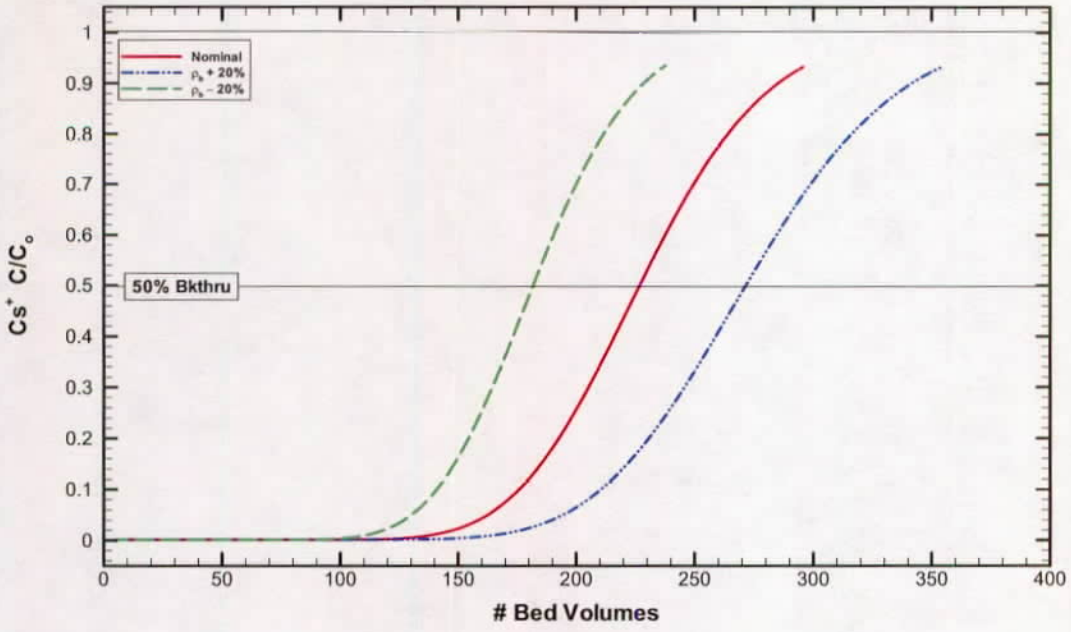

Figure 10-14. VERSE-LC cesium breakthrough prediction for the lead column under Hot Commissioning Operations feed. The impact on breakthrough with variation in bed density is shown for the first cycle.

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Appendix A (Detailed Thermodynamic Isotherm Model)

The Thermodynamic Modeling of IX Processes (TMIXP) code is software developed by the Savannah River National Laboratory to simulate ion-exchange equilibria of electrolytic solutions and SuperLig® 644 or Resorcinol-Formaldehyde (RF) solid resin. TMIXP is written in FORTRAN 90 and compiled with Compaq Visual Fortran Version 6.6.B. For applications at SRNL, a Win32 version running under Windows 2000 Professional is used. This appendix contains or references the necessary material for using version 1.0 of TMIXP (i.e., executable referred to as tmixp.exe).

A.1 Model Description

The TMIXP model solves a set of equations for solid-liquid equilibrium. This model includes the competitive ion exchange at SuperLig® 644 or RF exchange sites between the following homovalent cations: Na^+, Cs^+, H^+ and K^+. Non-idealities within the aqueous phase are handled using Pitzer's model for calculating ionic activity coefficients and water activity. Since Pitzer only established modeling parameters for some of the most common ions up to an ionic strength of ~6 molal, errors may occur when one uses the TMIXP code beyond 6 molal or when addressing solutions containing ions whose Pitzer parameters do not exist. A listing of the currently available ionic species contained within the TMIXP database is provided in Table A-1.

Table A-1. Ionic species available within the TMIXP ion-exchange equilibrium model

ID	Cations	MW	Anions	MW
1	Al+++	26.9815	Al(OH)4-	95.0107
2	Ba++	137.327	C2O4--	88.019
3	Ca++	40.078	CH3COO-	59.0439
4	Cd++	112.411	Cl-	35.453
5	Co++	58.9332	COOH-	45.0174
6	Cr+++	51.9961	CO3--	60.0089
7	Cs+	132.905	F-	18.9984
8	Cu++	63.546	HCO3-	61.0168
9	Fe+++	55.845	HPO4--	95.9793
10	H+	1.0079	NO2-	46.0055
11	K+	39.0983	NO3-	62.0049
12	Li+	6.941	OH-	17.0073
13	Mg++	24.305	PO4---	94.9714
14	Mn++	54.938	SO4--	96.0626
15	Na+	22.9898	na	na
16	Ni++	58.6934	na	na

ID	Cations	MW	Anions	MW
17	Pb++	207.2	na	na
18	Sr++	87.62	na	na
19	UO2++	270.028	na	na
20	Zn++	65.409	na	na

Surface non-idealities on the solid phase SuperLig® 644 or RF material are handled by assuming that solid phase is ideal.

Mass-action relationships are written for each of the potential competitors (Na^+, Cs^+, H^+ and K^+). Also species material balance equations are written relating the amount of each species within the liquid and solid phases in the initial state to amounts in the final ("equilibrium") state. To obtain these material balances the mass of SuperLig® 644 or RF and mass of liquid (i.e., volume of liquid and its density) must also be specified. Solution of this set of nonlinear algebraic equations is achieved using a modified Powell hybrid algorithm and a finite-difference approximation to the Jacobian (Visual Numerics Inc., 1997, IMSL® DNEQNF subroutine).

The solid-liquid equilibrium model solves the various mass-action equations involving ion exchange in conjunction with the appropriate material balance equations. The user must also supply coefficients to a two-parameter hyperbolic fit of apparent cesium capacity as a function of hydroxide concentration. At a specified operating temperature (C) and solution density (g/L) TMIXP performs a simulated batch contact ("K_d") test where the quantity of the following variables at their initial state must be specified:

- Initial composition of aqueous solution (M)
- Amount of aqueous solution present (L)
- Amount of SuperLig® 644 or RF material present (g)
- Initial form of SuperLig® 644 or RF (loading fractions in Na^+, Cs^+, H^+ and K^+ form, must total to 1.0, typically resin is in Na^+ or H^+)

Upon solving the simulated batch contact test, TMIXP outputs the following detailed information:

- Header and title
- Liquid temperature
- Species name (cations to anions), molecular weight, valence and initial molar concentration
- Initial moles of water

- Initial ionic strength of solution
- Equilibrium constants
- Liquid volume and resin mass
- Total ion exchange capacity
- Cs^+, K^+, Na^+, H^+ initial fractional and total solid loadings
- Convergence criterion and maximum number of nonlinear iterations
- Normalized residual and L2 norm of residual
- Species equilibrium molarities, molalities and ionic activity coefficients
- Equilibrium moles of water and water activity
- Equilibrium ionic strength and pH
- Equilibrium Cs^+, K^+, Na^+, and H^+ aqueous concentration, K_d and solid loading.

In order to mathematically predict the state of the solid-electrolyte system, there are three essential steps involved. These are

1. Formulating a proper set of nonlinear algebraic equations in order to represent the system.
2. Obtaining, via published material and/or nonlinear regression, the required coefficients for the equilibrium constants and species interaction parameters for activity coefficient calculations.
3. Solving the nonlinear algebraic system numerically.

A.2 Model Formulation

Formulating a model for an isothermal solid-electrolyte system requires stating in mathematical expressions the following

1. Mass-action or reaction equilibria
2. Phase equilibria
3. Material balances
4. Electroneutrality

The following mass-action expressions apply for a waste solution in contact with SuperLiq® 644 or RF resin assuming a single site ion-exchange model

$$\overline{K^+} + Cs^+ \xleftrightarrow{K_{12}} \overline{Cs^+} + K^+, \quad K_{12}(T) = \frac{\hat{\gamma}_{Cs^+} Q_{Cs^+} \gamma_{K^+} m_{K^+}}{\hat{\gamma}_{K^+} Q_{K^+} \gamma_{Cs^+} m_{Cs^+}} \tag{A-1}$$

$$\overline{Na^+} + Cs^+ \xleftrightarrow{K_{13}} \overline{Cs^+} + Na^+, \quad K_{13}(T) = \frac{\hat{\gamma}_{Cs^+} Q_{Cs^+} \gamma_{Na^+} m_{Na^+}}{\hat{\gamma}_{Na^+} Q_{Na^+} \gamma_{Cs^+} m_{Cs^+}} \tag{A-2}$$

$$\overline{H^+} + Cs^+ \xleftrightarrow{K_{14}} \overline{Cs^+} + H^+, \quad K_{14}(T) = \frac{\hat{\gamma}_{Cs^+} Q_{Cs^+} \gamma_{H^+} m_{H^+}}{\hat{\gamma}_{H^+} Q_{H^+} \gamma_{Cs^+} m_{Cs^+}} \tag{A-3}$$

where the bar over the cation designates the concentration in the solid phase and

K_{ij} .....equilibrium constant of cation i and cation j reaction

$\hat{\gamma}_i$ .....solid phase activity coefficient of ion i

Q_i .....solid-phase loading of cation i, mmol/g

γ_i .....liquid-phase activity coefficient of ion i

m_i .....molality of ion i

The dissociation of water is

$$H_2O \xleftrightarrow{K_w} H^+ + OH^-, \quad K_w(T) = \frac{\gamma_{H^+} m_{H^+} \gamma_{OH^-} m_{OH^-}}{a_w} \tag{A-4}$$

where a_w is the activity of water.

The total cesium, potassium and sodium ionic solid loadings are

$$Q_{Cs^+} = Q^\circ_{Cs^+} + (c^\circ_{Cs^+} - c_{Cs^+})\phi \tag{A-5}$$

$$Q_{K^+} = Q^\circ_{K^+} + (c^\circ_{K^+} - c_{K^+})\phi \tag{A-6}$$

$$Q_{Na^+} = Q^\circ_{Na^+} + (c^\circ_{Na^+} - c_{Na^+})\phi \tag{A-7}$$

where

Q°_i .....initial solid-phase loading of cation i, mmol/g

c°_i .....initial concentration of ion i, mmol/ml

c_i .....equilibrium concentration of ion i, mmol/ml

ϕ .....phase ratio of liquid to resin mass, ml/g

The total ionic capacity of the resin is computed as

$$C_T = C_T^{max}[OH^-]/(C_T^{coef} + [OH^-]) = Q_{K^+} + Q_{Na^+} + Q_{Cs^+} + Q_{H^+} \quad \text{(A-8)}$$

where:

C_T^{max} .....maximum ionic capacity of resin, mmol/g

C_T^{coef} .....coefficient in hyperbolic fit of C_T vs hydroxide concentration

$[OH^-]$ .....hydroxide concentration in solution, M

The electroneutrality balance is

$$\sum_{i=1}^{cations} z_i m_i = \sum_{j=1}^{anions} z_j m_j \quad \text{(A-9)}$$

where z_i is the ionic species charge. A hydrogen balance is the last required material balance and is expressed as

$$\begin{aligned} &2H_2O(in) + V\left(c^{\circ}_{H^+} + c^{\circ}_{OH^-} + 4c^{\circ}_{Al(OH)_4^-} + 3c^{\circ}_{CH_3O_2^-} + c^{\circ}_{COOH^-} + c^{\circ}_{HCO_3^-} + c^{\circ}_{HPO_4^-}\right) \\ &+ m_s Q^{\circ}_{H^+} = 2H_2O + \frac{H_2O}{\Omega}\left(m_{H^+} + m_{OH^-} + 4m_{Al(OH)_4^-} + 3m_{CH_3O_2^-} + m_{COOH^-}\right. \\ &\left. + m_{HCO_3^-} + m_{HPO_4^-}\right) + m_s Q_{H^+} \end{aligned} \quad \text{(A-10)}$$

where:

$H_2O(in)$ .....moles of water input

H_2O .....moles of water in solution

V .....volume of solution, M

m_s .....mass of resin

Ω .....conversion of moles of water to kg, $1000/M_W$

The set of nonlinear equations (A-1) to (A-10) completes the formulation of the solid-electrolyte system with the following unknowns:

$$\begin{aligned} &H_2O, m_{H^+}, m_{OH^-}, m_{Na^+}, m_{K^+}, m_{Cs^+}, \\ &Q_{H^+}, Q_{Na^+}, Q_{K^+} \text{ and } Q_{Cs^+} \end{aligned} \quad \text{(A-11)}$$

A.3 Pitzer Activity Coefficient Model

A.3.1 Overview

The derivation of the Pitzer activity coefficient model is based on Appendix C of "Aspen Physical Property System Physical Property Methods and Models 11.1" (2001, Aspen Technology, Inc).

A.3.2 Working Equations

Fürst and Renon (1982) propose the following expression as the Pitzer equation for the excess Gibbs energy:

$$\frac{G^E}{RT} = n_w \left[\begin{array}{l} f(I) + \sum_i \sum_j B_{ij} m_i m_j + \sum_i \sum_j \theta_{ij} m_i m_j + \tfrac{1}{2} \sum_i \sum_j \left(\sum_k m_k |z_k| \right) C_{ij} m_i m_j \\ + \tfrac{1}{6} \sum_i \sum_j \sum_k \Psi_{ijk} m_i m_j m_k \end{array} \right] \quad \text{(A-12)}$$

$$B_{ij} = f(\beta_{ij}^{(0)}, \beta_{ij}^{(1)}, \beta_{ij}^{(2)}) \quad \text{(A-13a)}$$

$$C_{ij} = f(C_{ij}^{\phi}, z_i, z_j) \quad \text{(A-13b)}$$

where

G^E .....excess Gibbs energy
R .....gas constant
T .....temperature
n_w .....kilograms of water
z_i .....charge number of ion i
m_i .....molality of ion i
i, j, k .....loop over all cations and anions

B, **C**, **θ** and **Ψ** are interaction parameters, f(I) is an electrostatic term that expresses the effect of long-range electrostatic forces between ions. This takes into account the hard-core effects of the Debye-Hückel theory. The cation-anion parameters **B** and **C** are characteristic for an aqueous single-electrolyte system. These parameters can be determined by the properties of pure (apparent) electrolytes. **B** is expressed as a function of **β** (Eqs. (A-24) and (A-25)). **C** is expressed as a function of C^{ϕ} and z.

The parameters **θ** and **Ψ** are for the difference of interaction of unlike ions of the same sign from the mean of like ions. These parameters can be measured from common-ion mixtures.

The modified Pitzer expression for the excess Gibbs energy orders cations before anions. Fürst and Renon do not. All summations are taken over all ions i and j (both cations and anions). This involves making the parameter matrices B_{ij}, C_{ij}, θ_{ij} and Ψ_{ij} symmetric as follows:

Second-order parameters are written B_{ij} if i and j are ions of different sign. $B_{ij} = 0$ if the sign of z_i = sign of z_j, and $B_{ii} = 0$. Since cations are not ordered before anions, $B_{ij} = B_{ji}$. Second-order parameters are written θ_{ij} if i and j are ions of same sign. Thus $\theta_{ij} = 0$ if the sign of z_i is different from the sign of z_j, and $\theta_{ii} = 0$ with $\theta_{ij} = \theta_{ji}$.

Third-order parameters are written C_{ij} if i and j are ions of different sign. $C_{ij} = 0$ if the sign of z_i = sign of z_j, and $C_{ii} = 0$ with $C_{ij} = C_{ji}$. The matrix **C** is symmetric and $\sum_k m_k|z_k|$ is extended to all ions to make the equation symmetric.

Ψ_{ijk} is written for three different ions $\Psi_{ijk} = \Psi_{kij} = \Psi_{jki}$, and $\Psi_{ikk} = 0$. $\Psi_{ijk} = 0$ if the sign of z_i = sign of z_j = sign of z_k. Fürst and Renon's expression, Eq. (A-12), calculates the expressions for the activity coefficients and osmotic coefficients.

A.3.3 Calculation of Activity Coefficients

Taking the partial derivative of the expression for G^E yields expressions for the ionic activity coefficient

$$\begin{aligned}\ln\gamma_i &= \frac{\partial\left(G^E/RT\right)}{\partial n_i} \\ &= \tfrac{1}{2} z_i^2 f' + 2\sum_j B_{ij} m_j + \tfrac{1}{2} z_i^2 \sum_j \sum_k B'_{jk} m_j m_k + 2\sum_j \theta_{ij} m_j \\ &+ \tfrac{1}{2}|z_i| \sum_j \sum_k C_{jk} m_j m_k + \sum_j \left(\sum_k m_k |z_k| \right) C_{ij} m_j + \tfrac{1}{2} \sum_j \sum_k \Psi_{ijk} m_j m_k\end{aligned} \qquad \text{(A-14)}$$

where $B'_{jk} = dB_{jk}/dI$, $f' = df/dI$, and where the dependence of θ_{ij} on ionic strength is neglected $\left(\theta'_{ij} = 0\right)$. f and parameters B_{ij} are functions of ionic strength.

For water the logarithm of the activity is calculated as follows:

$$\ln a_w = \ln x_w + \ln \gamma_w \qquad \text{(A-15)}$$

The mole fraction of water x_w is computed as

$$x_w = \frac{\Omega}{\Omega + \sum_i m_i} \tag{A-16}$$

where $\Omega = 1000/M_w$ and M_w is the molecular weight of water. For water the logarithm of the activity coefficient is calculated as follows:

$$\ln \gamma_w = \frac{\partial\left(G^E/RT\right)}{\partial N_w} = \frac{\partial\left(G^E/RT\right)}{\Omega \partial n_w} \tag{A-17}$$

where N_w is the number of moles of water. Rearranging Eqn. (A-17) yields

$$\begin{aligned}\Omega \ln \gamma_w = f - If' - \sum_i \sum_j B_{ij} m_i m_j - I \sum_i \sum_j B'_{ij} m_i m_j - \sum_i \sum_j \theta_{ij} m_i m_j \\ - \sum_i \sum_j \left(\sum_k m_z |z_k| \right) C_{ij} m_i m_j - \tfrac{1}{3} \sum_i \sum_j \sum_k \Psi_{ijk} m_i m_j m_k\end{aligned} \tag{A-18}$$

$f(I)$ is the function describing the long-range electrostatic effects as a function of ionic strength as

$$f(I) = -A^{DH} \left(\frac{4I}{b} \right) \ln\left(1 + b\sqrt{I}\right) \tag{A-19}$$

where I is the ionic strength, defined as

$$I = \tfrac{1}{2} \sum_i m_i z_i^2 \tag{A-20}$$

b is an adjustable parameter, which has been optimized in this model to equal 1.2. Taking the derivative of Eq. (A-19) with respect to I, gives

$$f'(I) = \frac{df}{dI} = -2A^{DH} \left[\frac{\sqrt{I}}{1 + b\sqrt{I}} + \frac{2}{b} \ln\left(1 + b\sqrt{I}\right) \right] \tag{A-21}$$

so that

$$f - If' = \frac{2A^{DH} I^{3/2}}{1 + b\sqrt{I}} \tag{A-22}$$

This equation is used in Eq. (A-18). In Eqs. (A-19) and (A-21), A^{DH} is the Debye-Hückel constant for the osmotic coefficient on a log e basis, computed as

$$A^{DH} = \frac{1}{3}\left(\frac{2\pi N_A d_w}{1000}\right)^{1/2}\left(\frac{e}{\sqrt{DkT}}\right)^3 \qquad \text{(A-23)}$$

where

N_A .....Avogadro's number
d_w .....water density
e .....electronic charge
D .....dielectric constant of solvent
k .....Boltzmann's constant
T .....absolute temperature

B_{ij} and B'_{ij} need expressions so that Eqs. (A-14) and (A-18) can be completely solved for the activity coefficients. The parameter B_{ij} is determined differently for different electrolyte pairings. For 1-N electrolytes (1-1, 1-2, 2-1, and so on) the following expression gives the parameter B_{ij}:

$$B_{ij} = \beta_{ij}^{(0)} + \frac{2\beta_{ij}^{(1)}}{\alpha_1^2 I}\left[1-\left(1+\alpha_1 I^{1/2}\right)e^{-\alpha_1 I^{1/2}}\right] \qquad \text{(A-24)}$$

with $\alpha_1 = 2.0$.

For 2-2 electrolytes, B_{ij} is determined by the following expression:

$$B_{ij} = \beta_{ij}^{(0)} + \frac{2\beta_{ij}^{(1)}}{\alpha_1^2 I}\left[1-\left(1+\alpha_1 I^{1/2}\right)e^{-\alpha_1 I^{1/2}}\right] + \frac{2\beta_{ij}^{(2)}}{\alpha_2^2 I}\left[1-\left(1+\alpha_2 I^{1/2}\right)e^{-\alpha_2 I^{1/2}}\right] \qquad \text{(A-25)}$$

with $\alpha_1 = 1.4$ and $\alpha_2 = 12.0$.

By taking appropriate derivatives, expressions for B'_{ij} can be derived for 1-n electrolytes:

$$B'_{ij} = \frac{2\beta_{ij}^{(1)}}{(\alpha_1 I)^2}\left[-1+\left(1+\alpha_1 I^{1/2}+0.5\alpha_1^2 I\right)e^{-\alpha_1 I^{1/2}}\right] \qquad \text{(A-26)}$$

and for 2-2 electrolytes:

$$B'_{ij} = \frac{2\beta_{ij}^{(1)}}{(\alpha_1 I)^2}\left[-1+\left(1+\alpha_1 I^{1/2}+0.5\alpha_1^2 I\right)e^{-\alpha_1 I^{1/2}}\right] + \frac{2\beta_{ij}^{(2)}}{(\alpha_2 I)^2}\left[-1+\left(1+\alpha_2 I^{1/2}+0.5\alpha_2^2 I\right)e^{-\alpha_2 I^{1/2}}\right] \quad \text{(A-27)}$$

The parameters $\beta_{ij}^{(0)}$, $\beta_{ij}^{(1)}$, $\beta_{ij}^{(2)}$ and also C_{ij}^{ϕ}, θ_{ij}, and Ψ_{ijk} can be found in Pitzer's articles (Pitzer, 1991) and other relevant publications (Weber, 2001, and Zemaitis et al., 1986).

A.3.4 Pitzer Parameters

The Pitzer model in the TMIXP code involves user-supplied parameters. These parameters are used in the calculation of binary and ternary parameters for the electrolyte system. These parameters include the binary cation-anion parameters $\beta_{ij}^{(0)}$, $\beta_{ij}^{(1)}$, $\beta_{ij}^{(3)}$ and C_{ij} in Table A-2 at 25 °C, ternary cation-cation parameters θ_{ij} in Table A-3, ternary anion-anion parameters θ_{ij} in Table A-4, ternary cation-anion-anion parameters Ψ_{ijk} in Table A-5 and ternary cation-cation-anion parameters Ψ_{ijk} in Table A-6.

Table A-2. Binary Pitzer Cation-Anion Parameters at 25 °C

Cation	Anion	β_0	β_1	β_2	C
Al^{3+}	Cl^-	0.6993	5.845	0.0	0.7794E-03
Ba^{2+}	Cl^-	0.2628	1.496	0.0	-.6859E-02
Ba^{2+}	NO_3^-	-.3230E-01	0.8025	0.0	0.000
Ba^{2+}	OH^-	0.1717	1.200	0.0	0.000
Ca^{2+}	Cl^-	0.3159	1.614	0.0	-.1202E-03
Ca^{2+}	NO_3^-	0.2108	1.409	0.0	-.7106E-02
Ca^{2+}	SO_4^{2-}	0.2000	2.650	-55.70	0.000
Cd^{2+}	NO_3^-	0.2865	1.668	0.0	-.9051E-02
Cd^{2+}	SO_4^{2-}	0.2053	2.617	-48.07	0.2850E-02
Co^{2+}	Cl^-	0.3643	1.475	0.0	-.4388E-02
Co^{2+}	NO_3^-	0.3119	1.690	0.0	-.2194E-02
Co^{2+}	SO_4^{2-}	0.2000	2.700	0.0	0.000
Cr^{3+}	Cl^-	0.7364	5.255	0.0	-.1302E-01
Cr^{3+}	NO_3^-	0.7040	5.185	0.0	-.1703E-01
Cs^+	$CH_3CO_2^-$	0.1628	0.3605	0.0	-.2775E-02
Cs^+	Cl^-	0.3000E-01	0.5580E-01	0.0	0.1900E-03
Cs^+	F^-	0.1306	0.2570	0.0	-.2150E-02
Cs^+	NO_2^-	0.4270E-01	0.6000E-01	0.0	-.2550E-02
Cs^+	NO_3^-	-.7580E-01	-.6690E-01	0.0	0.000
Cs^+	OH^-	0.1500	0.3000	0.0	0.000
Cs^+	SO_4^{2-}	0.8880E-01	1.111	0.0	-.2121E-02
Cu^{2+}	Cl^-	0.2966	1.391	0.0	-.1273E-01
Cu^{2+}	NO_3^-	0.3168	1.430	0.0	-.7743E-02
Cu^{2+}	SO_4^{2-}	0.2340	2.527	-48.33	0.1100E-02

Cation	Anion	β_0	β_1	β_2	C
H^+	Cl^-	0.1775	0.2945	0.0	0.4000E-03
H^+	NO_3^-	0.1119	0.3206	0.0	0.5000E-03
K^+	$Al(OH)_4^-$	0.1276	0.9700E-01	0.0	-.6000E-02
K^+	$C_2O_4^{2-}$	0.6430E-01	1.524	0.0	0.5000E-03
K^+	$CH_3CO_2^-$	0.1587	0.3251	0.0	-.3300E-02
K^+	Cl^-	0.4750E-01	0.2148	0.0	-.3000E-03
K^+	CO_3^{2-}	0.1288	1.433	0.0	-.1800E-03
K^+	F^-	0.8089E-01	0.2021	0.0	0.4650E-03
K^+	HCO_3^-	-.1071E-01	0.4780E-01	0.0	0.000
K^+	HPO_4^{2-}	0.2480E-01	1.274	0.0	0.5798E-02
K^+	NO_2^-	0.1280E-01	0.6680E-01	0.0	-.5000E-03
K^+	NO_3^-	-.8060E-01	0.7640E-01	0.0	0.2500E-02
K^+	OH^-	0.1632	0.9700E-01	0.0	-.7000E-03
K^+	PO_4^{3-}	0.3729	3.972	0.0	-.2506E-01
K^+	SO_4^{2-}	0.4995E-01	0.7793	0.0	0.000
Li^+	$CH_3CO_2^-$	0.1124	0.2483	0.0	-.2625E-02
Li^+	Cl^-	0.1494	0.3074	0.0	0.1795E-02
Li^+	NO_2^-	0.1336	0.3250	0.0	-.2650E-02
Li^+	NO_3^-	0.1420	0.2780	0.0	-.2755E-02
Li^+	OH^-	0.1500E-01	0.1400	0.0	0.000
Li^+	SO_4^{2-}	0.1363	1.270	0.0	-.1414E-02
Mg^{2+}	Cl^-	0.3524	1.681	0.0	0.1838E-02
Mg^{2+}	NO_3^-	0.3671	1.585	0.0	-.7283E-02
Mg^{2+}	SO_4^{2-}	0.2210	3.343	-37.23	0.6250E-02
Mn^{2+}	Cl^-	0.3272	1.550	0.0	-.7248E-02
Mn^{2+}	SO_4^{2-}	0.2010	2.980	0.0	0.4550E-02
Na^+	$Al(OH)_4^-$	0.5130E-01	0.2481	0.0	0.1300E-02
Na^+	$C_2O_4^{2-}$	0.1621	1.453	0.0	-.8220E-01
Na^+	$CH_3CO_2^-$	0.1426	0.3237	0.0	-.3145E-02
Na^+	Cl^-	0.7430E-01	0.2744	0.0	0.8000E-03
Na^+	HCO_3^-	0.8200E-01	0.2872	0.0	-.2615E-02
Na^+	CO_3^{2-}	0.3620E-01	1.510	0.0	0.1840E-02
Na^+	F^-	0.3300E-01	0.2456	0.0	0.2810E-02
Na^+	HCO_3^-	0.2800E-01	0.4400E-01	0.0	0.000
Na^+	HPO_4^{2-}	-.3045E-01	1.350	0.0	0.3590E-02
Na^+	NO_2^-	0.4980E-01	0.2177	0.0	-.1200E-02
Na^+	NO_3^-	0.2040E-02	0.2368	0.0	0.8000E-04
Na^+	OH^-	0.8690E-01	0.2481	0.0	0.3900E-02
Na^+	PO_4^{3-}	0.2534	3.738	0.0	-.2260E-01
Na^+	SO_4^{2-}	0.2620E-01	1.028	0.0	0.1260E-02
Ni^{2+}	Cl^-	0.3479	1.581	0.0	-.1308E-02
Ni^{2+}	SO_4^{2-}	0.1702	2.907	-40.06	0.9150E-02
Pb^{2+}	NO_3^-	-.3610E-01	0.2850	0.0	0.1874E-02
Sr^{2+}	Cl^-	0.2857	1.667	0.0	-.4596E-03
Sr^{2+}	NO_3^-	0.1346	1.380	0.0	-.7036E-02
UO_2^{2+}	Cl^-	0.4607	1.613	0.0	-.1115E-01
UO_2^{2+}	CO_3^{2-}	0.4607	1.613	0.0	-.1115E-01
UO_2^{2+}	HCO_3^-	0.3220	1.827	0.0	-.1760E-01

Cation	Anion	β_0	β_1	β_2	C
UO_2^{2+}	NO_3^-	0.4607	1.613	0.0	-.1115E-01
UO_2^{2+}	OH^-	0.4274	1.644	0.0	-.1303E-01
UO_2^{2+}	SO_4^{2-}	0.3220	1.827	0.0	-.4400E-02
Zn^{2+}	Cl^-	0.2602	1.643	0.0	-.3111E-01
Zn^{2+}	NO_3^-	0.3481	1.691	0.0	-.5551E-02
Zn^{2+}	SO_4^{2-}	0.1949	2.883	-32.81	0.7250E-02

Table A-3. Ternary Pitzer Cation-Cation Parameters

Cation	Cation	0
Ba^{2+}	Cs^+	-.1500
Ba^{2+}	H^+	-.3600E-01
Ba^{2+}	K^+	-.7200E-01
Ba^{2+}	Li^+	-.7000E-01
Ba^{2+}	Na^+	-.3000E-02
Ca^{2+}	Co^{2+}	-.5500E-01
Ca^{2+}	K^+	-.4000E-01
Ca^{2+}	Mg^{2+}	0.1000E-01
Co^{2+}	Ca^{2+}	-.5500E-01
Co^{2+}	Na^+	-.1600E-01
Cs^+	Ba^{2+}	-.1500
Cs^+	H^+	-.4400E-01
Cs^+	Li^+	-.9500E-01
Cs^+	Na^+	-.3300E-01
H^+	Ba^{2+}	-.3600E-01
H^+	Cs^+	-.4400E-01
H^+	K^+	0.5000E-02
H^+	Li^+	0.1500E-01
H^+	Na^+	0.3600E-01
H^+	Sr^{2+}	-.2000E-01
K^+	Ba^{2+}	-.7200E-01
K^+	Ca^{2+}	-.4000E-01
K^+	H^+	0.5000E-02
K^+	Na^+	-.1200E-01
Li^+	Ba^{2+}	-.7000E-01
Li^+	Cs^+	-.9500E-01
Li^+	H^+	0.1500E-01
Li^+	Na^+	0.1200E-01
Mg^{2+}	Ca^{2+}	0.1000E-01
Na^+	Ba^{2+}	-.3000E-02
Na^+	Co^{2+}	-.1600E-01
Na^+	Cs^+	-.3300E-01
Na^+	H^+	0.3600E-01
Na^+	K^+	-.1200E-01
Na^+	Li^+	0.1200E-01
Sr^{2+}	H^+	-.2000E-01

Table A-4. Ternary Pitzer Anion-Anion Parameters

Anion	Anion	θ
$Al(OH)_4^-$	NO_2^-	0.1970E-02
$Al(OH)_4^-$	NO_3^-	-.2720E-01
$Al(OH)_4^-$	OH^-	0.1400E-01
$C_2O_4^{2-}$	NO_3^-	-.1093
$C_2O_4^{2-}$	OH^-	-.1118
Cl^-	CO_3^{2-}	-.5300E-01
Cl^-	F^-	-.1000E-01
Cl^-	HCO_3^-	0.3600E-01
Cl^-	NO_3^-	0.1600E-01
Cl^-	OH^-	-.5000E-01
Cl^-	PO_4^{3-}	0.2559
Cl^-	SO_4^{2-}	0.3000E-01
CO_3^{2-}	Cl^-	-.5300E-01
CO_3^{2-}	HCO_3^-	0.9000E-01
CO_3^{2-}	OH^-	-.1632
CO_3^{2-}	SO_4^{2-}	0.2000E-01
F^-	Cl^-	-.1000E-01
F^-	OH^-	0.1193
F^-	PO_4^{3-}	0.5500
HCO_3^-	Cl^-	0.3600E-01
HCO_3^-	CO_3^{2-}	0.9000E-01
HCO_3^-	SO_4^{2-}	0.1000E-01
NO_2^-	$Al(OH)_4^-$	0.1970E-02
NO_2^-	PO_4^{3-}	0.1047
NO_3^-	$Al(OH)_4^-$	-.2720E-01
NO_3^-	$C_2O_4^{2-}$	-.1093
NO_3^-	Cl^-	0.1600E-01
NO_3^-	OH^-	-.5470E-01
NO_3^-	SO_4^{2-}	0.6730E-01
OH^-	$Al(OH)_4^-$	0.1400E-01
OH^-	$C_2O_4^{2-}$	-.1118
OH^-	Cl^-	-.5000E-01
OH^-	CO_3^{2-}	-.1632
OH^-	F^-	0.1193
OH^-	NO_3^-	-.5470E-01
OH^-	PO_4^{3-}	0.1000
OH^-	SO_4^{2-}	-.1300E-01
PO_4^{3-}	Cl^-	0.2559
PO_4^{3-}	F^-	0.5500
PO_4^{3-}	NO_2^-	0.1047
PO_4^{3-}	OH^-	0.1000
SO_4^{2-}	Cl^-	0.3000E-01
SO_4^{2-}	CO_3^{2-}	0.2000E-01
SO_4^{2-}	HCO_3^-	0.1000E-01
SO_4^{2-}	NO_3^-	0.6730E-01
SO_4^{2-}	OH^-	-.1300E-01

Table A-5. Ternary Pitzer Cation-Anion-Anion Parameters

Cation	Anion	Anion	Ψ
K^+	$C_2O_4^{2-}$	OH^-	0.5000E-01
K^+	Cl^-	CO_3^{2-}	0.4000E-02
K^+	Cl^-	F^-	-.1350E-01
K^+	Cl^-	HCO_3^-	-.1500E-01
K^+	Cl^-	NO_3^-	-.3100E-02
K^+	Cl^-	OH^-	-.3200E-02
K^+	Cl^-	SO_4^{2-}	-.5000E-02
K^+	CO_3^{2-}	Cl^-	0.4000E-02
K^+	CO_3^{2-}	OH^-	-.1000E-01
K^+	CO_3^{2-}	SO_4^{2-}	-.9000E-02
K^+	F^-	Cl^-	-.1350E-01
K^+	HCO_3^-	Cl^-	-.1500E-01
K^+	HCO_3^-	SO_4^{2-}	0.5000E-02
K^+	NO_3^-	Cl^-	-.3100E-02
K^+	NO_3^-	OH^-	-.3200E-02
K^+	OH^-	$C_2O_4^{2-}$	0.5000E-01
K^+	OH^-	Cl^-	-.3200E-02
K^+	OH^-	CO_3^{2-}	-.1000E-01
K^+	OH^-	NO_3^-	-.3200E-02
K^+	OH^-	SO_4^{2-}	-.5000E-01
K^+	SO_4^{2-}	Cl^-	-.5000E-02
K^+	SO_4^{2-}	CO_3^{2-}	-.9000E-02
K^+	SO_4^{2-}	HCO_3^-	0.5000E-02
K^+	SO_4^{2-}	OH^-	-.5000E-01
Na^+	$Al(OH)_4^-$	NO_2^-	0.5400E-02
Na^+	$Al(OH)_4^-$	NO_3^-	0.4700E-02
Na^+	$Al(OH)_4^-$	OH^-	-.4800E-02
Na^+	$C_2O_4^{2-}$	NO_2^-	0.2300
Na^+	$C_2O_4^{2-}$	NO_3^-	0.1895
Na^+	$C_2O_4^{2-}$	OH^-	0.1000
Na^+	Cl^-	CO_3^{2-}	0.8500E-02
Na^+	Cl^-	F^-	-.2180E-02
Na^+	Cl^-	HCO_3^-	-.1500E-01
Na^+	Cl^-	NO_3^-	-.6000E-02
Na^+	Cl^-	OH^-	-.6300E-02
Na^+	CO_3^{2-}	Cl^-	0.8500E-02
Na^+	CO_3^{2-}	HCO_3^-	0.2000E-02
Na^+	CO_3^{2-}	OH^-	0.1720E-01
Na^+	CO_3^{2-}	SO_4^{2-}	-.5000E-02
Na^+	F^-	Cl^-	-.2180E-02
Na^+	F^-	OH^-	-.3500E-01
Na^+	HCO_3^-	Cl^-	-.1500E-01
Na^+	HCO_3^-	CO_3^{2-}	0.2000E-02
Na^+	HCO_3^-	SO_4^{2-}	-.5000E-02
Na^+	NO_2^-	$Al(OH)_4^-$	0.5400E-02

Cation	Anion	Anion	Ψ
Na^+	NO_2^-	$C_2O_4^{2-}$	0.2300
Na^+	NO_2^-	PO_4^{3-}	0.5370E-01
Na^+	NO_3^-	$Al(OH)_4^-$	0.4700E-02
Na^+	NO_3^-	$C_2O_4^{2-}$	0.1895
Na^+	NO_3^-	Cl^-	-.6000E-02
Na^+	NO_3^-	OH^-	0.2000E-03
Na^+	NO_3^-	SO_4^{2-}	0.3350E-02
Na^+	OH^-	$Al(OH)_4^-$	-.4800E-02
Na^+	OH^-	$C_2O_4^{2-}$	0.1000
Na^+	OH^-	Cl^-	-.6300E-02
Na^+	OH^-	CO_3^{2-}	0.1720E-01
Na^+	OH^-	F^-	-.3500E-01
Na^+	OH^-	NO_3^-	0.2000E-03
Na^+	OH^-	PO_4^{3-}	0.3000E-01
Na^+	OH^-	SO_4^{2-}	-.9000E-02
Na^+	PO_4^{3-}	NO_2^-	0.5370E-01
Na^+	PO_4^{3-}	OH^-	0.3000E-01
Na^+	SO_4^{2-}	CO_3^{2-}	-.5000E-02
Na^+	SO_4^{2-}	HCO_3^-	-.5000E-02
Na^+	SO_4^{2-}	NO_3^-	0.3350E-02
Na^+	SO_4^{2-}	OH^-	-.9000E-02

Table A-6. Ternary Pitzer Cation-Cation-Anion Parameters

Cation	Cation	Anion	Ψ
Ba^{2+}	H^+	Cl^-	0.2400E-01
Ba^{2+}	Li^+	Cl^-	0.1900E-01
Ca^{2+}	Co^{2+}	Cl^-	0.1300E-01
Ca^{2+}	K^+	Cl^-	-.1500E-01
Co^{2+}	Ca^{2+}	Cl^-	0.1300E-01
Co^{2+}	Na^+	Cl^-	-.1100E-01
Cs^+	H^+	Cl^-	-.1900E-01
Cs^+	K^+	Cl^-	-.1000E-02
Cs^+	Li^+	Cl^-	-.9000E-02
Cs^+	Na^+	Cl^-	-.3000E-02
Cu^{2+}	Na^+	Cl^-	-.1400E-01
Cu^{2+}	Na^+	NO_3^-	-.1400E-01
H^+	Ba^{2+}	Cl^-	0.2400E-01
H^+	Cs^+	Cl^-	-.1900E-01
H^+	K^+	Cl^-	-.1100E-01
H^+	K^+	NO_3^-	-.1030E-01
H^+	Na^+	Cl^-	-.4000E-02
H^+	Na^+	NO_3^-	-.2740E-02
H^+	Sr^{2+}	Cl^-	0.1800E-01
K^+	Ca^{2+}	Cl^-	-.1500E-01
K^+	Cs^+	Cl^-	-.1000E-02
K^+	H^+	Cl^-	-.1100E-01

Cation	Cation	Anion	Ψ
K^+	H^+	NO_3^-	-.1030E-01
K^+	Li^+	Cl^-	-.1000E-01
K^+	Na^+	Cl^-	-.1800E-02
K^+	Na^+	CO_3^{2-}	0.3000E-02
K^+	Na^+	HCO_3^-	0.3000E-02
K^+	Na^+	NO_3^-	-.6000E-02
K^+	Na^+	OH^-	0.4000E-02
K^+	Na^+	SO_4^{2-}	-.1000E-01
Li^+	Ba^{2+}	Cl^-	0.1900E-01
Li^+	Cs^+	Cl^-	-.9000E-02
Li^+	K^+	Cl^-	-.1000E-01
Li^+	Na^+	Cl^-	-.3000E-02
Li^+	Na^+	NO_3^-	-.7000E-02
Mn^{2+}	Na^+	Cl^-	-.3000E-02
Na^+	Co^{2+}	Cl^-	-.1100E-01
Na^+	Cs^+	Cl^-	-.3000E-02
Na^+	Cu^{2+}	Cl^-	-.1400E-01
Na^+	Cu^{2+}	SO_4^{2-}	-.1400E-01
Na^+	H^+	Cl^-	-.4000E-02
Na^+	H^+	NO_3^-	-.2740E-02
Na^+	K^+	Cl^-	-.1800E-02
Na^+	K^+	CO_3^{2-}	0.3000E-02
Na^+	K^+	HCO_3^-	0.3000E-02
Na^+	K^+	NO_3^-	-.6000E-02
Na^+	K^+	OH^-	0.4000E-02
Na^+	K^+	SO_4^{2-}	-.1000E-01
Na^+	Li^+	Cl^-	-.3000E-02
Na^+	Li^+	NO_3^-	-.7000E-02
Na^+	Mn^{2+}	Cl^-	-.3000E-02
Na^+	UO_2^{2+}	NO_3^-	0.3879
Na^+	UO_2^{2+}	OH^-	-.2556
Sr^{2+}	H^+	Cl^-	0.1800E-01
UO_2^{2+}	Na^+	NO_3^-	0.3879
UO_2^{2+}	Na^+	OH^-	-.2556

A.4 Data Structure

The input and output files associated with the TMIXP code and their contents are described below.

A.4.1 Super File

The TMIXP super file is a special type of file used to organize the individual files for input and output operations. The super file is a text file that contains the names of input/output files. The super file is read from standard input (UNIT=5). The first line of the super file is an identifier card, "TMIXPSUP". After the identifier line, each subsequent line is preceded by a four-letter category code and a filename. The category code and filename have to be enclosed in single or double quotes. The MAIN, LIST, PIT1 and KVAL categories are required. The other categories are specified based on the type of simulation, spline specifications and output options. Table A-7 shows the format of a typical super file.

Table A-7. TMIXP Super File Format

Category	File Name
TMIXPSUP	
'MAIN'	'CXP01-AD.dat'
'SPLN'	'CXP01-AD.spl'
'LIST'	'..\..\databank\Species-Data.dat'
'PIT1'	'..\..\databank\Pitzer-Cation-Anion.dat'
'KVAL'	'..\..\databank\Equilibrium-Constants-SL644.dat'
'PRNT'	'..\..\output\LAW_IX_Feeds\CXP01-AD.out'
'DIAG'	'..\..\output\LAW_IX_Feeds\CXP01-AD.log'
'PLOT'	'..\..\output\LAW_IX_Feeds\CXP01-AD.plt'

A.4.2 File Content and Organization

Table A-8 summarizes the input and output (I/O) files specified within the TMIXP super file. The detailed content and organization of each file is presented in the next section.

TMIXP uses list-directed **READ** statements to process numeric data in the main input, species data, Pitzer parameters, equilibrium constants and spline profile data file. Therefore, there are no data formatting requirements and the data associated with a given **READ** statement may occupy multiple lines in the main input file. Data groups are delineated by required comment lines that serve the purpose of annotating the input.

Besides a main output file and optional diagnostic file, TMIXP can create an additional output file intended for Tecplot™ post-processing.

Table A-8. Summary of TMIXP Input and Output Files

File	Name	Unit	I/O	Category
super file	user-specified	5	input	
main input	user-specified in	10	input	MAIN

File	Name	Unit	I/O	Category
	super file			
spline data	user-specified in super file	11	input	SPLN
species data	user-specified in super file	12	input	LIST
Pitzer cation-anion parameters	user-specified in super file	13	input	PIT1
Pitzer cation-cation parameters	user-specified in super file	14	input	PIT2
Pitzer anion-anion parameters	user-specified in super file	15	input	PIT3
Pitzer cation-anion-anion parameters	user-specified in super file	16	input	PIT4
Pitzer cation-cation-anion parameters	user-specified in super file	17	input	PIT5
equilibrium constants	user-specified in super file	18	input	KVAL
print file	user-specified in super file	20	output	PRNT
plot file	user-specified in super file	21	output	PLOT
diagnostic file	user-specified in super file	22	output	DIAG

A.4.3 Main Input File

The main input file is divided into 11 groups and arranged as follows:

1. Problem description
2. Simulation options
3. Number of cations and anions
4. List of cations
5. List of anions
6. Cation concentrations
7. Anion concentrations
8. Liquid properties
9. Nonlinear convergence parameters
10. Resin properties
11. Initial form of solid

The above sequence must be strictly followed, although not every item will be present for all simulations. Groups 10 and 11 are not required for the solution chemistry only option. A description of the input variables and data formats is presented below. The user should keep in mind the following items when preparing the main input file.

- The data associated with a given **READ** statement is termed a "data record" in the discussion below.
- A comment line is required before most data records as described below. A comment line cannot be greater than 80 characters.
- TMIXP uses list-directed **READ** statements to process numeric data. Therefore, there are no data formatting requirements and the data associated with a given **READ** statement may occupy multiple lines in the main input file.

The following data records are required as indicated:

Group 1

1. Problem description

A comment line followed by ntitle+1 data records:

comment
ntitle
title(1)
:
title(ntitle)

ntitle: Number of title lines.

title: Title character array ($1 \le i \le$ ntitle). Each title line cannot be greater than 80 characters and must be enclosed in single or double quotes.

Group 2

2. Simulation options

A comment line followed by one data record:

comment
iopt icor iter Tc

iopt: Parameter indicating the type of simulation;
= 0 Solution chemistry only,
= 1 SuperLig 644®,
= 2 Resorcinol-Formaldehyde (RF),
= 3 SuperLig 639® (incomplete).

icor: Parameter indicating temperature correction of Pitzer parameters;
= 0 no,
= 1 yes.

iter: Parameter indicating the type of Pitzer parameters;
= 0 binary Pitzer parameters only,
= 1 binary and ternary Pitzer parameters.

Tc: Equilibrium temperature (C).

Group 3

3. Number of cations and anions

A comment line followed by one data record:

comment
ncation nanion

ncation: Number of cations: A minimum of 1 is required for iopt = 0. A minimum of 4 cations are required for iopt = 2 because Na^+, Cs^+, H^+ and K^+ are competing cations for SuperLig 644® exchange sites.

nanion: Number of anions: A mimimum of 1 is required for iopt = 0. A minimum of 2 anions is required for iopt = 2 because OH^- and NO_3^- are assumed to be always considered within the aqueous phase solution formulation.

Group 4

4. List of cations

A comment line followed by ncation data records:

```
comment
cation
cation
cation
cation
  :
cation
```

cation: Name of cation. The cation name is a character string of length 8 enclosed within quotes and must be a member of the cation list in Table A-1. The minimum cation list is 'Na+', 'Cs+', 'H+' and 'K+' for iopt = 2.

Group 5

5. List of anions

A comment line followed by nanion data records:

```
comment
anion
anion
  :
anion
```

anion: Name of anion. The anon name is a character string of length 8 enclosed within quotes and must be a member of the anion list in Table A-1. The minimum anion list is 'OH-' and 'NO3-' for iopt = 2.

Group 6

6. Cation concentrations

A comment line followed by ncation data records:

comment	
cinmlt(1)	icinxy(1)
cinmlt(2)	icinxy(2)
cinmlt(3)	icinxy(3)
cinmlt(4)	icinxy(4)
:	:
cinmlt()	icinxy()

cinmlt: Cation input concentration (icinxy = 0) or concentration multiplier (icinxy > 0) to the spline dataset specified by the file given in the 'SPLN' category of the TMIXP super file. Here the concentrations should be listed in the same order as the cation list in Group 4. Zero concentrations can be used. If the solution is neutral or basic set the concentration of H^+ to zero and TMIXP will internally correct the H^+ concentration. Otherwise, specified the H^+ concentration if the solution is acidic.

icinxy: Parameter array indicating which spline dataset to use for computing cation concentration.

= 0 no spline dataset used, cinmlt is the input concentration,

> 0 integer indicating the index of the spline dataset specified by the file given in the 'SPLN' category of the TMIXP super file.

Group 7

7. Anion concentrations

A comment line followed by nanion data records:

comment	
cinmlt(ncation+1)	icinxy(ncation+1)
cinmlt(ncation+2)	icinxy(ncation+2)
:	:
cinmlt()	icinxy()

cinmlt: Anion input concentration (icinxy = 0) or concentration multiplier (icinxy > 0) to the spline dataset specified by the file given in the 'SPLN' category of the TMIXP super file. Here the concentrations should be listed in the same order as the anion list in Group 5. Zero concentrations can be used. If the solution is neutral or acidic set the concentration of OH^- to zero and TMIXP will internally correct the OH^- concentration. Otherwise, specified the OH^- concentration if the solution is basic.

icinxy: Parameter array indicating which spline dataset to use for computing anion concentration.
- = 0 no spline dataset used, cinmlt is the input concentration,
- > 0 integer indicating the index of the spline dataset specified by the file given in the 'SPLN' category of the TMIXP super file.

Group 8

8. Liquid properties

A comment line followed by one data record:

comment		
vol_liq	rhoin	H2Oin

vol_liq: Volume of liquid (L).

rhoin: Parameter indicating the method for computing liquid density;
- < 0 liquid density computed using HTWOS model,
- > 0 liquid density specified in g/L.

H2Oin: Parameter indicating the method for computing initial moles of water;
= 0 compute using liquid density specified above,
> 0 initial moles of water specified.

Group 9

9. Nonlinear convergence parameters

A comment line followed by one data record:

comment		
errrel	itmax	

errrel: Stopping criterion. The root is accepted if the relative error between two successive approximations to this root is less than errrel. A typical value is 1E-8.

itmax: The maximum allowable number of iterations. A suggested value is 200.

Group 10

10. Resin properties (iopt > 0)

A comment line followed by one data record:

comment		
m_resin	CTMax	CTcoef

m_resin: Mass of dry resin (g).

CTMax: Maximum apparent capacity of cesium in hyperbolic fit of apparent cesium capacity as a function of hydroxide concentration (mmol/g).

$$CT = CTMax[OH^-]/(CTcoef + [OH^-])$$

CTcoef: Hyperbolic coefficient in function above.

Group 11

11. Initial form of solid (iopt > 0)

A comment line followed by one data record:

comment
fQ(1) fQ(2) fQ(3) fQ(4)

fQ(1): Fractional initial loading of resin in Cs^+ form.

fQ(2): Fractional initial loading of resin in K^+ form.

fQ(3): Fractional initial loading of resin in Na^+ form.

fQ(4): Fractional initial loading of resin in H^+ form.

The fQ array must sum up to 1. The resin is typically in hydrogen form, fQ(4) = 1, or in sodium form, fQ(3) = 1.

A.4.4 Spline Data File

The spline data file is specified in the TMIXP super file under the 'SPLN' category (Table A-8). This data file is used to vary the concentrations of cations and anions in order to generate multiple numerical batch contacts within a single simulation. Otherwise, TMIXP computes a single numerical batch contact. Each spline dataset within the file is indexed starting at 1. To access the spline dataset, the user must set the icinxy (Groups 6 and 7) variable to the spline index of interest. Note, the spline data for cations and anions should be set up to maintain electroneutrality at each spline data point. An example of utilizing the spline data would be to generate points along a cesium isotherm (loading curve) as a function of aqueous cesium concentration. The structure of the spline data file is as follows:

A comment line followed by one data record:

comment	
nspl	nk

nspl: Number of spline datasets. Must be at least 1.

nk: Number of knots per spline.

The following block of data is repeated nspl times:

comment
itype() ninv
The following block of data is repeated ninv times:
ylo yhi n

itype(): Parameter integer array indicating the type of spline,
= -1 Heaviside spline,
= 0 Linear spline.

ninv: Number of spline intervals per spline dataset.

ylo: Lower concentration value of spline interval.

yhi: Upper concentration value of spline interval.

n: Number of spline data points in spline interval (includes endpoints). For example, if n = 3 TMIXP would generate y values at ylo, 0.5*(ylo+yhi) and yhi.

A.4.5 Species Data File

The species data file is specified in the TMIXP super file under the 'LIST' category (Table A-8). This data file is used primarily to provide cation and anion id numbers, names, molecular weights and valences. In addition, the isotopic fraction of Cs-137, molecular weight of Cs-137 and the molecular weight of water are specified at the end of the file. The current species data file includes 20 cations and 14 anions. The structure of the species data file is as follows:

A comment line followed by one data record:

comment
nc na

nc: Number of cations.

na: Number of anions.

A comment line followed by nc data records:

comment			
id	ion(1)	MW(1)	z(1)
:	:	:	:
id	ion(nc)	MW(nc)	z(nc)

A comment line followed by na data records:

comment			
id	ion(nc+1)	MW(nc+1)	z(nc+1)
:	:	:	:
id	ion(nc+na)	MW(nc+na)	z(nc+na)

id: Ion relative id number $(1 \le id \le nc)$ or $(1 \le id \le na)$.

ion(): Array of ion names. Ion name must be enclosed within quotes and not exceed 8 characters.

MW(): Array of ion molecular weights.

z(): Array of ion valences.

A comment line followed by one data record:

comment		
eta	MW_Cs137	MWw

eta: Isotopic fraction of ^{137}Cs $(0 \le eta \le 1)$.

MW_Cs137: Molecular weight of ^{137}Cs (g/gmole).

MWw: Molecular weight of water (g/gmole).

A.4.6 Pitzer Cation-Anion Parameter File

The Pitzer cation-anion parameter file is specified in the TMIXP super file under the 'PIT1' category (Table A-8). This parameter file provides the temperature dependent parameters for computing the binary Pitzer parameters. This file is always required. The structure of the Pitzer cation-anion parameter file is as follows:

A comment line followed by one data record:

comment ncap

ncap: Number of Pitzer cation-anion binary parameter records.

The following block of data is repeated ncap times:

comment						
ion1	ion2		i	j	etype	ref
comment						
A(1)	A(2)	A(3)	A(4)	A(5)	// $\beta_{ij}^{(0)}$ parameters //	
A(1)	A(2)	A(3)	A(4)	A(5)	// $\beta_{ij}^{(1)}$ parameters //	
A(1)	A(2)	A(3)	A(4)	A(5)	// $\beta_{ij}^{(2)}$ parameters, etype = '2-2' //	
A(1)	A(2)	A(3)	A(4)	A(5)	// C_{ij}^{ϕ} parameters, C_{ij} parameters if ref = 2//	

ion1: Cation name. Cation name must be enclosed within quotes and not exceed 8 characters.

ion2: Anion name. Anion name must be enclosed within quotes and not exceed 8 characters.

i: Relative id number of cation $(1 \le i \le nc)$.

j: Relative id number of anion $(1 \le j \le na)$.

etype: Electrolyte type. For example, barium chloride would be considered a '2-1' electrolyte and calcium sulfate would be considered a '2-2' electrolyte.

ref: Parameter integer indicating reference source for Pitzer parameters.
= 1 K.S. Pitzer (1979),
= 2 C. F. Weber (2001),
= 3 V. Neck et al. (1998)

A(1:5): Coefficients to temperature dependent functional form of Pitzer

parameter. The functional form is

$$A(1)+A(2)(T-T_{ref})+A(3)(1/T_{ref}-1/T)+A(4)\ln(T/T_{ref})+A(5)(T^2-T_{ref}^2)$$

where $T_{ref} = 298.15\,°K$.

A.4.7 Pitzer Cation-Cation Parameter File

The Pitzer cation-cation parameter file is specified in the TMIXP super file under the 'PIT2' category (Table A-8). This parameter file provides the temperature dependent parameters for computing the ternary Pitzer cation-cation parameters. This file is required if iter = 1 in the main input file. The structure of the Pitzer cation-cation parameter file is as follows:

A comment line followed by one data record:

comment
nccp

nccp: Number of Pitzer cation-cation ternary parameter records.

The following block of data is repeated nccp times:

comment					
ion1	ion2	i	j		
comment					
A(1)	A(2)	A(3)	A(4)	A(5)	// θ_{ij} parameters //

ion1: Cation 1 name. Cation 1 name must be enclosed within quotes and not exceed 8 characters.

ion2: Cation 2 name. Cation 2 name must be enclosed within quotes and not exceed 8 characters.

i: Relative id number of cation 1 $(1 \le i \le nc)$.

j: Relative id number of cation 2 $(1 \le j \le nc)$.

A(1:5): Coefficients to temperature dependent functional form of Pitzer θ_{ij} parameter. The functional form is

$$A(1)+A(2)(T-T_{ref})+A(3)(1/T_{ref}-1/T)+A(4)\ln(T/T_{ref})+A(5)(T^2-T_{ref}^2)$$

where $T_{ref} = 298.15\,°K$.

A.4.8 Pitzer Cation-Anion-Anion Parameter File

The Pitzer cation-anion-anion parameter file is specified in the TMIXP super file under the 'PIT4' category (Table A-8). This parameter file provides the temperature dependent parameters for computing the ternary Pitzer cation-anion-anion parameters. This file is required if iter = 1 in the main input file. The structure of the Pitzer cation-anion-anion parameter file is as follows:

A comment line followed by one data record:

comment
ncaap

nccap: Number of Pitzer cation-anion-anion ternary parameter records.

The following block of data is repeated ncaap times:

comment						
ion1	ion2	ion3	i	j	k	
comment						
A(1)	A(2)	A(3)	A(4)	A(5)	// ψ_{ijk} parameters //	

ion1: Cation name. Cation name must be enclosed within quotes and not exceed 8 characters.

ion2: Anion 1 name. Anion 1 name must be enclosed within quotes and not exceed 8 characters.

ion3: Anion 2 name. Anion 2 name must be enclosed within quotes and not exceed 8 characters.

i: Relative id number of cation $(1 \le i \le nc)$.

j: Relative id number of anion 1 $(1 \le j \le na)$.

k: Relative id number of anion 2 $(1 \le k \le na)$.

A(1:5): Coefficients to temperature dependent functional form of Pitzer ψ_{ijk} parameter. The functional form is

$$A(1) + A(2)(T - T_{ref}) + A(3)(1/T_{ref} - 1/T) + A(4)\ln(T/T_{ref}) + A(5)(T^2 - T_{ref}^2)$$

where $T_{ref} = 298.15\,°K$.

A.4.9 Pitzer Cation-Cation-Anion Parameter File

The Pitzer cation-cation-anion parameter file is specified in the TMIXP super file under the 'PIT5' category (Table A-8). This parameter file provides the temperature dependent parameters for computing the ternary Pitzer cation-cation-anion parameters. This file is required if iter = 1 in the main input file. The structure of the Pitzer cation-cation-anion parameter file is as follows:

A comment line followed by one data record:

comment
nccap

nccap: Number of Pitzer cation-cation-anion ternary parameter records.

The following block of data is repeated nccap times:

comment						
ion1		ion2		ion3	i j k	
comment						
A(1)	A(2)	A(3)	A(4)	A(5)	// ψ_{ijk} parameters //	

ion1: Cation 1 name. Cation 1 name must be enclosed within quotes and not exceed 8 characters.

ion2: Cation 2 name. Cation 2 name must be enclosed within quotes and not exceed 8 characters.

ion3: Anion name. Anion name must be enclosed within quotes and not exceed 8 characters.

i: Relative id number of cation 1 $(1 \le i \le nc)$.

j: Relative id number of cation 2 $(1 \le j \le nc)$.

k: Relative id number of anion $(1 \le k \le na)$.

A(1:5): Coefficients to temperature dependent functional form of Pitzer ψ_{ijk} parameter. The functional form is

$$A(1) + A(2)(T - T_{ref}) + A(3)(1/T_{ref} - 1/T) + A(4)\ln(T/T_{ref}) + A(5)(T^2 - T_{ref}^2)$$

where $T_{ref} = 298.15\,°K$.

A.4.10 Equilibrium Constant Parameter File

The equilibrium constant parameter file is specified in the TMIXP super file under the 'KVAL' category (Table A-8). This parameter file provides the temperature dependent parameters for computing equilibrium constants for the water dissociation reaction and mass action equations. The number of entries is simulation dependent. One entry is required for the solution thermodynamics option (iopt=0). The parameters for the water dissociation reaction (Eqn. A-4). The SuperLig® 644 or Resorcinol-Formaldehyde option (iopt=1 or2) requires 4 entries: the water dissociation reaction and parameters for three mass action reactions (Eqns. (A-1) to (A-3)). The structure of the equilibrium constant parameter file is as follows:

A comment line followed by one data record:

comment	
ncoef	nek

ncoef: Number of coefficients in expression for equilibrium constant (currently set to 4).

nek: Number of equilibrium constants;
= 1 solution chemistry only,
= 4 SuperLig 644®.

A comment line followed by nek data records:

comment				
coef(1,1)	coef(2,1)	coef(3,1)	coef(4,1)	// Eqn. A-4 //
coef(1,2)	coef(2,2)	coef(3,2)	coef(4,2)	// Eqn. A-1 //
coef(1,3)	coef(2,3)	coef(3,3)	coef(4,3)	// Eqn. A-2 //
coef(1,4)	coef(2,4)	coef(3,4)	coef(4,4)	// Eqn. A-3 //

coef(): Matrix of coefficients to temperature dependent parameters used to compute equilibrium constants. The equilibrium constants are computed as $K_j = \mathbf{exp}(\mathrm{coef}(1,j)1/T + \mathrm{coef}(2,j)\mathbf{ln}(T) + \mathrm{coef}(3,j)T + \mathrm{coef}(4,j))$

A.4.11 Printed Ouput File

The printed output file is specified in the TMIXP super file under the 'PRNT' category (Table A-8). This file provides the following information

- Header and title

- Liquid temperature
- Species name (cations to anions), molecular weight, valence and initial molar concentration
- Initial moles of water
- Initial ionic strength of solution
- Equilibrium constants
- Liquid volume and resin mass
- Total ion exchange capacity (iopt=2)
- Cs^+, K^+, Na^+, H^+ initial fractional and total solid loadings (iopt=2)
- Convergence criterion and maximum number of nonlinear iterations
- Normalized residual and L2 norm of residual
- Species equilibrium molarities, molalities and ionic activity coefficients
- Equilibrium moles of water and water activity
- Equilibrium ionic strength and pH
- Equilibrium Cs^+, K^+, Na^+, and H^+ aqueous concentration, K_d and solid loading (iopt=2).

A.4.12 Tecplot Datafile

The Tecplot datafile is specified in the TMIXP super file under the 'PLOT' category (Table A-8). The output of the Tecplot datafile is simulation dependent. For a solution chemistry only simulation (iopt=0), the Tecplot datafile will dump the following variables at each numerical batch contact.

- Equilibrium concentrations and molalities of ionic species provided in Groups 4 and 5.
- Activity of water
- Ionic strength of solution
- pH of solution
- osmotic coefficient of solution

For a SuperLig 644 or Resorcinol-Formaldehyde simulation (iopt=1 or 2), the Tecplot data file will dump the following variables at each numerical batch contact.

- Equilibrium concentrations and molalities of ionic species provided in Groups 4 and 5.
- Equilibrium ionic solid loadings of Cs^+, K^+, Na^+ and H^+.

A.4.13 Diagnostic Log File

The diagnostic log file is specified in the TMIXP super file under the 'DIAG' category (Table A-8). This file provides the following diagnostic information

- Ionic species charge balance summary
- Pitzer parameters evaluated at the simulation temperature
- Spline profile data and coefficients

A.5 TMIXP-OPT Parameter Estimation Code

The TMIXP with OPTimization (TMIXP-OPT) code computes the nonlinear least squares estimate of equilibrium constants and total ionic capacity using experimental batch contact data for SuperLig® 644 or Resorcinol-Formaldehyde in an electrolyte solution. TMIXP-OPT is a separate code that contains the engine of TMIXP and utilizes the IMSL® subroutine DBCLSF (Visual Numerics, 1999). The IMSL® subroutine DBCLSF is called to solve a nonlinear least squares problem subject to bounds on the variables using a modified Levenberg-Marquardt algorithm and a finite-difference Jacobian. The bounds on the variables are that they be nonnegative. The cost function minimized is a vector of log-difference, normalized or inverse difference residuals of cesium solid loadings.

A.5.1 Model Description

The TMIXP-OPT code processes a series of batch contact datasets (TMIXP MAIN input files). The initial ionic concentrations, liquid and resin properties are loaded into arrays for each batch contact dataset. Using initial guesses for the equilibrium constants and total ionic capacity (user selected through input), TMIXP-OPT performs a numerical batch contact simulation for each dataset. As the program loops over batch contact datasets, the cost function is generated based on a user specified residual (log-difference, normalized or inverse-difference). Once the cost function vector of residuals is generated, the program proceeds to perturb one of the parameters in an effort to minimize the cost function in a nonlinear least squares fashion. This process continues until the convergence criteria is satisfied or unsatisfactory progress is achieved.

A.5.2 Data Structure

The data structure of TMIXP-OPT is very similar to that of TMIXP. It utilizes the familiar super file for organizing the input and output files.

A.5.2.1Super File

The TMIXP-OPT super file is a special type of file used to organize the individual files for input and output operations. The super file is a text file that contains the names of input/output files. The super file is read from standard input (UNIT=5). The first line of the super file is an identifier card, "TMIXPSUP". After the identifier line, each subsequent line is preceded by a four-letter category code and a filename. The category code and filename have to be enclosed in single or double quotes. The NLSQ, LIST, PIT1 and KVAL categories are required. The other categories are specified based on the Pitzer and output options. Table A-9 shows the format of a typical super file

Table A-9. TMIXP-OPT Super File Format

Category	File Name
TMIXPOPTSUP	
'NLSQ'	'SL644-WK.opt'
'LIST'	'..\databank\Species-Data.dat'
'PIT1'	'..\databank\Pitzer-Cation-Anion.dat'
'KVAL'	'..\databank\Equilibrium-Constants.dat'
'PRNT'	'..\output\SL644-WK.out'
'DIAG'	'..\output\SL644-WK.log'
'PLOT'	'..\output\SL644-WK.plt'
'POUT'	'..\output\SL644-WK.par'

A.5.2.2File Content and Organization

Table A-10 summarizes the input and output (I/O) files specified within the TMIXP-OPT super file. The detailed content and organization of each file that is not part of TMIXP are presented in the next section.

TMIXP-OPT uses list-directed **READ** statements to process numeric data in the nlsq input, species data, Pitzer parameters and equilibrium constants. Therefore, there are no data formatting requirements and the data associated with a given **READ** statement may occupy multiple lines in the main input file. Data groups are delineated by required comment lines that serve the purpose of annotating the input.

Besides a main output file and optional diagnostic file, TMIXP-OPT can create an additional output file intended for Tecplot™ post-processing and a file summarizing the parameter estimation.

Table A-10. Summary of TMIXP-OPT Input and Output Files

File	Name	Unit	I/O	Category
super file	user-specified	5	input	
main input	user-specified in nlsq file	10	input	
nlsq input	user-specified in super file	11	input	NLSQ
species data	user-specified in	12	input	LIST

File	Name	Unit	I/O	Category
	super file			
Pitzer cation-anion parameters	user-specified in super file	13	input	PIT1
Pitzer cation-cation parameters	user-specified in super file	14	input	PIT2
Pitzer anion-anion parameters	user-specified in super file	15	input	PIT3
Pitzer cation-anion-anion parameters	user-specified in super file	16	input	PIT4
Pitzer cation-cation-anion parameters	user-specified in super file	17	input	PIT5
equilibrium constants	user-specified in super file	18	input	KVAL
print file	user-specified in super file	20	output	PRNT
plot file	user-specified in super file	21	output	PLOT
diagnostic file	user-specified in super file	22	output	DIAG
parameter file	user-specified in super file	23	output	POUT

The main input file structure is the same as the TMIXP main input in Section A.4.3. There are multiple main input files read by TMIXP-OPT, one for each batch contact simulation. The names of the main input files are specified in the NLSQ input file.

A.5.2.3NLSQ Input File

The NLSQ input file is divided into 8 groups and arranged as follows:

1. Parameter estimation options
2. Simulation options
3. Number of cations and anions
4. List of cations
5. List of anions
6. Apparent cesium capacity coefficients
7. Nonlinear convergence parameters
8. Batch contact datasets

Group 1

1. Parameter estimation options

A comment line followed by one data record:

comment
nbc icost iP(1) iP(2) iP(3) iP(4) iP(5)

nbc: Number of batch contact datasets.

icost: Parameter indicating the type of cost function to minimize;

= 0 log-difference residual, $\text{resid(i)} = w(i)(\ln(q_i^{obs}) - \ln(q_i^{mod}))$

= 1 normalized residual, $\text{resid(i)} = w(i)(q_i^{obs} - q_i^{mod})/q_i^{obs}$

= 2 inverse-difference residual, $\text{resid(i)} = w(i)(1/q_i^{obs} - 1/q_i^{mod})$

iP(1): Parameter indicating whether to estimate K_{12} equilibrium constant (Eq. (A-1);

= 0 no

= 1 yes

iP(2): Parameter indicating whether to estimate K_{13} equilibrium constant (Eq. (A-2);

= 0 no

= 1 yes

iP(3): Parameter indicating whether to estimate K_{14} equilibrium constant (Eq. (A-3);

= 0 no

= 1 yes

iP(4): Parameter indicating whether to estimate C_T total ionic capacity of resin (Eq. (A-9);

= 0 no

= 1 yes

iP(5): Parameter indicating whether to estimate C_T coef in hyperbolic fit of total ionic capacity as a function of hydroxide concentration;

= 0 no

= 1 yes

Group 2

2. Simulation options

A comment line followed by one data record:

comment
iopt icor iter Tc

iopt: Parameter indicating the type of simulation;
= 0 solution chemistry only (no parameter estimation),
= 1 SuperLig 644®,
= 2 Resorcinol-Formaldehyde (RF),
= 3 SuperLig 639® (incomplete).

icor: Parameter indicating temperature correction of Pitzer parameters;
= 0 no,
= 1 yes.

iter: Parameter indicating the type of Pitzer parameters;
= 0 binary Pitzer parameters only,
= 1 binary and ternary Pitzer parameters.

Tc: Equilibrium temperature (C).

The parameters in Group 2 override the values specified in Group 2 of each batch contact dataset.

Group 3

3. Number of cations and anions

A comment line followed by one data record:

comment
ncation nanion

ncation: Number of cations: An integer whose number must exceed 3. A minimum of 4 cations are required because Na^+, Cs^+, H^+ and K^+ are competing cations for SuperLig 644® exchange sites.

nanion: Number of anions: An integer whose number must exceed 1. A minimum of 2 anions is required because OH^- and NO_3^- are assumed to be always considered within the aqueous phase solution formulation.

The parameters in Group 3 should be identical to values in Group 3 of each batch contact dataset.

Group 4

4. List of cations

A comment line followed by ncation data records:

comment
'Na+'
'Cs+'
'H+'
'K+'
:
cation

cation: Name of cation. The cation name is a character string of length 8 enclosed within quotes and must be a member of the cation list in Table A-1. The minimum cation list is 'Na+', 'Cs+', 'H+' and 'K+'.

The list of cations in Group 4 should be identical to the list of cations in Group 4 of each batch contact dataset.

Group 5

5. List of anions

A comment line followed by nanion data records:

comment
'OH-'
'NO3-'
:
anion

anion: Name of anion. The anion name is a character string of length 8 enclosed within quotes and must be a member of the anion list in Table

A-1. The minimum anion list is 'OH-' and 'NO3-'.

The list of anions in Group 5 should be identical to the list of anions in Group 5 of each batch contact dataset.

Group 6

6. Apparent cesium capacity coefficients

A comment line followed by one data record:

comment	
CTin	CTcoef

CTin: Maximum cesium capacity of resin;
= use value (iP(4)=0),
= initial guess of value (iP(4)=1).

CTcoef: Coefficient in hyperbolic fit of C_T to hydroxide concentration [OH-]
= use value (iP(5)=0),
= initial guess of value (iP(5)=1).

The parameters in Group 6 override the values specified in Group 10 of each batch contact dataset.

Group 7

7. Nonlinear convergence parameters

A comment line followed by one data record:

comment	
errrel	itmax

errrel: Stopping criterion. The root is accepted if the relative error between two successive approximations to this root is less than errrel. A typical value is 1E-8.

itmax: The maximum allowable number of iterations. A suggested value is 200.

The parameters in Group 7 override the values specified in Group 9 of each batch contact dataset.

Group 8

8. Batch contact datasets

A comment line followed by nbc data records:

comment			
w(1)	cobs(1)	qobs(1)	fname(1)
w(2)	cobs(2)	qobs(2)	fname(2)
:	:	:	:
w()	cobs()	qobs()	fname()

w(): Statistical weight of batch contact dataset.

cobs(): Equilibrium experimental cesium concentration, mmol/ml.

qobs(): Equilibrium experimental cesium solid loading, mmol/g.

fname(): Name of batch contact dataset file including full or relative path enclosed within quotes. The length of the file name cannot exceed 80 characters. The format of the dataset is that of the main input file for TMIXP.

A.5.2.4Tecplot Datafile

The Tecplot datafile is specified in the TMIXP-OPT super file under the 'PLOT' category (Table A-10). The Tecplot datafile will dump the following variables for each numerical batch contact simulation.

- Equilibrium experimental cesium concentration.
- Equilibrium computed cesium concentration.
- Equilibrium experimental cesium solid loading.
- Equilibrium computed cesium solid loading.

A.5.2.5Parameter Output File

The parameter output file is specified in the TMIXP-OPT super file under the 'POUT' category (Table A-10). The parameter output file summarizes the results of the parameter estimation. The following information is provided by the file:

- Cs^+ to K^+ rational selectivity coefficient.
- Cs^+ to Na^+ rational selectivity coefficient.
- Cs^+ to H^+ rational selectivity coefficient.
- K^+ to Na^+ rational selectivity coefficient.
- K^+ to Cs^+ rational selectivity coefficient.
- Na^+ to Cs^+ rational selectivity coefficient.
- H^+ to Cs^+ rational selectivity coefficient.
- Na^+ to K^+ rational selectivity coefficient.
- Type of cost function (log-difference, normalized or inverse-difference).
- Estimated parameters
- Experimental and computed cesium solid loadings for each batch contact dataset.
- Experimental and computed cesium concentrations for each batch contact dataset.

Appendix B (250 Gallon Batch Contact, Kinetics, and Property Data)

A series of tests were conducted at SRNL to support the final stages of development of the SuperLig® 644 (SL644) performance modeling effort. All tests were conducted with the 250 gallon batch of SuperLig® 644 (manufacturer batch #C-01-11-05-02-35-60). The intent of this testing was to thoroughly characterize the cesium loading isotherm, cesium loading kinetics, competitor effects on cesium sorption, and physical properties of a single, carefully-controlled sample of SuperLig® 644 resin from a large-scale manufacturer batch. This data was intended to provide a basis set for the performance model using the most prototypic resin available, which would allow for prediction of cesium breakthrough profiles from full-scale columns under the range of potential processing conditions and waste feeds. A column test was also conducted under prototypical processing conditions using the same resin sample and the same simulant utilized for other tests. The column test was conducted under a separate test plan (Serkiz, 2002). The column data allowed for verification of the predictive capabilities of the model without the confounding effects of variability in resin batch, sample handling, and simulant composition. To our knowledge, this is the only complete set of data obtained in this way. Therefore this data was utilized as the basis set for the model.

The initial resin sub-sample was obtained for testing from the 250 gallon batch by multiple sampling of each shipping container following protocols developed at SRNL (Steimke, 2003a) which were based on an ASTM standard method (ASTM 2676). The samples were collected using a simple glass sampling tube (1-in. ID). Each sampling event involved the collection and compositing of multiple vertical core sub-samples of resin/water slurry from the storage vessels after some initial mixing of the material by tilting the vessels. The resin was received from the vendor as a water slurry in sodium form (typical cover liquid pH: 12). The sub-sample composite was conditioned by two sequential shrink/swell cycles as described below. The sample was then sieved with deionized water using a Gilson Wet-Vac sieve unit following an established protocol developed at SRNL (King, 2003). The –20 to +30 mesh portion was isolated from the sieves as a water slurry and the cover solution was readjusted to pH 12 with 0.25 M NaOH solution to convert the resin back to the sodium form. The pH of the solution was periodically measured and readjusted over a period of 24 hours until a stable pH of 12 was obtained. The –20 to +30 mesh size range was utilized for testing based on initial results from the hydraulic testing program conducted at SRNL which indicated that this would be the optimum size range for plant operations. The conditioned and sieved test sample was stored in a closed container and sub-samples were collected for specific tests following the sampling protocol mentioned previously. 1-inch or 1-cm ID sampling tubes were used depending on the sample size needed.

Resin Conditioning Cycle

5 BV of 0.5 M HNO_3 for 1.5 hours
5 BV of 0.5 M HNO_3 for 1.5 hours
5 BV of deionized water for 0.5 hours

5 BV of deionized water for 0.5 hours
5 BV of 0.25 M NaOH for 1.5 hours
5 BV of 0.25 M NaOH for 1.5 hours
5 BV of deionized water for 0.5 hours
5 BV of deionized water for 0.5 hours

Resin mass measurements for specific tests were conducted following an established protocol (Steimke, 2003b). Sample dry mass determination involved rapid removal of free-flowing liquid from the resin by filtration, followed by essentially simultaneous collection of a test sub-sample and multiple small (0.1 g) samples for the determination of water content. Water content was determined by drying known masses of damp resin in a vacuum oven (45 °C, -30 in. Hg) until a dry weight was determined. A weight correction factor (F-factor) was calculated for determination of the dry mass of the actual test sample. (The F-factor was defined as the resin dry mass divided by the damp mass.)

Tests conducted with the –20 to +30 mesh resin sub-sample are summarized below and in Table B-1. 5 M Na^+ AN-105 simulant used as the primary test simulant was prepared following the recipe published by Eibling (2001). The target AN-105 simulant composition based on reagents added is provided in Table B-2. Bench-scale column and loading kinetics tests were performed with the base AN-105 simulant as well as numerous batch contact equilibrium tests. Details and results of the column test are reported elsewhere (Serkiz et al., 2004). The kinetics tests were conducted using a specially-designed test apparatus following procedures described elsewhere (Duffey et al., 2003). Resin samples for the kinetics tests were added to the apparatus in damp sodium form. In contrast to previous tests, no resin preconditioning was performed in the apparatus. Additional kinetics test details and results are provided in Tables B-7 through B-9, as well as Figure B-3.

Batch contact equilibrium tests were conducted in an orbital shaker oven (Innova 4230). Each test sample contained 1.000 +/- 0.002 g (dry mass) of Na-form resin and 100 +/- 2 mL of simulant. The samples were placed in 250 mL polyethylene bottles that were sealed with rubber septa. The bottles were purged with argon for 10-15 minutes and then placed on the shaker table in a horizontal orientation. The agitation rate was set to 100 RPM and the oven was maintained at 25 +/- 0.5 °C throughout the test. The samples were agitated for 72 hours based on preliminary tests that confirmed that equilibrium is attained under these conditions within this time period. At the conclusion of the tests the samples were removed from the oven and filtered through 0.45 um Nalgene Nylon disposable filter units. Sub-samples of the filtrate were then submitted for cesium analysis by ICP-MS.

A 4-point cesium loading isotherm was determined by varying the initial cesium concentration within the base 5 M Na^+ AN-105 simulant matrix. Results are provided in Table B-5 and Figure B-1. Modified AN-105 simulants were also used for batch contact equilibrium testing in order to evaluate the impacts of competitors on cesium loading. The target concentrations for Na^+, K^+, Cs^+, and OH^- are provided in Table B-3. The modified AN-105 simulants were tested with the high and low target cesium concentrations as shown in the test matrix in Table B-4 in order to obtain the isotherm endpoints. Results of batch contact equilibrium testing with the modified simulants are provided in Table B-6 and Figure B-2.

During bench-scale chemical testing of the –20 to +30 mesh sub-sample, the plant design particle sieve range was broadened to –20 to +40 mesh. A large sample of resin from the 250 gallon resin batch was sieved by personnel at the Engineering Development Laboratory at SRNL to provide sufficient material in the –20 to +40 mesh range for pilot-scale testing in a 24-inch ID column. Equilibrium isotherms were obtained for a sub-sample of this sieved resin following the batch contact procedures described above. After completion of the multiple cycle testing in the 24-inch ID column, the cesium loading isotherm was measured for another sub-sample of the composited material removed from the column. Results of testing the –20 to +40 mesh sub-samples are also provided in Table B-5 and Figure B-1.

The drainable void volume of a SL644 resin bed packed in a prototypical manner with the –20 to +30 mesh sub-sample was determined by a liquid drainage technique. An apparatus was constructed and the method was refined using 1-mm diameter borosilicate glass beads as a surrogate for the resin. The apparatus consisted of a clear plastic tube (1-inch ID, 1/8-inch wall) approximately twelve inches long (Figure B-4). The tube was mounted vertically at eye level by means of a stainless steel block with internal manifolds accommodating an in-line drain valve and a de-ionized water supply valve at a right angle. The tube was sealed into the block with an o-ring and set screws. A fine mesh stainless steel screen was supported by three one-sixteenth inch by one-eighth inch stainless steel bars evenly spaced across the diameter at the bottom end of the tube within the block. Two viewing slots were machined into the valve block below the screen level to facilitate the observation of water flow.

The top of the tube was opened for filling with the porous medium. A tight fitting rubber stopper with a central one-quarter inch diameter hard walled plastic tube that served as an air supply line was used to blow air down through the media. This was done to ensure the complete capture of all of the water held within the voids during the drainage for subsequent weighing. The supply air was fully saturated with water by flowing through a large six-inch diameter quarter-inch wall clear acrylic pipe approximately six feet tall, maintained to a level approximately half full of water. From the laboratory air compressor, the air was regulated to no more than 20 psig, and then controlled with a needle valve into the bottom of the water column. The air outlet at the top of the water column was directed through a tee fitting through another needle control valve into a rotometer type flow meter and finally ending through the stopper at the top of the measurement column. The other air path through the center of the tee fitting was piped into a twelve foot vertical u-tube, half full of water, that served as a pressure relief valve and a visual air pressure gauge. The saturated air was blown down through the sample column only with the drain valve in the open position and the collection beaker in place. The airflow was set to approximately one scfm for two-minute time intervals. The intervals were repeated until the weighing results stabilized. This maximum cumulative weight was used directly to relate to the void space in the test column media.

Results of the drainable void tests are provided in Tables B-10 and B-11. After subtracting the weight of the volume of water below the screen (41.85 grams) and converting the weight of the water into equivalent volume, the average void space of the three runs through the glass beads was 33.71 cubic centimeters per 100 cc (33.7% porosity of glass beads, +/- 1%). This data demonstrated good reproducibility and reasonable results for this method. After subtracting the weight of the volume of water below the screen (41.85 grams) and converting the weight of the

water into equivalent volume, the average void space of the three runs through the resin was 34.44 cubic centimeters per 89.84 cc (38.0% porosity of resin, +/- 1%). Raw data are recorded in lab notesbooks.

A sample of preconditioned Na-form SuperLig® 644 resin from the –20 to +30 mesh sub-sample was isolated using the core sampling method. Half of the sample was converted to the H-form using 0.5 M HNO_3. The Na- and H-form portions of the resin were then dried to a constant weight in a vacuum oven at 45°C and –30 inches Hg for skeletal density determination. The method used roughly followed ASTM D 854 – 02. The skeletal density of the resin in Na-form was determined in DI H_2O and standard AN-105 simulant. The skeletal density of the resin in H-form was determined in DI H_2O and 0.5 M HNO_3. All measurements were taken using ~25 mL glass pycnometers. Results are provided in Table B-15. The dry mass of each pycnometer (including the lid) was obtained. The mass of the pycnometer and indicated liquid was obtained as follows. The pycnometer was filled near the top with the indicated liquid, the lid pushed on tightly, all the liquid wiped from the outside of the vessel, and the vessel was then weighed. When wiping the lid, special care was taken not to wick any liquid from the top. Care was also taken not to warm the pycnometer by excessive rubbing or handling. Once the mass was obtained the liquid was removed from the pycnometer. Approximately one gram of the indicated dry resin was weighed into the appropriate pycnometer. The pycnometer was filled ¾ full with the indicated liquid and the vessel was gently agitated to remove entrapped air. A small piece of parafilm was placed over the top and the resin was allowed to rehydrate overnight. The pycnometer was then filled near the top and the above procedure followed to determine the mass of the pycnometer, liquid, and resin. The density of each liquid was then determined by weighing an exact volume.

The skeletal density was calculated for each sample as follows:

$$\rho_{skeletal} = \frac{M_R}{M_{P+L} - (M_{P+L+R} - M_R)} \times \rho_L$$

where

- $\rho_{skeletal}$ - skeletal density of resin (g/mL)
- M_R - mass of dry resin (g)
- M_{P+L} - mass of pycnometer and liquid (g)
- M_{P+L+R} - mass of pycnometer, liquid, and resin (g)
- ρ_L - density of liquid (g/mL)

Particle size measurements were conducted for each resin sample by wet sieving and Microtrac (laser diffraction) analysis. Results are provided in Tables B-12 through B-14 and Figures B-5 through B-14.

Table B-1. Summary of Tests Conducted with the –20 to +30 mesh Sub-sample of the 250 Gallon Batch.

Test Description	Distribution Used (mesh)	Temperatur (°C)	Simulant
Batch Contact Equilibrium	-20 to +30	25 ± 0.5	Base AN-105 Modified AN-105
Sorption Kinetics	-20 to +30 -20 to +25 -25 to +30	25 ± 0.5	Base AN-105
Column Loading	-20 to +30	25 ± 1.0	Base AN-105
Drainable Void	-20 to +30	ambient	Base AN-105 water
Skeletal Density	-20 to +30	ambient	Base AN-105 water
Particle Size Analysis (Wet Sieving)	-20 to +30	ambient	water
Particle Size Analysis (Microtrac)	-20 to +30	ambient	water

Table B-2. Target Composition for the Base AN-105 Simulant.

Simulant	AN-105 [M]
Na	5.000
K	0.090
Al	0.687
S	0.004
P	0.003
Cr	0.012
Mg	1.04E-04
Ca	4.66E-04
Cd	1.37E-05
B	2.21E-03
Si	3.51E-03
Mo	4.00E-04
Pb	1.20E-04
Nitrate	1.243
Nitrite	1.126
Sulfate	0.004
Phosphate	0.003
Chloride	0.120
Fluoride	0.005
Oxalate	3.24E-03
Formate	2.99E-02
Added OH^-	1.60
Carbonate	0.098
TIC	0.098
TOC	0.140

Table B-3. Target Concentration Levels for Various Species in AN-105 Simulant Matrix for Batch Contact Equilibrium Testing with SL644.

Component	Low	Nominal	Intermediate	High	Base AN-105 Adjustments	Basis
Cs^+	1.58E-04	6.71E-04	2.65E-03	6.20E-03	varied $CsNO_3$ spike levels	values selected to determine full isotherm
K^+	0.00	0.09	---	0.7	varied KNO_3 spike levels	high value based on tank composition extreme
Na^+	---	5.0	---	6.0	concentration and spiking to 6 M Na^+	high/low values based on possible processing extremes
Free OH^-	0.2	1.4	---	2.0	exchanged $NaNO_3$ and NaOH to maintain $[Na^+]$	high/low values based on tank composition extremes

Table B-4. AN-105 Simulant Matrix for Batch Contact Equilibrium Testing with SL644.

Simulant ID	Simulant Description	$[Cs^+]$	$[K^+]$	$[OH^-]$	Comments
A	Nominal	N	N	N	---
B	High Cs/Nominal	H	N	N	minimal variation in nitrate
C	Intermediate Cs/Nominal	I	N	N	minimal variation in nitrate
D	Low Cs/Nominal	L	N	N	minimal variation in nitrate
E	High Cs/ Low OH	H	N	L	low Al, high $[NO_3^-]$
F	Low Cs/ Low OH	L	N	L	low Al, high $[NO_3^-]$
G	High Cs/ High OH	H	N	H	low $[NO_3^-]$[a]
H	Low Cs/ High OH	L	N	H	low $[NO_3^-]$[a]
I	High Cs/Low K	H	L	N	slightly lower $[NO_3^-]$
J	Low Cs/Low K	L	L	N	slightly lower $[NO_3^-]$
K	High Cs/High K	H	H	N	high nitrate[b]
L	Low Cs/High K	L	H	N	high nitrate[b]
M	High Cs/6 M Na^+ Concentrate	H	N	N	concentrated nominal recipe
N	Low Cs/6 M Na^+ Concentrate	L	N	N	concentrated nominal recipe
O	High Cs/6 M $NaNO_3$ Spike	H	N	N	spiking nominal to 6 M[c]
P	Low Cs/6 M $NaNO_3$ Spike	L	N	N	spiking nominal to 6 M[c]

[a] total added NO_3^-: 0.75 M
[b] total added NO_3^-: 3.24 M
[c] total added NO_3^-: 2.24 M

Table B-5. Cesium Equilibrium Loading Isotherm Data for SL644 Samples with the Base AN-105 Simulant

SL644 Sample	Liquid-Phase Equilibrium [Cs] (M)	Solid-Phase Equilibrium Cs Loading (mmol Cs/g resin)
-20 to +30 (Bench-Scale Chemical)	3.31E-06	0.0163
-20 to +30 (Bench-Scale Chemical)	1.85E-05	0.0656
-20 to +30 (Bench-Scale Chemical)	2.03E-04	0.2488
-20 to +30 (Bench-Scale Chemical)	8.40E-04	0.4767
-20 to +40 (Pilot-Scale Hydraulic - Before)	3.23E-06	0.0159
-20 to +40 (Pilot-Scale Hydraulic - Before)	1.47E-05	0.0570
-20 to +40 (Pilot-Scale Hydraulic - Before)	2.35E-04	0.2747
-20 to +40 (Pilot-Scale Hydraulic - Before)	1.60E-03	0.5358
-20 to +40 (Pilot-Scale Hydraulic - After)	2.86E-06	0.0136
-20 to +40 (Pilot-Scale Hydraulic - After)	1.68E-05	0.0483
-20 to +40 (Pilot-Scale Hydraulic - After)	2.44E-04	0.2325
-20 to +40 (Pilot-Scale Hydraulic - After)	1.50E-03	0.4640

*"before" and "after" refer to samples tested before or after testing in the 24-in. ID column

Table B-6. Cesium Equilibrium Loading Isotherm Data for Modified AN-105 Simulants using the –20 to +30 Mesh SL644 Sub-sample.

Simulant	Liquid-Phase Equilibrium [Cs] (M)	Solid-Phase Equilibrium Cs Loading (mmol Cs/g resin)
E	0.3788	2.38E-03
F	0.0159	5.93E-06
G	0.4639	1.40E-03
H	0.0156	2.78E-06
I	0.4863	1.21E-03
J	0.0172	6.96E-07
K	0.3834	2.15E-03
L	0.0152	1.32E-05
M	0.4569	1.61E-03
N	0.0231	3.08E-06
O	0.4397	1.73E-03
P	0.0160	4.05E-06

Table B-7. Experimental variables for particle size dependent kinetics testing.

Variable		Experiment 1	Experiment 2	Experiment 3	Experiment 4
Start Date		08/02/03	08/02/03	08/09/03	08/09/03
Simulant		AN-105	AN-105	AN-105	AN-105
Avg. Temperature (°C)		25.1	25.0	25.2	25.0
Sieve Fraction		-20+30	-20+30	-20+25	-25+30
Resin Dry Wt. (g)		0.3386	0.3388	0.3096	0.3097
Feed Volume (mL)		120	120	120	120
Phase Ratio (ϕ)		354	354	388	387
c_i (Cs)	(µg/L)	7.72E+04	7.72E+04	7.82E+04	7.82E+04
	(M)	5.81E-04	5.81E-04	5.88E-04	5.88E-04
Flow Rate	(mL/min)	30	30	30	30
	(BV/hr)	1385	1385	1385	1385
	(cm/min)	12.5	12.5	12.5	12.5

Table B-8. F-factor values of SuperLig® 644 resin based on oven- and filter-dried resin masses during kinetics testing.

Kinetics Experiment [a]	Experiment Date	Sieve Fraction [b] (mesh)	F-factor
Experiment 1/2 [c]	08/02/03	-20+30	0.4424
Experiments 3	08/09/03	-20+25	0.4039
Experiment 4	08/09/03	-25+30	0.4053

[a] F-factor determination was performed immediately prior to the kinetics experiment(s) indicated.
[b] Indicated particle size is based on wet sieve analysis of conditioned resin.
[c] Experiments 1 and 2 used resin from the same sub-sample of filter-dried resin. Thus, only one F-factor was performed.

Table B-9. Results summary for particle size dependent kinetics testing.

Experiment (Sieve Fraction)	Time, t (hr)	Liquid Cs Concentration (c_f)		Loading, Q (mmol Cs/g resin)	K_d (mL/g)
		(µg/L)	(M)		
Experiment 1 (-20+30)	0.00	7.72E+04	5.81E-04	0.00E+00	---
	0.25	5.32E+04	4.00E-04	6.40E-02	160
	1.00	4.36E+04	3.28E-04	8.96E-02	273
	4.00	2.90E+04	2.18E-04	1.29E-01	589
	8.00	2.00E+04	1.50E-04	1.53E-01	1014
	24.00	1.45E+04	1.09E-04	1.67E-01	1532
	48.00	1.28E+04	9.63E-05	1.72E-01	1783
	72.00	1.30E+04	9.78E-05	1.71E-01	1750
	120.00	1.35E+04	1.02E-04	1.70E-01	1672
	144.00	1.37E+04	1.03E-04	1.70E-01	1643
Experiment 2 (-20+30)	0.00	7.72E+04	5.81E-04	0.00E+00	---
	0.25	5.91E+04	4.45E-04	4.82E-02	108
	1.00	4.16E+04	3.13E-04	9.49E-02	303
	4.00	2.60E+04	1.96E-04	1.36E-01	697
	24.00	1.68E+04	1.26E-04	1.61E-01	1273
	48.00	1.43E+04	1.08E-04	1.68E-01	1558
	72.00	1.46E+04	1.10E-04	1.67E-01	1519
	120.00	1.46E+04	1.10E-04	1.67E-01	1519
	144.00	1.49E+04	1.12E-04	1.66E-01	1481
Experiment 3 (-20+25)	0.00	7.82E+04	5.88E-04	0.00E+00	---
	0.25	5.82E+04	4.38E-04	5.82E-02	133
	1.00	4.49E+04	3.38E-04	9.70E-02	287
	4.00	3.06E+04	2.30E-04	1.39E-01	603
	7.00	2.55E+04	1.92E-04	1.54E-01	801
	24.50	1.84E+04	1.38E-04	1.74E-01	1260
	48.00	1.92E+04	1.44E-04	1.72E-01	1191
	72.00	1.97E+04	1.48E-04	1.70E-01	1151
	120.50	1.78E+04	1.34E-04	1.76E-01	1315
Experiment 4 (-25+30)	0.00	7.82E+04	5.88E-04	0.00E+00	---
	0.25	5.86E+04	4.41E-04	5.70E-02	130
	1.00	4.52E+04	3.40E-04	9.61E-02	283
	4.00	3.09E+04	2.32E-04	1.38E-01	593
	7.00	2.58E+04	1.94E-04	1.53E-01	787
	24.50	1.94E+04	1.46E-04	1.71E-01	1174
	48.00	1.76E+04	1.32E-04	1.77E-01	1334
	72.00	1.74E+04	1.31E-04	1.77E-01	1354
	121.00	1.93E+04	1.45E-04	1.72E-01	1182

Table B-10. Drainable Void Measurement for 100 mL Bed of 1mm Diameter Glass Beads.

Weighing Sequence Number:	Trial #1 Weight of Drainage (grams)	Trial #2 Weight of Drainage (grams)	Trial #3 Weight of Drainage (grams)
1	65.53	63.92	66.77
2	75.98	74.77	75.27
3	76.17	74.74	75.26
4	76.24	74.66	---
5	76.19	---	---

*100 ml of DI water weighs 99.16 grams

Table B-11. Drainable Void Measurement for 89.84 mL Bed of SL644 Resin (250 Gallon Batch, -20 to +30 Mesh Sub-sample).

Weighing Sequence Number:	Trial #1 Weight of Drainage (grams)	Trial #2 Weight of Drainage (grams)	Trial #3 Weight of Drainage (grams)
1	53.99	54.36	61.01
2	74.95	75.68	75.86
3	75.01	76.06	76.10
4	75.06	76.43	76.07
5	75.02	76.62	---
6	---	76.86 (max)	---

*100 ml of DI water weighs 99.16 grams

Table B-12. Wet Sieve Data for the –20 to +30 mesh SL644 Sub-sample Used for Bench-Scale Chemical Testing

Mesh	Empty Beaker Wt. (g)	Beaker + Sample Wt. (g)	Sample Wt. (g)	Cumulative % Passing	Mesh Opening (μm)
>18			Total	100.00	>1000
18	28.5205	28.5292	0.0087	99.94	1000
20	29.1472	32.1072	2.96	80.37	850
30	101.83	113.64	11.81	2.28	600
40	28.7879	29.0893	0.3014	0.29	425
50	29.0296	29.0619	0.0323	0.07	300
70	29.3545	29.3618	0.0073	0.03	212
100	31.0239	31.0279	0.004	0.00	150

Table B-13. Wet Sieve Data for the –20 to +40 mesh SL644 Sub-sample Prior to Pilot-Scale Hydraulic Testing

Mesh	Empty Beaker Wt. (g)	Beaker + Sample Wt. (g)	Sample Wt. (g)	Cumulative % Passing	Mesh Opening (μm)
>18			Total	100.00	>1000
18	28.9894	29.0081	0.0187	99.91	1000
20	29.1124	31.9247	2.8123	86.24	850
30	108.1	121.73	13.63	19.97	600
40	28.5953	32.5454	3.9501	0.76	425
50	29.6132	29.7328	0.1196	0.18	300
70	29.0768	29.1036	0.0268	0.05	212
100	28.6876	28.6983	0.0107	0.00	150

Table B-14. Wet Sieve Data for the –20 to +40 mesh SL644 Sub-sample Following Pilot-Scale Hydraulic Testing

Mesh	Empty Beaker Wt. (g)	Beaker + Sample Wt. (g)	Sample Wt. (g)	Cumulative % Passing	Mesh Opening (μm)
>18			Total	100.00	>1000
18	29.2896	29.2929	0.0033	99.99	1000
20	29.1874	29.2247	0.0373	99.84	850
30	103.40	113.67	10.27	60.33	600
40	108.37	120.15	11.78	15.01	425
50	29.4804	32.274	2.7936	4.26	300
70	29.1258	30.0448	0.919	0.72	212
100	29.1224	29.3104	0.188	0.00	150

Table B-15. Skeletal densities of SuperLig® 644 resin.

Sample	M_{P+L}	M_R	M_{P+L+R}	ρ_L	$\rho_{skeletal}$	Average $\rho_{skeletal}$
Na/H_2O-1	45.1499	1.0186	45.4883	0.9978	1.494	1.489
Na/H_2O-2	43.5667	1.0687	43.9171	0.9978	1.485	
Na/Sim-1	50.0041	1.2139	50.1911	1.2300	1.454	1.451
Na/Sim-2	50.0210	1.0879	50.1845	1.2300	1.448	
H/H_2O-1	44.3881	1.1132	44.6689	0.9978	1.334	1.343
H/H_2O-2	43.7347	1.0816	44.0180	0.9978	1.352	
H/HNO_3-1	44.2048	1.0929	44.4532	1.0080	1.304	1.308
H/HNO_3-2	45.0582	1.1177	45.3172	1.0080	1.312	

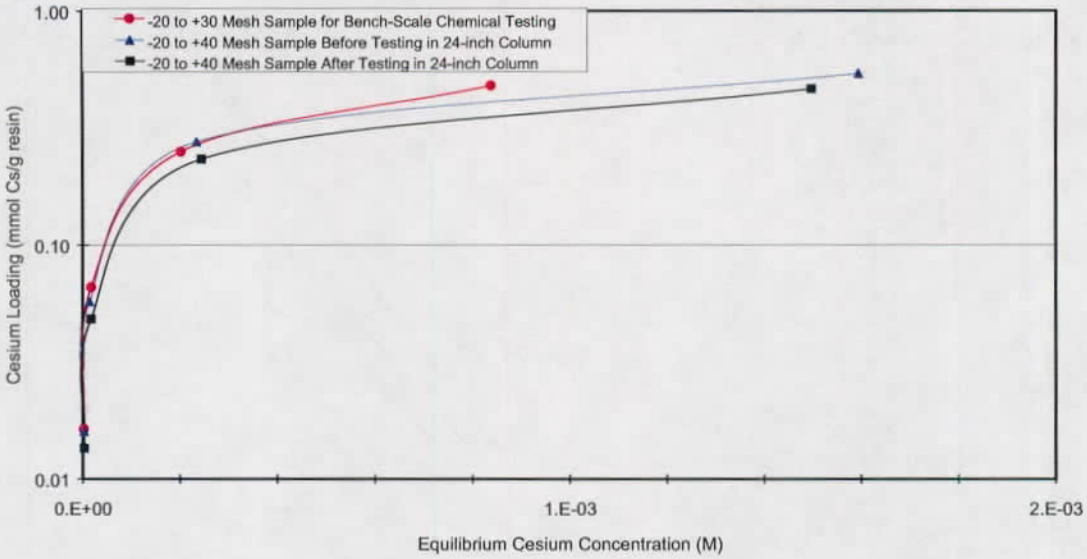


Figure B-1. Cesium Sorption Isotherms for SuperLig 644 Samples with the Standard AN-105 Simulant.

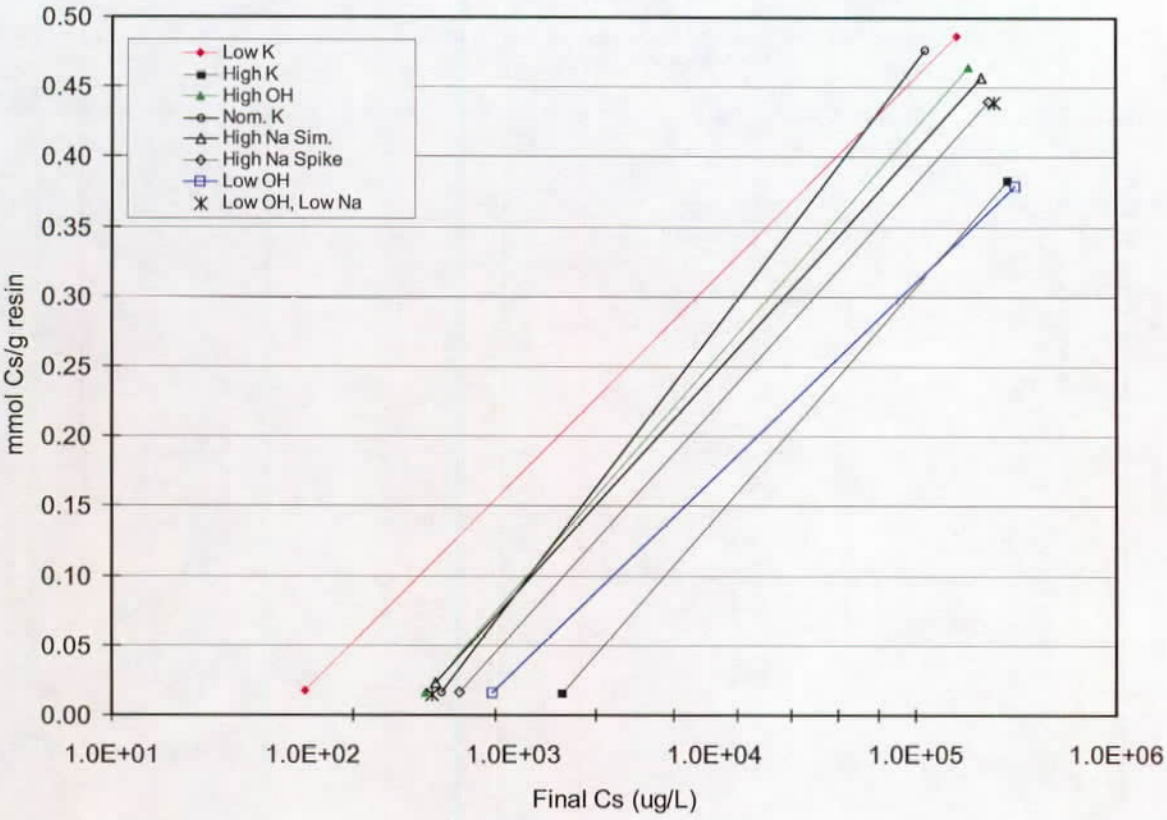


Figure B-2. Cesium Sorption Isotherms for –20 to +30 Mesh SuperLig 644 with Modifed AN-105 Simulants.

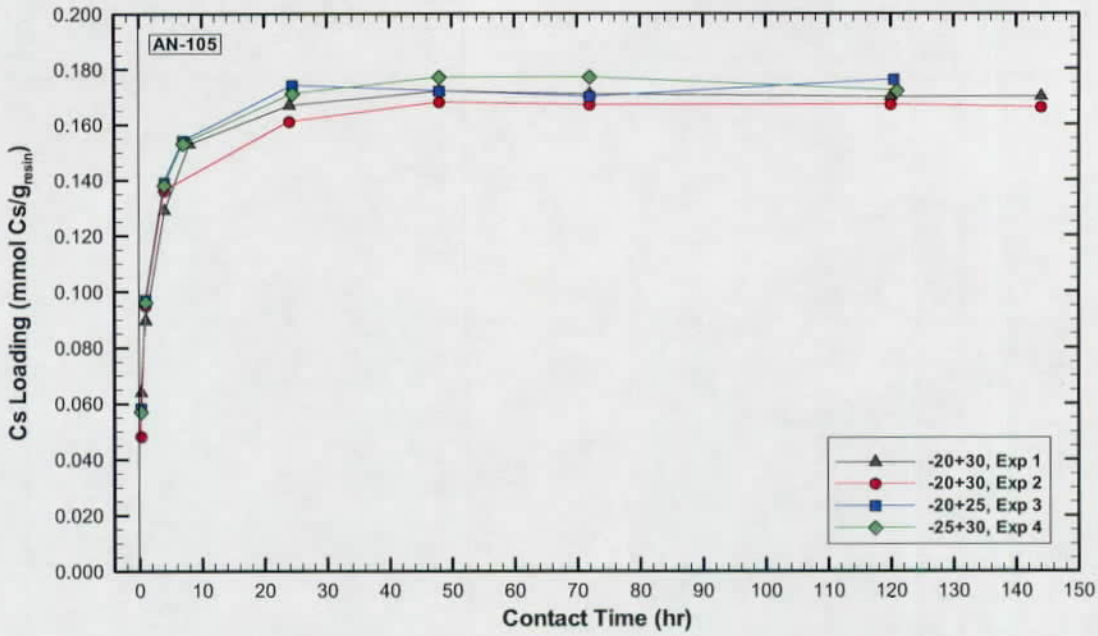


Figure B-3. Transient cesium loading levels for the sieve fractions studied.

Figure B-4. Drainable Void Test Apparatus.

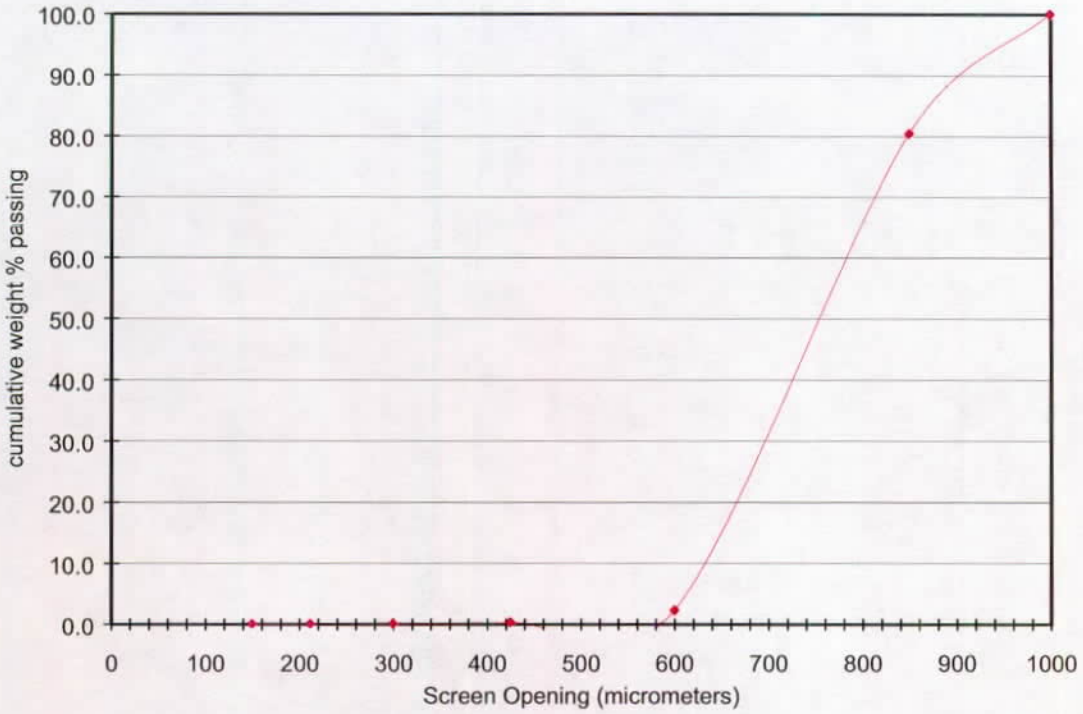


Figure B-5. Wet Sieve Data for the –20 to +30 Mesh SuperLig 644 Sample Used for Bench-Scale Chemical Testing.

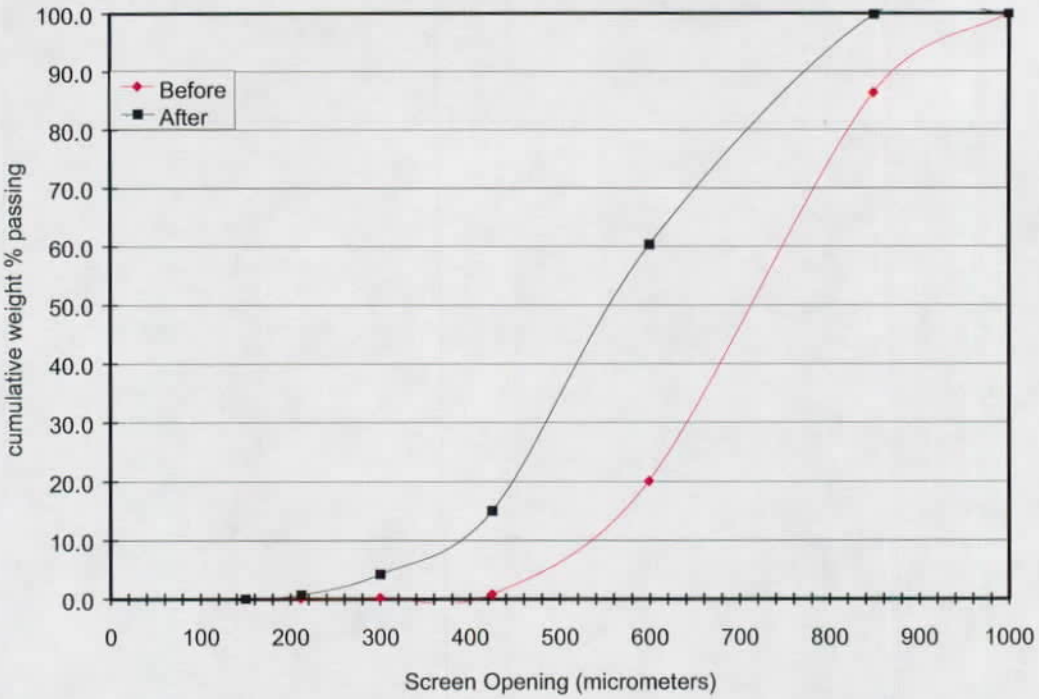


Figure B-6. Wet Sieve Data for the SuperLig 644 Sample Used for Testing with the 24-inch Column at the SRNL Engineering Development Laboratory. "Before" represents the original test sample prior to testing which had been sieved to give a –20 to +40 size distribution. "After" represents the composited sample after removal from the 24-inch column.

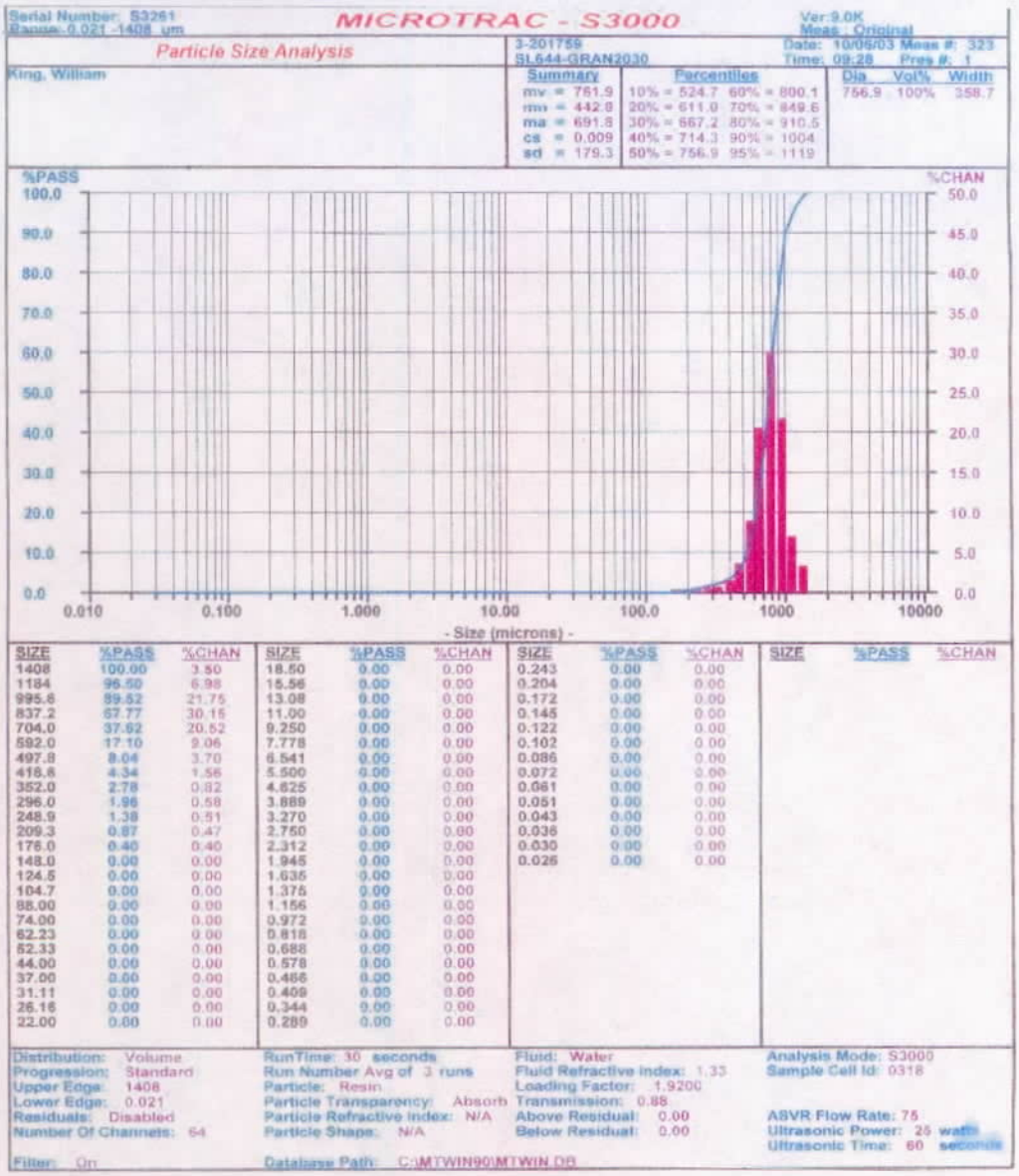
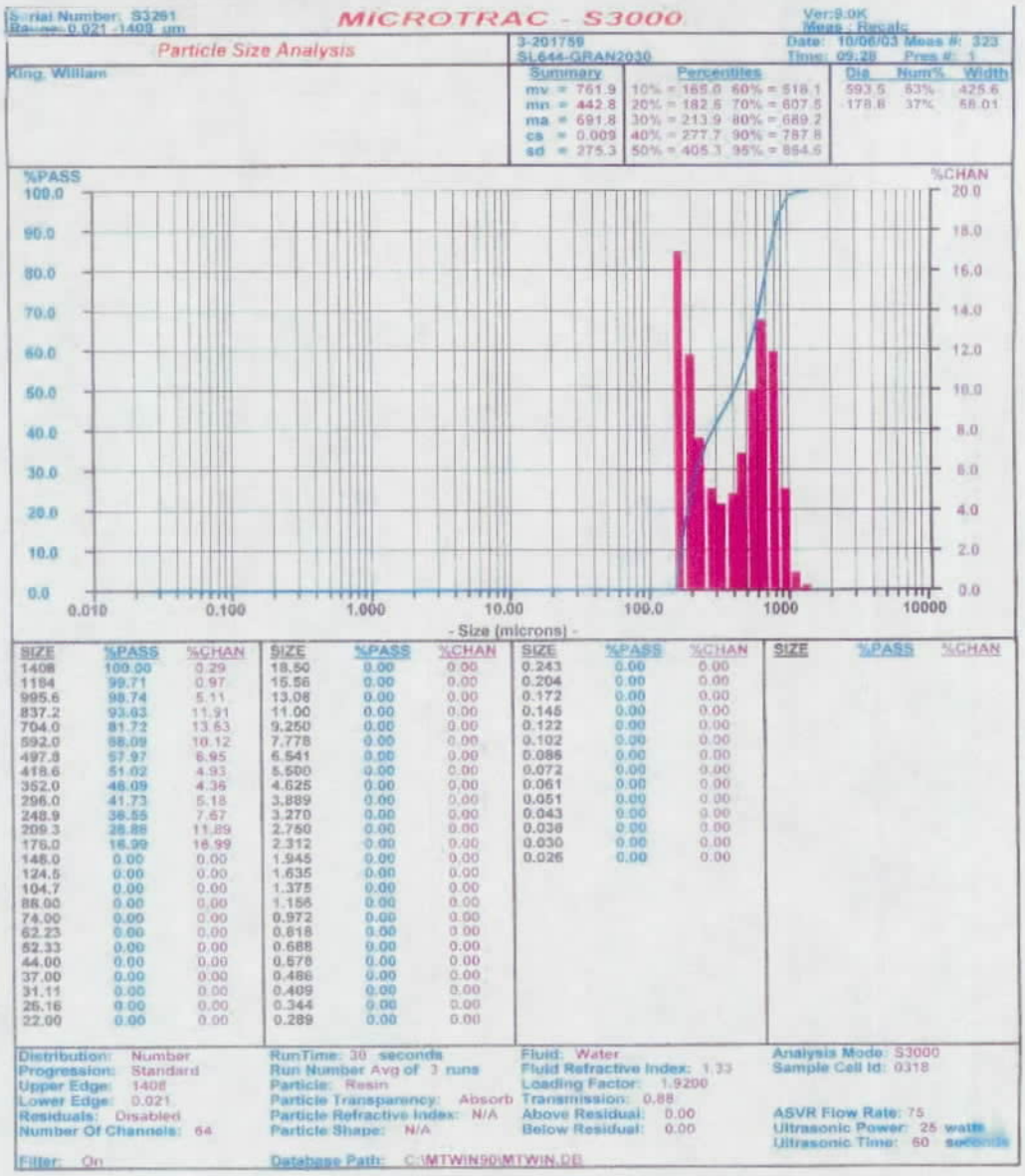


Figure B-7. Microtrac Particle Size Analysis Data for the –20 to +30 Mesh Sub-sample of SL644 Resin (volume-based data)



SIZE	%PASS	%CHAN	SIZE	%PASS	%CHAN	SIZE	%PASS	%CHAN	SIZE	%PASS	%CHAN
1408	100.00	0.29	18.50	0.00	0.00	0.243	0.00	0.00			
1194	99.71	0.97	15.56	0.00	0.00	0.204	0.00	0.00			
995.6	98.74	5.11	13.08	0.00	0.00	0.172	0.00	0.00			
837.2	93.63	11.91	11.00	0.00	0.00	0.145	0.00	0.00			
704.0	81.72	13.63	9.250	0.00	0.00	0.122	0.00	0.00			
592.0	68.09	10.12	7.778	0.00	0.00	0.102	0.00	0.00			
497.8	57.97	6.95	6.541	0.00	0.00	0.086	0.00	0.00			
418.6	51.02	4.93	5.500	0.00	0.00	0.072	0.00	0.00			
352.0	46.09	4.36	4.625	0.00	0.00	0.061	0.00	0.00			
296.0	41.73	5.18	3.889	0.00	0.00	0.051	0.00	0.00			
248.9	36.55	7.67	3.270	0.00	0.00	0.043	0.00	0.00			
209.3	28.88	11.89	2.750	0.00	0.00	0.036	0.00	0.00			
176.0	16.99	16.99	2.312	0.00	0.00	0.030	0.00	0.00			
148.0	0.00	0.00	1.945	0.00	0.00	0.026	0.00	0.00			
124.5	0.00	0.00	1.635	0.00	0.00						
104.7	0.00	0.00	1.375	0.00	0.00						
88.00	0.00	0.00	1.156	0.00	0.00						
74.00	0.00	0.00	0.972	0.00	0.00						
62.23	0.00	0.00	0.818	0.00	0.00						
52.33	0.00	0.00	0.688	0.00	0.00						
44.00	0.00	0.00	0.578	0.00	0.00						
37.00	0.00	0.00	0.486	0.00	0.00						
31.11	0.00	0.00	0.409	0.00	0.00						
26.16	0.00	0.00	0.344	0.00	0.00						
22.00	0.00	0.00	0.289	0.00	0.00						

Figure B-8. Microtrac Particle Size Analysis Data for the –20 to +30 Mesh Sub-sample of SL644 Resin (number-based data).

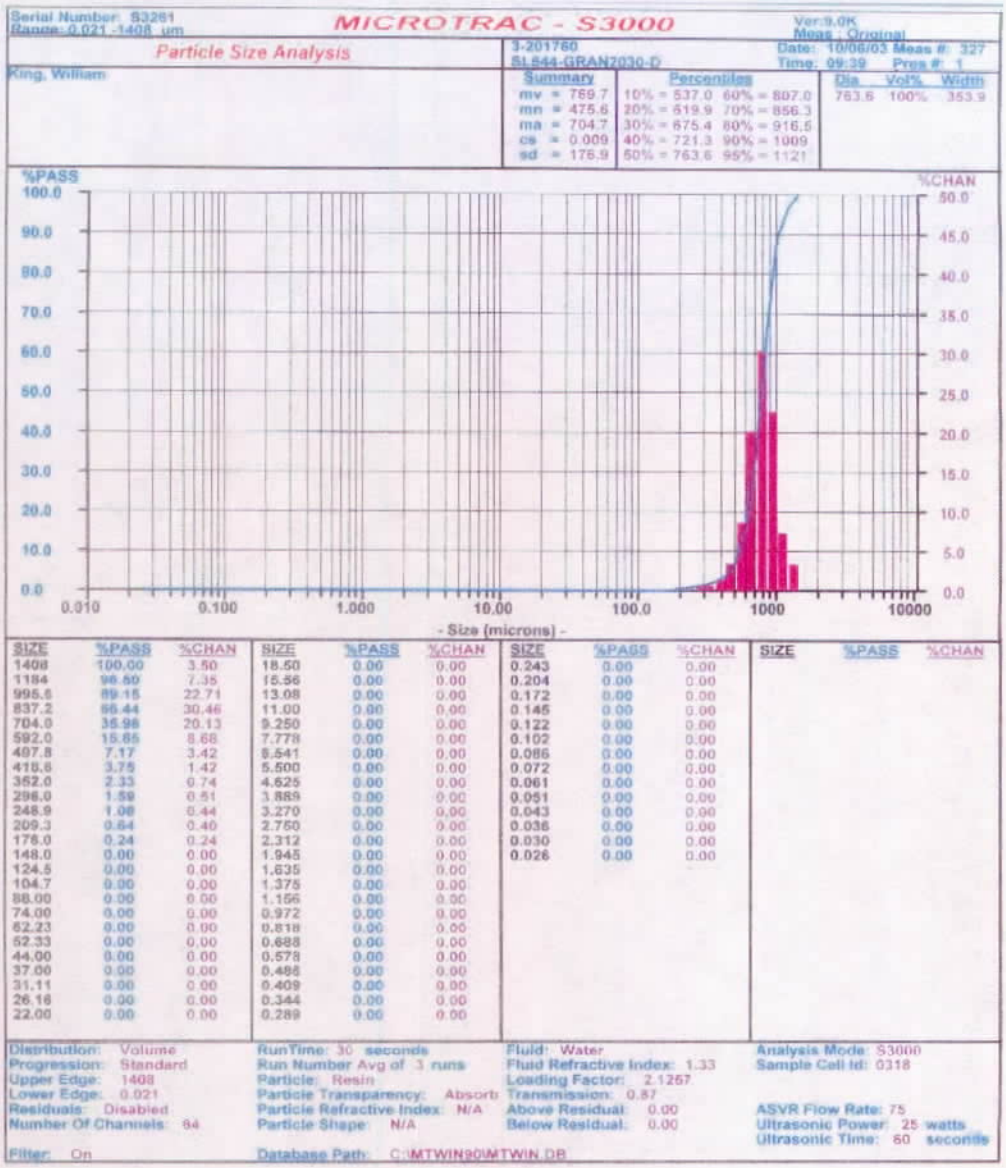


Figure B-9. Microtrac Particle Size Analysis Data for the –20 to +30 Mesh Sub-sample of SL644 Resin – Replicate (volume-based data)

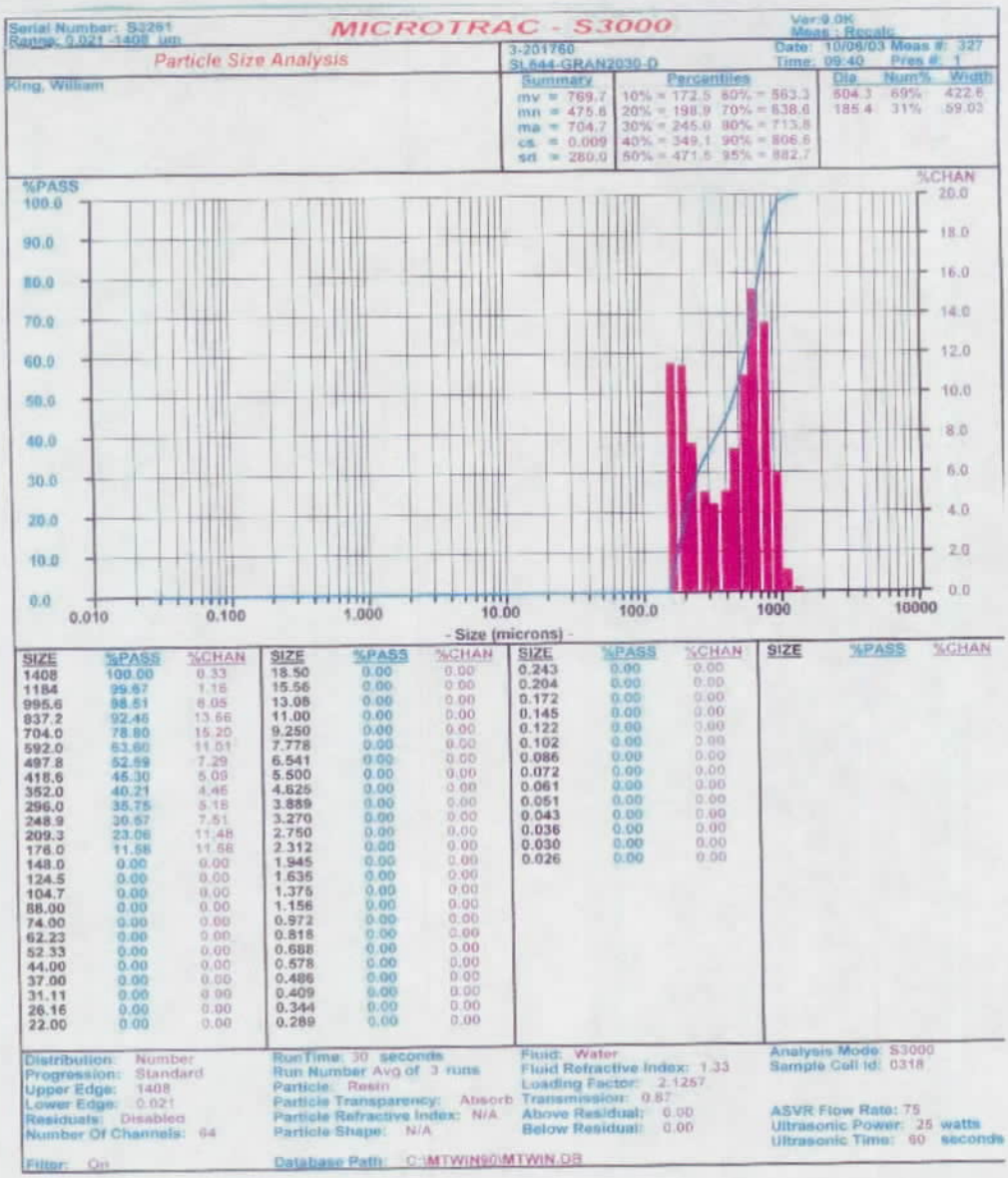


Figure B-10. Microtrac Particle Size Analysis Data for the –20 to +30 Mesh Sub-sample of SL644 Resin – Replicate (number-based data).

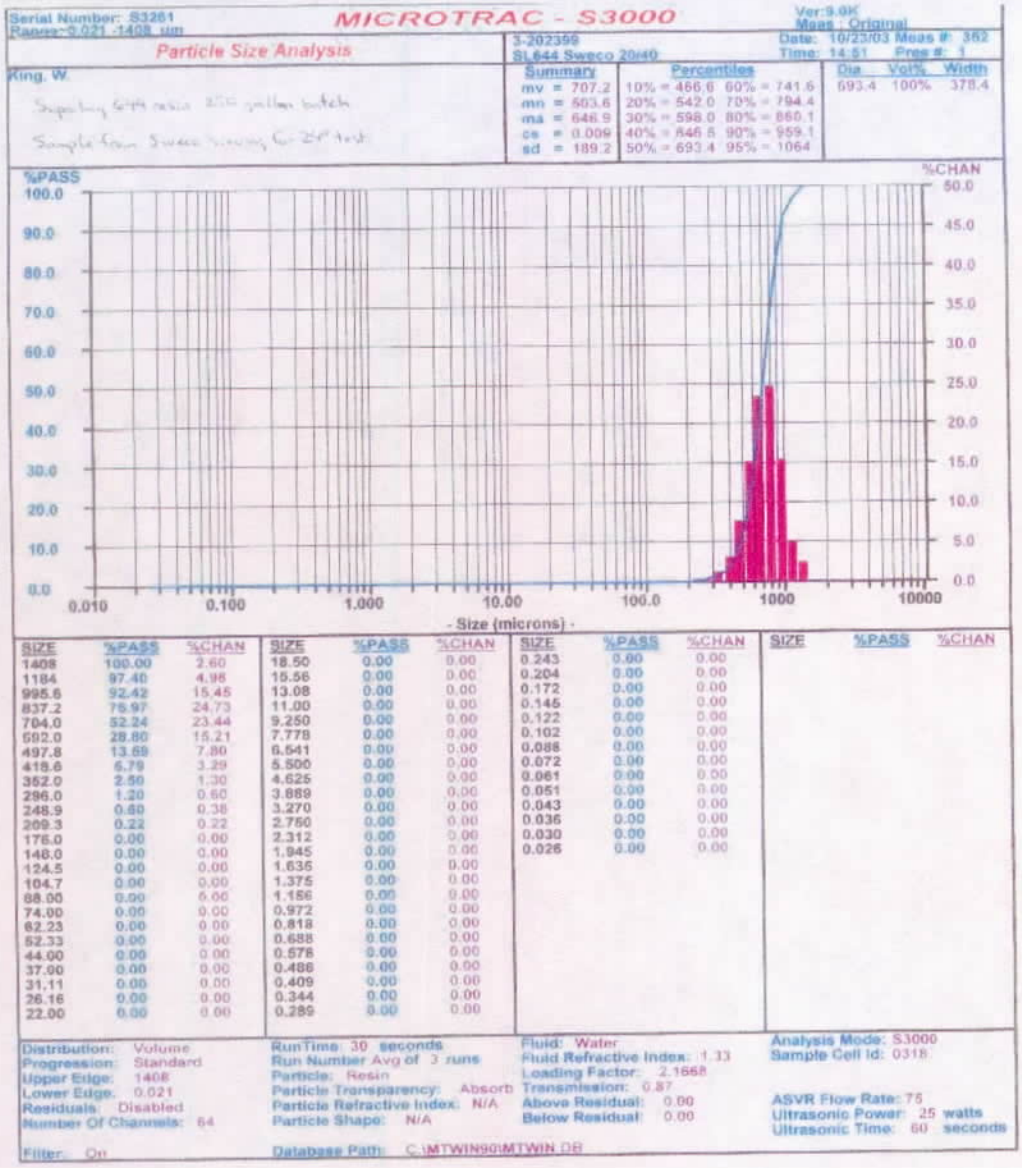


Figure B-11. Microtrac Particle Size Analysis Data for the –20 to +40 Mesh SuperLig 644 Resin Before Testing with the 24-inch Column (volume-based data)

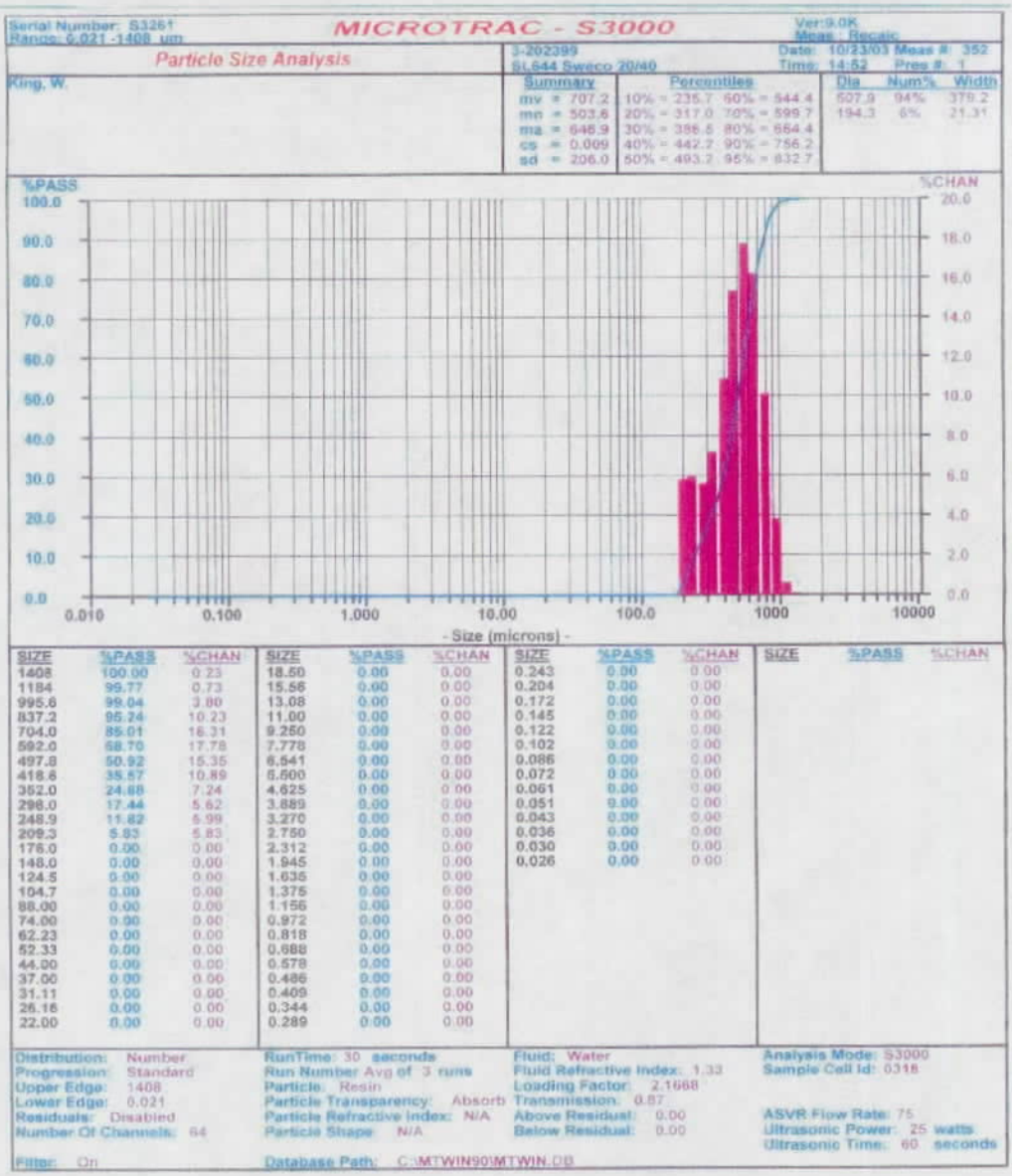


Figure B-12. Microtrac Particle Size Analysis Data for the –20 to +40 Mesh SuperLig 644 Resin Before Testing with the 24-inch Column (number-based data).

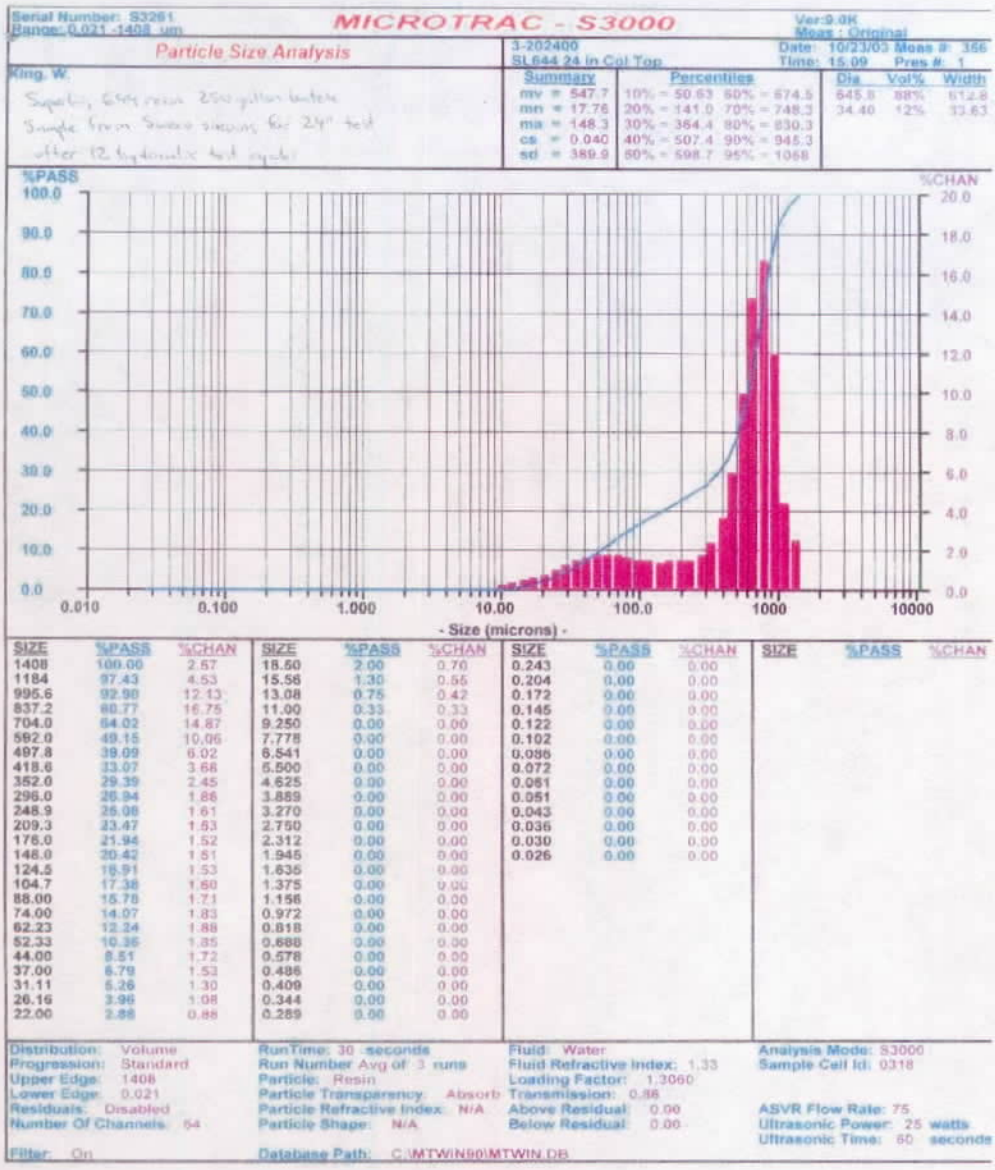
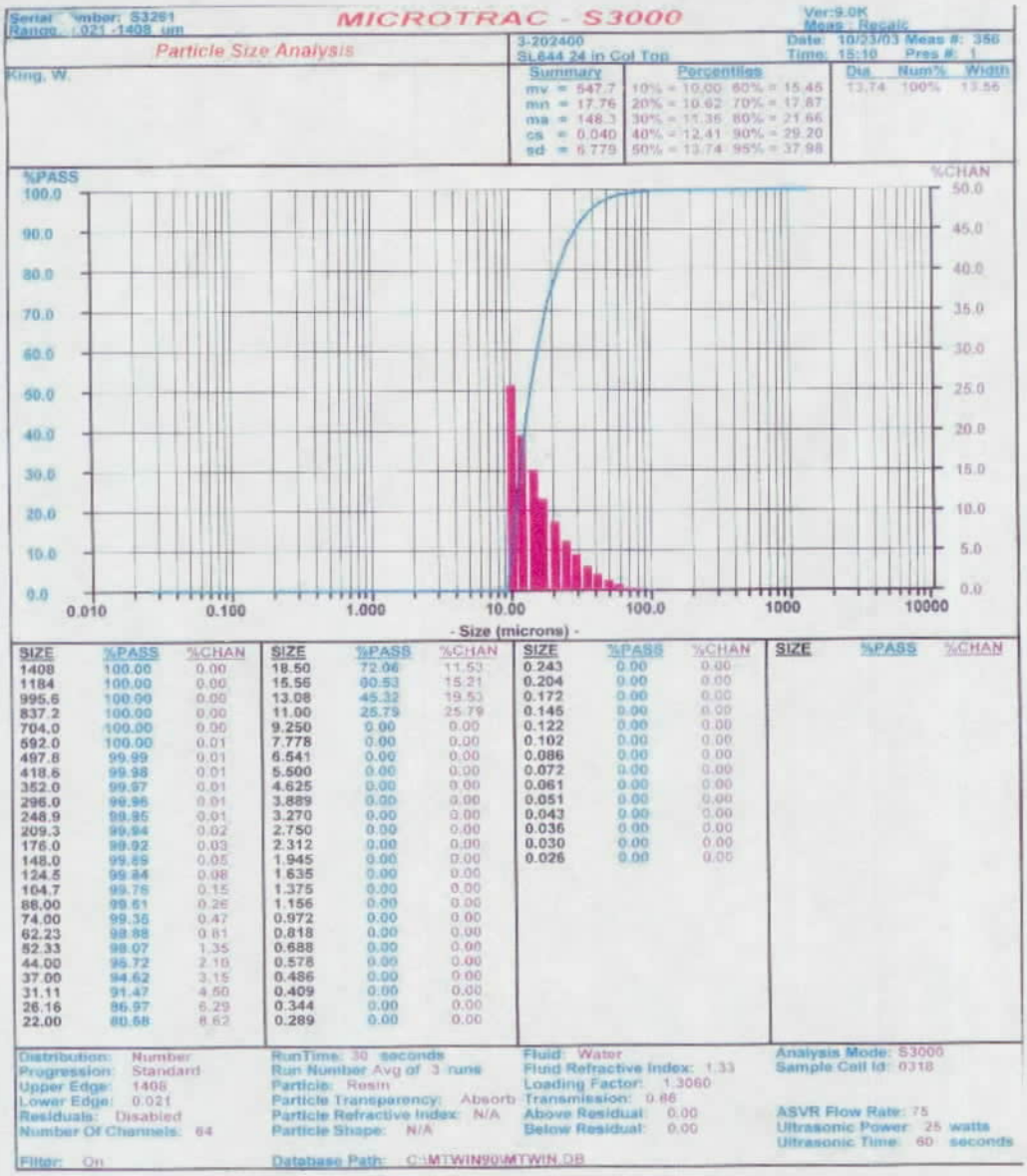


Figure B-13. Microtrac Particle Size Analysis Data for the –20 to +40 Mesh SuperLig 644 Resin After Testing with the 24-inch Column (volume-based data)



SIZE	%PASS	%CHAN	SIZE	%PASS	%CHAN	SIZE	%PASS	%CHAN	SIZE	%PASS	%CHAN
1408	100.00	0.00	18.50	72.06	11.53	0.243	0.00	0.00			
1184	100.00	0.00	15.56	60.53	15.21	0.204	0.00	0.00			
995.6	100.00	0.00	13.08	45.32	19.53	0.172	0.00	0.00			
837.2	100.00	0.00	11.00	25.79	25.79	0.145	0.00	0.00			
704.0	100.00	0.00	9.250	0.00	0.00	0.122	0.00	0.00			
592.0	100.00	0.01	7.778	0.00	0.00	0.102	0.00	0.00			
497.8	99.99	0.01	6.541	0.00	0.00	0.086	0.00	0.00			
418.6	99.98	0.01	5.500	0.00	0.00	0.072	0.00	0.00			
352.0	99.97	0.01	4.625	0.00	0.00	0.061	0.00	0.00			
296.0	99.96	0.01	3.889	0.00	0.00	0.051	0.00	0.00			
248.9	99.95	0.01	3.270	0.00	0.00	0.043	0.00	0.00			
209.3	99.94	0.02	2.750	0.00	0.00	0.036	0.00	0.00			
176.0	99.92	0.03	2.312	0.00	0.00	0.030	0.00	0.00			
148.0	99.89	0.05	1.945	0.00	0.00	0.026	0.00	0.00			
124.5	99.84	0.08	1.635	0.00	0.00						
104.7	99.76	0.15	1.375	0.00	0.00						
88.00	99.61	0.26	1.156	0.00	0.00						
74.00	99.35	0.47	0.972	0.00	0.00						
62.23	98.88	0.81	0.818	0.00	0.00						
52.33	98.07	1.35	0.688	0.00	0.00						
44.00	96.72	2.10	0.578	0.00	0.00						
37.00	94.62	3.15	0.486	0.00	0.00						
31.11	91.47	4.50	0.409	0.00	0.00						
26.16	86.97	6.29	0.344	0.00	0.00						
22.00	80.68	8.62	0.289	0.00	0.00						

Figure B-14. Microtrac Particle Size Analysis Data for the –20 to +40 Mesh SuperLig 644 Resin After Testing with the 24-inch Column (number-based data).

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Appendix C (Particle Kinetics and Column Assessment Input and Output Files)

VERSE-LC input and output files for the particle kinetics rig and laboratory-scale test columns are provided in this appendix. Six simulations were run. The input and output files for each case are listed below. A datafile.yio file was required for each of the models for the SRNL particle kinetics experiments, but not for the SRNL or PNNL column experiments. The datafile.yio file for SRNL particle kinetics Experiments 1 and 2 differed from that required for Experiments 3 and 4. In this appendix, the datafile.yio files are listed after their corresponding datafile.

C.1 SRNL Particle Kinetics Experiments 1 and 2

C.1.1 VERSE Datafile

```
SRNL Kinetics Rig - Experiments 1 and 2, SL644 -20+30 AN-105

Particle radius = 0.70*number median radius, Dp = Dinf/3
1, 2, 1, 6                          ncomp, nelem, ncol-bed, ncol-part
FCWNA                               isotherm,axial-disp,film-coef,surf-diff,BC-col
NNNYN                               input-only,perfusable,feed-equil,datafile.yio
M                                   comp-conc units
0.472, 1.75, 30.0, 60.0             Length(cm),Diam(cm),Q-flow(ml/min),CSTR-vol(ml)
238.09, 0.380, 0.668159,  0.0       part-rad(um), bed-void, part-void, sorb-cap()
0.0d-4                              initial concentrations (M)
S                                   COMMAND - conc step change
1, 0.0, 5.809d-4, 1, 0.0            spec id, time(min), conc(M), freq, dt(min)
R                                   COMMAND - Total recycle
0.0001, 9000.0, 1, 0.0              start time(min), duration(min), freq, wait time(min)
V                                   COMMAND - viscosity/density change
0.02736, 1.216                      fluid viscosity(poise), density(g/cm^3)
h                                   COMMAND - effluent history dump
0, 2.0d-4, 5.2E-2, 2.55E-6, 4.252E-4       unit op#, ptscale(1-4) filtering
h                                   COMMAND - effluent history dump
1, 2.0d-4, 5.2E-2, 2.55E-6, 4.252E-4       unit op#, ptscale(1-4) filtering
h                                   COMMAND - effluent history dump
2, 2.0d-4, 5.2E-2, 2.55E-6, 4.252E-4       unit op#, ptscale(1-4) filtering
h                                   COMMAND - effluent history dump
3, 2.0d-4, 5.2E-2, 2.55E-6, 4.252E-4       unit op#, ptscale(1-4) filtering
D                                   COMMAND - Dump Column Profile
-1, 15, 1, 0.0                      part. pt.(-1=>all), time(min), # of repeats, prd. of repet.
D
-1, 60, 1, 0.0
D
-1, 240, 1, 0.0
D
-1, 480, 1, 0.0
D
-1, 1440, 1, 0.0
D
-1, 2880, 1, 0.0
D
-1, 4320, 1, 0.0
D
-1, 7200, 1, 0.0
D
-1, 8640, 1, 0.0
-                                   end of commands
8640.0, 1.0                         end time(min), max dt in B.V.s
1.0d-7, 1.0d-4                      abs-tol, rel-tol
-                                   non-negative conc constraint
1.0d0                               size exclusion factor
5.2657d-5                           part-pore diffusivities(cm^2/min)
1.5797d-4                           Brownian diffusivities(cm^2/min)
```

```
1.2517d-01                  Freundlich/Langmuir Hybrid a     (moles/L B.V.)
1.0                         Freundlich/Langmuir Hybrid b     (1/M)
1.0                         Freundlich/Langmuir Hybrid Ma    (-)
1.0                         Freundlich/Langmuir Hybrid Mb    (-)
1.5758d-04                  Freundlich/Langmuir Hybrid beta  (-)
```

C.1.2 VERSE Datafile.yio

```
0.0000,    0.0000

0.0000,    0.0000
0.0000,    0.0000
0.0000,    0.0000
0.0000,    0.0000
0.0000,    0.0000
0.0000,    0.0000
0.0000,    0.0000
0.0000,    0.0000
0.0000,    0.0000
0.0000,    0.0000
0.0000,    0.0000
0.0000,    0.0000
0.0000,    0.0000
0.0000,    0.0000
0.0000,    0.0000
0.0000,    0.0000
0.0000,    0.0000
0.0000,    0.0000
0.0000,    0.0000
0.0000,    0.0000
0.0000,    0.0000
0.0000,    0.0000
0.0000,    0.0000
0.0000,    0.0000
0.0000,    0.0000
0.0000,    0.0000

0.0000,    0.0000
0.0000,    0.0000
0.0000,    0.0000
0.0000,    0.0000
0.0000,    0.0000
0.0000,    0.0000
0.0000,    0.0000
0.0000,    0.0000
0.0000,    0.0000
0.0000,    0.0000
0.0000,    0.0000
0.0000,    0.0000
0.0000,    0.0000
0.0000,    0.0000
5.809d-4,  0.0000
5.809d-4,  0.0000
```

C.1.3 VERSE Datafile.run

```
================================================================================

VERSE v7.80  by R. D. Whitley and N.-H. L. Wang, c1999 PRF
================================================================================
Input file: case.$
SRNL Kinetics Rig - Experiments 1 and 2, SL644 -20+30 AN-105
Particle radius = 0.70*number median radius, Dp = Dint/3
Begin Run:  13:04:10 on 04-12-2004   running under Windows 95/8
Finite elements    - axial:  2  particle: 1
Collocation points - axial:  1  particle: 6 => Number of eqns:    42
Inlet species at equilib.? N   Perfusable sorbent? N   Feed profile only? N
Use Profile File? Y   Generate Profile File? N
Axial dispersion correlation:   Chung & Wen (1968)
Film mass transfer correlation: Wilson & Geankoplis (1966)
================================================================================
SYSTEM PARAMETERS (at initial conditions):
```

```
t(stop)         =   8640.00000 min          dtheta max      =      1.00000 BV
abs. tol.       =       .10000E-06          rel. tol.       =       .10000E-03
Total Length    =       .47200 cm           D               =      1.75000 cm
Tot. Capacity   =       .00000 eq/L solid   Col. Vol.       =      1.13529 mL
F               =     30.00000 mL/min       Uo (linear)     =     32.82250 cm/min
R               =    238.09000 microns      L/R             =     19.82444
Bed Void frac.  =       .38000              Pcl. Porosity   =       .66816
Spec. Area      =     78.12172 1/cm         Time/BV         =       .01438 min
Vol CSTRs       =     60.00000 mL

Component no.   =       1
Ke   [-]        =  .10000E+01
Eb   [cm2/min]  =  .28634E+01
Dp   [cm2/min]  =  .52657E-04
Doo  [cm2/min]  =  .15797E-03
kf   [cm/min]   =  .14797E+00
Ds   [cm2/min]  =  .00000E+00

Dimensionless Groups:
Re              =  .43994E+00
Sc(i)           =  .85459E+04
Peb(i)          =  .54104E+01
Bi(i)           =  .10013E+03
Nf(i)           =  .43744E+00
Np(i)           =  .89253E-03
Pep(i)          =  .22211E+05

Isotherm        =  Freundlich/Langmuir Hybrid
Iso. Const. 1   =  .12517E+00
Iso. Const. 2   =  .10000E+01
Iso. Const. 3   =  .10000E+01
Iso. Const. 4   =  .10000E+01
Iso. Const. 5   =  .15758E-03
Init. Conc.     =  .00000E+00
Conc. at eqb.   =  .00000E+00
Conc. units             M
================================================================================
COMMAND LIST:
  1: Step conc. of component 1 at .0000     min to .5809E-03 M
     Execute   1 times, every .0000     mins.
  2: Full Recycle from .1000E-03 min to 9000.     min.
     Execute   1 times, every .0000     mins.
  3: User set viscosity to .2736E-01 poise and density to 1.216     g/cm3
  4: Monitor conc. history at stream  0.  Filename = case.$.h01
     Output density adjustments:
     .20E-03*default abs conc delta,      .52E-01*default rel conc delta,
     .26E-05*default force w/ conc delta, .43E-03*default force w/o conc delta
  5: Monitor conc. history at stream  1.  Filename = case.$.h02
     Output density adjustments:
     .20E-03*default abs conc delta,      .52E-01*default rel conc delta,
     .26E-05*default force w/ conc delta, .43E-03*default force w/o conc delta
  6: Monitor conc. history at stream  2.  Filename = case.$.h03
     Output density adjustments:
     .20E-03*default abs conc delta,      .52E-01*default rel conc delta,
     .26E-05*default force w/ conc delta, .43E-03*default force w/o conc delta
  7: Monitor conc. history at stream  3.  Filename = case.$.h04
     Output density adjustments:
     .20E-03*default abs conc delta,      .52E-01*default rel conc delta,
     .26E-05*default force w/ conc delta, .43E-03*default force w/o conc delta
  8: Dump full profile file at  15.00     min
     Execute   1 times, every .0000     mins.
  9: Dump full profile file at  60.00     min
     Execute   1 times, every .0000     mins.
 10: Dump full profile file at  240.0     min
     Execute   1 times, every .0000     mins.
 11: Dump full profile file at  480.0     min
     Execute   1 times, every .0000     mins.
 12: Dump full profile file at  1440.     min
     Execute   1 times, every .0000     mins.
 13: Dump full profile file at  2880.     min
     Execute   1 times, every .0000     mins.
 14: Dump full profile file at  4320.     min
     Execute   1 times, every .0000     mins.
```

```
 15: Dump full profile file at  7200.     min
     Execute   1 times, every .0000     mins.
 16: Dump full profile file at  8640.     min
     Execute   1 times, every .0000     mins.
================================================================================
VERSE-LC finished in ***** steps.  Average step size .1438E-01 minutes
End run:  13:05:37 on 04-12-2004
Integrated Areas in History Files:
case.$.h01                  .989671
case.$.h02                  .990621
case.$.h03                  .988720
case.$.h04                  .989671
```

C.2 SRNL Particle Kinetics Experiment 3

C.2.1 VERSE Datafile

```
SRNL Kinetics Rig - Experiments 3, SL644 -20+25 AN-105

Particle radius = 0.70*number median radius, Dp = Dinf/3
1, 2, 1, 6                          ncomp, nelem, ncol-bed, ncol-part
FCWNA                               isotherm,axial-disp,film-coef,surf-diff,BC-col
NNNYN                               input-only,perfusable,feed-equil,datafile.yio
M                                   comp-conc units
0.431, 1.75, 30.0, 60.0             Length(cm),Diam(cm),Q-flow(ml/min),CSTR-vol(ml)
266.61, 0.380, 0.668159,  0.0        part-rad(um), bed-void, part-void, sorb-cap()
0.0d-4                              initial concentrations (M)
S                                   COMMAND - conc step change
1, 0.0, 5.880d-4, 1, 0.0            spec id, time(min), conc(M), freq, dt(min)
R                                   COMMAND - Total recycle
0.0001, 9000.0, 1, 0.0              start time(min), duration(min), freq, wait time(min)
V                                   COMMAND - viscosity/density change
0.02736, 1.216                      fluid viscosity(poise), density(g/cm^3)
h                                   COMMAND - effluent history dump
0, 2.0d-4, 5.2E-2, 2.55E-6, 4.252E-4       unit op#, ptscale(1-4) filtering
h                                   COMMAND - effluent history dump
1, 2.0d-4, 5.2E-2, 2.55E-6, 4.252E-4       unit op#, ptscale(1-4) filtering
h                                   COMMAND - effluent history dump
2, 2.0d-4, 5.2E-2, 2.55E-6, 4.252E-4       unit op#, ptscale(1-4) filtering
h                                   COMMAND - effluent history dump
3, 2.0d-4, 5.2E-2, 2.55E-6, 4.252E-4       unit op#, ptscale(1-4) filtering
D                                   COMMAND - Dump Column Profile
-1, 15, 1, 0.0                      part. pt.(-1=>all), time(min), # of repeats, prd. of repet.
D
-1, 60, 1, 0.0
D
-1, 240, 1, 0.0
D
-1, 480, 1, 0.0
D
-1, 1440, 1, 0.0
D
-1, 2880, 1, 0.0
D
-1, 4320, 1, 0.0
D
-1, 7200, 1, 0.0
D
-1, 8640, 1, 0.0
-                                   end of commands
8640.0, 1.0                         end time(min), max dt in B.V.s
1.0d-7, 1.0d-4                      abs-tol, rel-tol
-                                   non-negative conc constraint
1.0d0                               size exclusion factor
5.2657d-5                           part-pore diffusivities(cm^2/min)
1.5797d-4                           Brownian diffusivities(cm^2/min)
1.1436d-01                          Freundlich/Langmuir Hybrid a     (moles/L B.V.)
1.0                                 Freundlich/Langmuir Hybrid b     (1/M)
1.0                                 Freundlich/Langmuir Hybrid Ma    (-)
1.0                                 Freundlich/Langmuir Hybrid Mb    (-)
```

```
1.5758d-04                    Freundlich/Langmuir Hybrid beta (-)
```

C.2.2 VERSE Datafile.yio

```
0.0000,    0.0000

0.0000,    0.0000
0.0000,    0.0000
0.0000,    0.0000
0.0000,    0.0000
0.0000,    0.0000
0.0000,    0.0000
0.0000,    0.0000
0.0000,    0.0000
0.0000,    0.0000
0.0000,    0.0000
0.0000,    0.0000
0.0000,    0.0000
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0.0000,    0.0000
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0.0000,    0.0000
0.0000,    0.0000
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0.0000,    0.0000
0.0000,    0.0000
0.0000,    0.0000
0.0000,    0.0000
0.0000,    0.0000
0.0000,    0.0000
0.0000,    0.0000
5.880d-4,  0.0000
5.880d-4,  0.0000
```

C.2.3 VERSE Datafile.run

```
================================================================================

VERSE v7.80  by R. D. Whitley and N.-H. L. Wang, c1999 PRF
================================================================================
Input file: case.$
SRNL Kinetics Rig - Experiments 3, SL644 -20+25 AN-105
Particle radius = 0.70*number median radius, Dp = Dinf/3
Begin Run:  13:23:52 on 04-15-2004   running under Windows 95/8
Finite elements    - axial:  2  particle: 1
Collocation points - axial:  1  particle: 6 => Number of eqns:    42
Inlet species at equilib.? N   Perfusable sorbent? N   Feed profile only? N
Use Profile File? Y   Generate Profile File? N
Axial dispersion correlation:   Chung & Wen (1968)
Film mass transfer correlation: Wilson & Geankoplis (1966)
================================================================================
SYSTEM PARAMETERS (at initial conditions):

t(stop)        =   8640.00000 min        dtheta max     =      1.00000 BV
abs. tol.      =       .10000E-06        rel. tol.      =       .10000E-03
```

```
Total Length   =       .43100 cm          D              =      1.75000 cm
Tot. Capacity  =       .00000 eq/L solid  Col. Vol.       =      1.03668 mL
F              =     30.00000 mL/min      Uo (linear)    =     32.82250 cm/min
R              =    266.61000 microns     L/R            =     16.16594
Bed Void frac. =       .38000            Pcl. Porosity  =       .66816
Spec. Area     =     69.76483 1/cm        Time/BV        =       .01313 min
Vol CSTRs      =     60.00000 mL

Component no.  =      1
Ke  [-]        =  .10000E+01
Eb  [cm2/min]  =  .32000E+01
Dp  [cm2/min]  =  .52657E-04
Doo [cm2/min]  =  .15797E-03
kf  [cm/min]   =  .13722E+00
Ds  [cm2/min]  =  .00000E+00

Dimensionless Groups:
Re             =  .49264E+00
Sc(i)          =  .85459E+04
Peb(i)         =  .44208E+01
Bi(i)          =  .10398E+03
Nf(i)          =  .33080E+00
Np(i)          =  .64996E-03
Pep(i)         =  .24872E+05

Isotherm       =  Freundlich/Langmuir Hybrid
Iso. Const. 1  =  .11436E+00
Iso. Const. 2  =  .10000E+01
Iso. Const. 3  =  .10000E+01
Iso. Const. 4  =  .10000E+01
Iso. Const. 5  =  .15758E-03
Init. Conc.    =  .00000E+00
Conc. at eqb.  =  .00000E+00
Conc. units       M
================================================================================
COMMAND LIST:
  1: Step conc. of component 1 at .0000     min to .5880E-03 M
     Execute   1 times, every .0000     mins.
  2: Full Recycle from .1000E-03 min to 9000.     min.
     Execute   1 times, every .0000     mins.
  3: User set viscosity to .2736E-01 poise and density to 1.216     g/cm3
  4: Monitor conc. history at stream  0.  Filename = case.$.h01
     Output density adjustments:
     .20E-03*default abs conc delta,      .52E-01*default rel conc delta,
     .26E-05*default force w/ conc delta, .43E-03*default force w/o conc delta
  5: Monitor conc. history at stream  1.  Filename = case.$.h02
     Output density adjustments:
     .20E-03*default abs conc delta,      .52E-01*default rel conc delta,
     .26E-05*default force w/ conc delta, .43E-03*default force w/o conc delta
  6: Monitor conc. history at stream  2.  Filename = case.$.h03
     Output density adjustments:
     .20E-03*default abs conc delta,      .52E-01*default rel conc delta,
     .26E-05*default force w/ conc delta, .43E-03*default force w/o conc delta
  7: Monitor conc. history at stream  3.  Filename = case.$.h04
     Output density adjustments:
     .20E-03*default abs conc delta,      .52E-01*default rel conc delta,
     .26E-05*default force w/ conc delta, .43E-03*default force w/o conc delta
  8: Dump full profile file at  15.00     min
     Execute   1 times, every .0000     mins.
  9: Dump full profile file at  60.00     min
     Execute   1 times, every .0000     mins.
 10: Dump full profile file at  240.0     min
     Execute   1 times, every .0000     mins.
 11: Dump full profile file at  480.0     min
     Execute   1 times, every .0000     mins.
 12: Dump full profile file at  1440.     min
     Execute   1 times, every .0000     mins.
 13: Dump full profile file at  2880.     min
     Execute   1 times, every .0000     mins.
 14: Dump full profile file at  4320.     min
     Execute   1 times, every .0000     mins.
 15: Dump full profile file at  7200.     min
     Execute   1 times, every .0000     mins.
 16: Dump full profile file at  8640.     min
```

```
     Execute   1 times, every .0000     mins.
================================================================================
VERSE-LC finished in ***** steps.  Average step size .1313E-01 minutes
End run:  13:25:24 on 04-15-2004
Integrated Areas in History Files:
case.$.h01                  1.25024
case.$.h02                  1.25115
case.$.h03                  1.24933
case.$.h04                  1.25024
```

C.3 SRNL Particle Kinetics Experiment 4

C.3.1 VERSE Datafile

```
SRNL Kinetics Rig - Experiments 4, SL644 -25+30 AN-105

Particle radius = 0.70*number median radius, Dp = Dinf/3
1, 2, 1, 6                          ncomp, nelem, ncol-bed, ncol-part
FCWNA                               isotherm,axial-disp,film-coef,surf-diff,BC-col
NNNYN                               input-only,perfusable,feed-equil,datafile.yio
M                                   comp-conc units
0.431, 1.75, 30.0, 60.0             Length(cm),Diam(cm),Q-flow(ml/min),CSTR-vol(ml)
226.58, 0.380, 0.668159,  0.0       part-rad(um), bed-void, part-void, sorb-cap()
0.0d-4                              initial concentrations (M)
S                                   COMMAND - conc step change
1, 0.0, 5.880d-4, 1, 0.0            spec id, time(min), conc(M), freq, dt(min)
R                                   COMMAND - Total recycle
0.0001, 9000.0, 1, 0.0              start time(min), duration(min), freq, wait time(min)
V                                   COMMAND - viscosity/density change
0.02736, 1.216                      fluid viscosity(poise), density(g/cm^3)
h                                   COMMAND - effluent history dump
0, 2.0d-4, 5.2E-2, 2.55E-6, 4.252E-4       unit op#, ptscale(1-4) filtering
h                                   COMMAND - effluent history dump
1, 2.0d-4, 5.2E-2, 2.55E-6, 4.252E-4       unit op#, ptscale(1-4) filtering
h                                   COMMAND - effluent history dump
2, 2.0d-4, 5.2E-2, 2.55E-6, 4.252E-4       unit op#, ptscale(1-4) filtering
h                                   COMMAND - effluent history dump
3, 2.0d-4, 5.2E-2, 2.55E-6, 4.252E-4       unit op#, ptscale(1-4) filtering
D                                   COMMAND - Dump Column Profile
-1, 15, 1, 0.0                      part. pt.(-1=>all), time(min), # of repeats, prd. of repet.
D
-1, 60, 1, 0.0
D
-1, 240, 1, 0.0
D
-1, 480, 1, 0.0
D
-1, 1440, 1, 0.0
D
-1, 2880, 1, 0.0
D
-1, 4320, 1, 0.0
D
-1, 7200, 1, 0.0
D
-1, 8640, 1, 0.0
-                                   end of commands
8640.0, 1.0                         end time(min), max dt in B.V.s
1.0d-7, 1.0d-4                      abs-tol, rel-tol
-                                   non-negative conc constraint
1.0d0                               size exclusion factor
5.2657d-5                           part-pore diffusivities(cm^2/min)
1.5797d-4                           Brownian diffusivities(cm^2/min)
1.0680d-01                          Freundlich/Langmuir Hybrid a     (moles/L B.V.)
1.0                                 Freundlich/Langmuir Hybrid b     (1/M)
1.0                                 Freundlich/Langmuir Hybrid Ma    (-)
1.0                                 Freundlich/Langmuir Hybrid Mb    (-)
1.5758d-04                          Freundlich/Langmuir Hybrid beta (-)
```

C.3.2 VERSE Datafile.yio

```
0.0000,     0.0000

0.0000,     0.0000
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0.0000,     0.0000
0.0000,     0.0000
0.0000,     0.0000
0.0000,     0.0000
0.0000,     0.0000
0.0000,     0.0000
5.880d-4,   0.0000
5.880d-4,   0.0000
```

C.3.3 VERSE Datafile.run

```
================================================================================

VERSE v7.80  by R. D. Whitley and N.-H. L. Wang, c1999 PRF
================================================================================
Input file: case.$
SRNL Kinetics Rig - Experiments 4, SL644 -25+30 AN-105
Particle radius = 0.70*number median radius, Dp = Dinf/3
Begin Run:  15:14:21 on 04-19-2004   running under Windows 95/8
Finite elements    - axial:  2  particle: 1
Collocation points - axial:  1  particle: 6 => Number of eqns:    42
Inlet species at equilib.? N   Perfusable sorbent? N   Feed profile only? N
Use Profile File? Y   Generate Profile File? N
Axial dispersion correlation:   Chung & Wen (1968)
Film mass transfer correlation: Wilson & Geankoplis (1966)
================================================================================
SYSTEM PARAMETERS (at initial conditions):

t(stop)         =   8640.00000 min          dtheta max      =      1.00000 BV
abs. tol.       =       .10000E-06          rel. tol.       =       .10000E-03
Total Length    =       .43100 cm           D               =      1.75000 cm
Tot. Capacity   =       .00000 eq/L solid   Col. Vol.       =      1.03668 mL
F               =     30.00000 mL/min       Uo (linear)     =     32.82250 cm/min
R               =    226.58000 microns      L/R             =     19.02198
```

```
Bed Void frac. =       .38000          Pcl. Porosity  =       .66816
Spec. Area     =     82.09021 1/cm       Time/BV        =       .01313 min
Vol CSTRs      =     60.00000 mL

Component no.  =       1
Ke   [-]       =  .10000E+01
Eb   [cm2/min] =  .27273E+01
Dp   [cm2/min] =  .52657E-04
Doo  [cm2/min] =  .15797E-03
kf   [cm/min]  =  .15294E+00
Ds   [cm2/min] =  .00000E+00

Dimensionless Groups:
Re             =  .41867E+00
Sc(i)          =  .85459E+04
Peb(i)         =  .51871E+01
Bi(i)          =  .98491E+02
Nf(i)          =  .43383E+00
Np(i)          =  .89991E-03
Pep(i)         =  .21138E+05

Isotherm       =  Freundlich/Langmuir Hybrid
Iso. Const. 1  =  .10680E+00
Iso. Const. 2  =  .10000E+01
Iso. Const. 3  =  .10000E+01
Iso. Const. 4  =  .10000E+01
Iso. Const. 5  =  .15758E-03
Init. Conc.    =  .00000E+00
Conc. at eqb.  =  .00000E+00
Conc. units            M
================================================================================
COMMAND LIST:
  1: Step conc. of component 1 at .0000     min to .5880E-03 M
     Execute   1 times, every .0000     mins.
  2: Full Recycle from .1000E-03 min to 9000.     min.
     Execute   1 times, every .0000     mins.
  3: User set viscosity to .2736E-01 poise and density to 1.216     g/cm3
  4: Monitor conc. history at stream  0.  Filename = case.$.h01
     Output density adjustments:
     .20E-03*default abs conc delta,      .52E-01*default rel conc delta,
     .26E-05*default force w/ conc delta, .43E-03*default force w/o conc delta
  5: Monitor conc. history at stream  1.  Filename = case.$.h02
     Output density adjustments:
     .20E-03*default abs conc delta,      .52E-01*default rel conc delta,
     .26E-05*default force w/ conc delta, .43E-03*default force w/o conc delta
  6: Monitor conc. history at stream  2.  Filename = case.$.h03
     Output density adjustments:
     .20E-03*default abs conc delta,      .52E-01*default rel conc delta,
     .26E-05*default force w/ conc delta, .43E-03*default force w/o conc delta
  7: Monitor conc. history at stream  3.  Filename = case.$.h04
     Output density adjustments:
     .20E-03*default abs conc delta,      .52E-01*default rel conc delta,
     .26E-05*default force w/ conc delta, .43E-03*default force w/o conc delta
  8: Dump full profile file at  15.00     min
     Execute   1 times, every .0000     mins.
  9: Dump full profile file at  60.00     min
     Execute   1 times, every .0000     mins.
 10: Dump full profile file at  240.0     min
     Execute   1 times, every .0000     mins.
 11: Dump full profile file at  480.0     min
     Execute   1 times, every .0000     mins.
 12: Dump full profile file at  1440.     min
     Execute   1 times, every .0000     mins.
 13: Dump full profile file at  2880.     min
     Execute   1 times, every .0000     mins.
 14: Dump full profile file at  4320.     min
     Execute   1 times, every .0000     mins.
 15: Dump full profile file at  7200.     min
     Execute   1 times, every .0000     mins.
 16: Dump full profile file at  8640.     min
     Execute   1 times, every .0000     mins.
================================================================================
VERSE-LC finished in ***** steps.  Average step size .1313E-01 minutes
End run:  15:15:52 on 04-19-2004
```

```
 Integrated Areas in History Files:
 case.$.h01                1.31727
 case.$.h02                1.31815
 case.$.h03                1.31638
 case.$.h04                1.31727
```

C.4 SRNL 250-Gallon -20 to +30 Column Test

C.4.1 VERSE Datafile

```
SRNL Column - SL644 250-Gallon Batch -20+30, AN-105

Particle radius = 0.70*number median radius, Dp = Dinf/3
1,50, 4, 6                          ncomp, nelem, ncol-bed, ncol-part
FCWNA                               isotherm,axial-disp,film-coef,surf-diff,BC-col
NNNNN                               input-only,perfusable,feed-equil,datafile.yio
M                                   comp-conc units
17.20, 2.67, 3.43, 38.1             Length(cm),Diam(cm),Q-flow(ml/min),CSTR-vol(ml)
238.09, 0.380, 0.668159,  0.0       part-rad(um), bed-void, part-void, sorb-cap()
0.0d-4                              initial concentrations (M)
S                                   COMMAND - conc step change
1, 0.0, 5.8275d-4, 1, 0.0           spec id, time(min), conc(M), freq, dt(min)
V                                   COMMAND - viscosity/density change
0.02736, 1.216                      fluid viscosity(poise), density(g/cm^3)
h                                           COMMAND - effluent history dump
0, 2.0d-4, 5.2E-2, 4.552E-3, 0.759          unit op#, ptscale(1-4) filtering
h                                           COMMAND - effluent history dump
1, 2.0d-4, 5.2E-2, 4.552E-3, 0.759          unit op#, ptscale(1-4) filtering
h                                           COMMAND - effluent history dump
2, 2.0d-4, 5.2E-2, 4.552E-3, 0.759          unit op#, ptscale(1-4) filtering
h                                           COMMAND - effluent history dump
3, 2.0d-4, 5.2E-2, 4.552E-3, 0.759          unit op#, ptscale(1-4) filtering
D                                   COMMAND - Dump Column Profile
-1, 15, 1, 0.0                      part. pt.(-1=>all), time(min), # of repeats, prd. of repet.
D
-1, 60, 1, 0.0
D
-1, 240, 1, 0.0
D
-1, 480, 1, 0.0
D
-1, 1440, 1, 0.0
D
-1, 2880, 1, 0.0
D
-1, 4320, 1, 0.0
D
-1, 7300, 1, 0.0
-                                   end of commands
8450.0, 1.0                         end time(min), max dt in B.V.s
1.0d-7, 1.0d-4                      abs-tol, rel-tol
-                                   non-negative conc constraint

1.0d0                               size exclusion factor
5.2657d-5                           part-pore diffusivities(cm^2/min)
1.5797d-4                           Brownian diffusivities(cm^2/min)
1.4962d-1                           Freundlich/Langmuir Hybrid a     (moles/L B.V.)
1.0                                 Freundlich/Langmuir Hybrid b     (1/M)
1.0                                 Freundlich/Langmuir Hybrid Ma    (-)
1.0                                 Freundlich/Langmuir Hybrid Mb    (-)
1.5758d-4                           Freundlich/Langmuir Hybrid beta  (-)
```

C.4.2 VERSE Datafile.run

```
================================================================================

VERSE v7.80  by R. D. Whitley and N.-H. L. Wang, c1999 PRF
================================================================================
Input file: case.$
SRNL Column - SL644 250-Gallon Batch -20+30, AN-105
```

```
Particle radius = 0.70*number median radius, Dp = Dinf/3
Begin Run:  08:39:58 on 04-19-2004   running under Windows 95/8
Finite elements    - axial: 50  particle: 1
Collocation points - axial:  4  particle: 6 => Number of eqns:  2010
Inlet species at equilib.? N   Perfusable sorbent? N   Feed profile only? N
Use Profile File? N   Generate Profile File? N
Axial dispersion correlation:   Chung & Wen (1968)
Film mass transfer correlation: Wilson & Geankoplis (1966)
================================================================================
SYSTEM PARAMETERS (at initial conditions):

t(stop)        =   8450.00000 min        dtheta max     =      1.00000 BV
abs. tol.      =       .10000E-06        rel. tol.      =       .10000E-03
Total Length   =     17.20000 cm         D              =      2.67000 cm
Tot. Capacity  =       .00000 eq/L solid Col. Vol.      =     96.30323 mL
F              =      3.43000 mL/min     Uo (linear)    =      1.61212 cm/min
R              =    238.09000 microns    L/R            =    722.41589
Bed Void frac. =       .38000           Pcl. Porosity  =       .66816
Spec. Area     =     78.12172 1/cm       Time/BV        =     10.66916 min
Vol CSTRs      =     38.10000 mL

Component no.  =      1
Ke  [-]        =  .10000E+01
Eb  [cm2/min]  =  .14459E+00
Dp  [cm2/min]  =  .52657E-04
Doo [cm2/min]  =  .15797E-03
kf  [cm/min]   =  .54188E-01
Ds  [cm2/min]  =  .00000E+00

Dimensionless Groups:
Re             =  .21608E-01
Sc(i)          =  .85459E+04
Peb(i)         =  .19177E+03
Bi(i)          =  .36670E+02
Nf(i)          =  .11886E+03
Np(i)          =  .66219E+00
Pep(i)         =  .10909E+04

Isotherm       =  Freundlich/Langmuir Hybrid
Iso. Const. 1  =  .14962E+00
Iso. Const. 2  =  .10000E+01
Iso. Const. 3  =  .10000E+01
Iso. Const. 4  =  .10000E+01
Iso. Const. 5  =  .15758E-03
Init. Conc.    =  .00000E+00
Conc. at eqb.  =  .00000E+00
Conc. units       M
================================================================================
COMMAND LIST:
  1: Step conc. of component 1 at .0000     min to .5828E-03 M
     Execute   1 times, every .0000     mins.
  2: User set viscosity to .2736E-01 poise and density to 1.216     g/cm3
  3: Monitor conc. history at stream  0.  Filename = case.$.h01
     Output density adjustments:
     .20E-03*default abs conc delta,       .52E-01*default rel conc delta,
     .46E-02*default force w/ conc delta, .76    *default force w/o conc delta
  4: Monitor conc. history at stream  1.  Filename = case.$.h02
     Output density adjustments:
     .20E-03*default abs conc delta,       .52E-01*default rel conc delta,
     .46E-02*default force w/ conc delta, .76    *default force w/o conc delta
  5: Monitor conc. history at stream  2.  Filename = case.$.h03
     Output density adjustments:
     .20E-03*default abs conc delta,       .52E-01*default rel conc delta,
     .46E-02*default force w/ conc delta, .76    *default force w/o conc delta
  6: Monitor conc. history at stream  3.  Filename = case.$.h04
     Output density adjustments:
     .20E-03*default abs conc delta,       .52E-01*default rel conc delta,
     .46E-02*default force w/ conc delta, .76    *default force w/o conc delta
  7: Dump full profile file at  15.00     min
     Execute   1 times, every .0000     mins.
  8: Dump full profile file at  60.00     min
     Execute   1 times, every .0000     mins.
  9: Dump full profile file at  240.0     min
     Execute   1 times, every .0000     mins.
```

```
 10: Dump full profile file at  480.0     min
     Execute   1 times, every .0000     mins.
 11: Dump full profile file at  1440.     min
     Execute   1 times, every .0000     mins.
 12: Dump full profile file at  2880.     min
     Execute   1 times, every .0000     mins.
 13: Dump full profile file at  4320.     min
     Execute   1 times, every .0000     mins.
 14: Dump full profile file at  7300.     min
     Execute   1 times, every .0000     mins.
================================================================================
VERSE-LC finished in  1059 steps.  Average step size 7.979     minutes
End run:  08:42:57 on 04-19-2004
Integrated Areas in History Files:
case.$.h01                  4.92423
case.$.h02                  4.91774
case.$.h03                  1.59868
case.$.h04                  1.59220
```

C.5 PNNL Column 1 Test

C.5.1 VERSE Datafile

```
PNNL Column 1 - Cycle 1, SL644 -20+70 AZ-102

Particle radius = 0.70*number median radius, Dp = Dinf/3
1,50, 4, 6                      ncomp, nelem, ncol-bed, ncol-part
FCWNA                           isotherm,axial-disp,film-coef,surf-diff,BC-col
NNNNN                           input-only,perfusable,feed-equil,datafile.yio
M                               comp-conc units
5.200, 2.0, 0.420, 13.0         Length(cm),Diam(cm),Q-flow(ml/min),CSTR-vol(ml)
108.21, 0.380, 0.668159,  0.0   part-rad(um), bed-void, part-void, sorb-cap()
0.0d-4                          initial concentrations (M)
S                               COMMAND - conc step change
1, 0.0, 3.66d-4, 1, 0.0         spec id, time(min), conc(M), freq, dt(min)
V                               COMMAND - viscosity/density change
0.027389, 1.24                  fluid viscosity(poise), density(g/cm^3)
h                                       COMMAND - effluent history dump
0, 2.0d-4, 5.2E-2, 4.552E-3, 0.759      unit op#, ptscale(1-4) filtering
h                                       COMMAND - effluent history dump
1, 2.0d-4, 5.2E-2, 4.552E-3, 0.759      unit op#, ptscale(1-4) filtering
h                                       COMMAND - effluent history dump
2, 2.0d-4, 5.2E-2, 4.552E-3, 0.759      unit op#, ptscale(1-4) filtering
h                                       COMMAND - effluent history dump
3, 2.0d-4, 5.2E-2, 4.552E-3, 0.759      unit op#, ptscale(1-4) filtering
D                               COMMAND - Dump Column Profile
-1, 15, 1, 0.0                  part. pt.(-1=>all), time(min), # of repeats, prd. of repet.
D
-1, 60, 1, 0.0
D
-1, 240, 1, 0.0
D
-1, 480, 1, 0.0
D
-1, 1440, 1, 0.0
D
-1, 2880, 1, 0.0
D
-1, 4320, 1, 0.0
D
-1, 7473, 1, 0.0
-                               end of commands
10500., 1.0                     end time(min), max dt in B.V.s
1.0d-7, 1.0d-4                  abs-tol, rel-tol
-                               non-negative conc constraint
1.0d0                           size exclusion factor
3.7993d-5                       part-pore diffusivities(cm^2/min)
1.1398d-4                       Brownian diffusivities(cm^2/min)
1.3910d-1                       Freundlich/Langmuir Hybrid a (moles/L B.V.)
1.0                             Freundlich/Langmuir Hybrid b    (1/M)
1.0                             Freundlich/Langmuir Hybrid Ma   (-)
```

```
1.0                          Freundlich/Langmuir Hybrid Mb   (-)
2.3835d-4                    Freundlich/Langmuir Hybrid beta (-)
```

C.5.2 VERSE Datafile.run

```
================================================================================

VERSE v7.80  by R. D. Whitley and N.-H. L. Wang, c1999 PRF
================================================================================
Input file: case.$
PNNL Column 1 - Cycle 1, SL644 -20+70 AZ-102
Particle radius = 0.70*number median radius, Dp = Dinf/3
Begin Run:  12:01:03 on 04-21-2004   running under Windows 95/8
Finite elements    - axial: 50  particle: 1
Collocation points - axial:  4  particle: 6 => Number of eqns:  2010
Inlet species at equilib.? N   Perfusable sorbent? N   Feed profile only? N
Use Profile File? N   Generate Profile File? N
Axial dispersion correlation:   Chung & Wen (1968)
Film mass transfer correlation: Wilson & Geankoplis (1966)
================================================================================
SYSTEM PARAMETERS (at initial conditions):

t(stop)        =  10500.00000 min        dtheta max     =      1.00000 BV
abs. tol.      =       .10000E-06        rel. tol.      =       .10000E-03
Total Length   =      5.20000 cm         D              =      2.00000 cm
Tot. Capacity  =       .00000 eq/L solid Col. Vol.      =     16.33628 mL
F              =       .42000 mL/min     Uo (linear)    =       .35182 cm/min
R              =    108.21000 microns    L/R            =    480.54708
Bed Void frac. =       .38000            Pcl. Porosity  =       .66816
Spec. Area     =    171.88800 1/cm       Time/BV        =     14.78045 min
Vol CSTRs      =     13.00000 mL

Component no.  =       1
Ke  [-]        =  .10000E+01
Eb  [cm2/min]  =  .14425E-01
Dp  [cm2/min]  =  .37993E-04
Doo [cm2/min]  =  .11398E-03
kf  [cm/min]   =  .44398E-01
Ds  [cm2/min]  =  .00000E+00

Dimensionless Groups:
Re             =  .21832E-02
Sc(i)          =  .11627E+05
Peb(i)         =  .12683E+03
Bi(i)          =  .18926E+02
Nf(i)          =  .29683E+03
Np(i)          =  .32043E+01
Pep(i)         =  .14997E+03

Isotherm       =  Freundlich/Langmuir Hybrid
Iso. Const. 1  =  .13910E+00
Iso. Const. 2  =  .10000E+01
Iso. Const. 3  =  .10000E+01
Iso. Const. 4  =  .10000E+01
Iso. Const. 5  =  .23835E-03
Init. Conc.    =  .00000E+00
Conc. at eqb.  =  .00000E+00
Conc. units          M
================================================================================
COMMAND LIST:
  1: Step conc. of component 1 at .0000     min to .3660E-03 M
     Execute   1 times, every .0000     mins.
  2: User set viscosity to .2739E-01 poise and density to 1.240     g/cm3
  3: Monitor conc. history at stream  0.  Filename = case.$.h01
     Output density adjustments:
     .20E-03*default abs conc delta,      .52E-01*default rel conc delta,
     .46E-02*default force w/ conc delta, .76    *default force w/o conc delta
  4: Monitor conc. history at stream  1.  Filename = case.$.h02
     Output density adjustments:
     .20E-03*default abs conc delta,      .52E-01*default rel conc delta,
     .46E-02*default force w/ conc delta, .76    *default force w/o conc delta
  5: Monitor conc. history at stream  2.  Filename = case.$.h03
```

```
     Output density adjustments:
     .20E-03*default abs conc delta,      .52E-01*default rel conc delta,
     .46E-02*default force w/ conc delta, .76    *default force w/o conc delta
  6: Monitor conc. history at stream  3.  Filename = case.$.h04
     Output density adjustments:
     .20E-03*default abs conc delta,      .52E-01*default rel conc delta,
     .46E-02*default force w/ conc delta, .76    *default force w/o conc delta
  7: Dump full profile file at  15.00     min
     Execute   1 times, every .0000     mins.
  8: Dump full profile file at  60.00     min
     Execute   1 times, every .0000     mins.
  9: Dump full profile file at  240.0     min
     Execute   1 times, every .0000     mins.
 10: Dump full profile file at  480.0     min
     Execute   1 times, every .0000     mins.
 11: Dump full profile file at  1440.     min
     Execute   1 times, every .0000     mins.
 12: Dump full profile file at  2880.     min
     Execute   1 times, every .0000     mins.
 13: Dump full profile file at  4320.     min
     Execute   1 times, every .0000     mins.
 14: Dump full profile file at  7473.     min
     Execute   1 times, every .0000     mins.
================================================================================
VERSE-LC finished in   769 steps.  Average step size 13.65     minutes
End run:  12:01:50 on 04-21-2004
Integrated Areas in History Files:
case.$.h01                  3.84300
case.$.h02                  3.83145
case.$.h03                  .544982
case.$.h04                  .533660
```

C.6 PNNL Column 9 Test

C.6.1 VERSE Datafile

```
PNNL Column 9 - Cycle 1, SL644 250-Gallon Batch -20+30, AZ-102

Particle radius = 0.70*number median radius, Dp = Dinf/3
1,50, 4, 6                        ncomp, nelem, ncol-bed, ncol-part
FCWNA                             isotherm,axial-disp,film-coef,surf-diff,BC-col
NNNNN                             input-only,perfusable,feed-equil,datafile.yio
M                                 comp-conc units
6.20, 2.0, 0.58, 13.0             Length(cm),Diam(cm),Q-flow(ml/min),CSTR-vol(ml)
238.09, 0.380, 0.668159,  0.0     part-rad(um), bed-void, part-void, sorb-cap()
0.0d-4                            initial concentrations (M)
S                                 COMMAND - conc step change
1, 0.0, 3.66d-4, 1, 0.0           spec id, time(min), conc(M), freq, dt(min)
V                                 COMMAND - viscosity/density change
0.027389, 1.24                    fluid viscosity(poise), density(g/cm^3)
h                                       COMMAND - effluent history dump
0, 2.0d-4, 5.2E-2, 4.552E-3, 0.759      unit op#, ptscale(1-4) filtering
h                                       COMMAND - effluent history dump
1, 2.0d-4, 5.2E-2, 4.552E-3, 0.759      unit op#, ptscale(1-4) filtering
h                                       COMMAND - effluent history dump
2, 2.0d-4, 5.2E-2, 4.552E-3, 0.759      unit op#, ptscale(1-4) filtering
h                                       COMMAND - effluent history dump
3, 2.0d-4, 5.2E-2, 4.552E-3, 0.759      unit op#, ptscale(1-4) filtering
D                                 COMMAND - Dump Column Profile
-1, 15, 1, 0.0                    part. pt.(-1=>all), time(min), # of repeats, prd. of repet.
D
-1, 60, 1, 0.0
D
-1, 240, 1, 0.0
D
-1, 480, 1, 0.0
D
-1, 1440, 1, 0.0
D
-1, 2880, 1, 0.0
D
```

```
-1, 4320, 1, 0.0
D
-1, 7473, 1, 0.0
-                          end of commands
10100.0, 1.0               end time(min), max dt in B.V.s
1.0d-7, 1.0d-4             abs-tol, rel-tol
-                          non-negative conc constraint
1.0d0                      size exclusion factor
3.7993d-5                  part-pore diffusivities(cm^2/min)
1.1398d-4                  Brownian diffusivities(cm^2/min)
1.1632d-1                  Freundlich/Langmuir Hybrid a (moles/L B.V.)
1.0                        Freundlich/Langmuir Hybrid b    (1/M)
1.0                        Freundlich/Langmuir Hybrid Ma   (-)
1.0                        Freundlich/Langmuir Hybrid Mb   (-)
2.3835d-4                  Freundlich/Langmuir Hybrid beta (-)
```

C.6.2 VERSE Datafile.run

```
================================================================================

VERSE v7.80  by R. D. Whitley and N.-H. L. Wang, c1999 PRF
================================================================================
Input file: case.$
PNNL Column 9 - Cycle 1, SL644 250-Gallon Batch -20+30, AZ-102
Particle radius = 0.70*number median radius, Dp = Dinf/3
Begin Run:  09:18:47 on 04-22-2004   running under Windows 95/8
Finite elements    - axial: 50  particle: 1
Collocation points - axial:  4  particle: 6 => Number of eqns:  2010
Inlet species at equilib.? N   Perfusable sorbent? N   Feed profile only? N
Use Profile File? N   Generate Profile File? N
Axial dispersion correlation:   Chung & Wen (1968)
Film mass transfer correlation: Wilson & Geankoplis (1966)
================================================================================
SYSTEM PARAMETERS (at initial conditions):

t(stop)        =  10100.00000 min        dtheta max     =      1.00000 BV
abs. tol.      =       .10000E-06        rel. tol.      =       .10000E-03
Total Length   =      6.20000 cm         D              =      2.00000 cm
Tot. Capacity  =       .00000 eq/L solid Col. Vol.      =     19.47787 mL
F              =       .58000 mL/min     Uo (linear)    =       .48584 cm/min
R              =    238.09000 microns    L/R            =    260.40573
Bed Void frac. =       .38000            Pcl. Porosity  =       .66816
Spec. Area     =     78.12172 1/cm       Time/BV        =     12.76137 min
Vol CSTRs      =     13.00000 mL

Component no.  =      1
Ke  [-]        =  .10000E+01
Eb  [cm2/min]  =  .43740E-01
Dp  [cm2/min]  =  .37993E-04
Doo [cm2/min]  =  .11398E-03
kf  [cm/min]   =  .29226E-01
Ds  [cm2/min]  =  .00000E+00

Dimensionless Groups:
Re             =  .66335E-02
Sc(i)          =  .11627E+05
Peb(i)         =  .68867E+02
Bi(i)          =  .27411E+02
Nf(i)          =  .76676E+02
Np(i)          =  .57148E+00
Pep(i)         =  .45567E+03

Isotherm       =  Freundlich/Langmuir Hybrid
Iso. Const. 1  =  .11632E+00
Iso. Const. 2  =  .10000E+01
Iso. Const. 3  =  .10000E+01
Iso. Const. 4  =  .10000E+01
Iso. Const. 5  =  .23835E-03
Init. Conc.    =  .00000E+00
Conc. at eqb.  =  .00000E+00
Conc. units       M
================================================================================
```

```
COMMAND LIST:
  1: Step conc. of component 1 at .0000     min to .3660E-03 M
     Execute   1 times, every .0000     mins.
  2: User set viscosity to .2739E-01 poise and density to 1.240     g/cm3
  3: Monitor conc. history at stream  0.  Filename = case.$.h01
     Output density adjustments:
     .20E-03*default abs conc delta,      .52E-01*default rel conc delta,
     .46E-02*default force w/ conc delta, .76    *default force w/o conc delta
  4: Monitor conc. history at stream  1.  Filename = case.$.h02
     Output density adjustments:
     .20E-03*default abs conc delta,      .52E-01*default rel conc delta,
     .46E-02*default force w/ conc delta, .76    *default force w/o conc delta
  5: Monitor conc. history at stream  2.  Filename = case.$.h03
     Output density adjustments:
     .20E-03*default abs conc delta,      .52E-01*default rel conc delta,
     .46E-02*default force w/ conc delta, .76    *default force w/o conc delta
  6: Monitor conc. history at stream  3.  Filename = case.$.h04
     Output density adjustments:
     .20E-03*default abs conc delta,      .52E-01*default rel conc delta,
     .46E-02*default force w/ conc delta, .76    *default force w/o conc delta
  7: Dump full profile file at  15.00     min
     Execute   1 times, every .0000     mins.
  8: Dump full profile file at  60.00     min
     Execute   1 times, every .0000     mins.
  9: Dump full profile file at  240.0     min
     Execute   1 times, every .0000     mins.
 10: Dump full profile file at  480.0     min
     Execute   1 times, every .0000     mins.
 11: Dump full profile file at  1440.     min
     Execute   1 times, every .0000     mins.
 12: Dump full profile file at  2880.     min
     Execute   1 times, every .0000     mins.
 13: Dump full profile file at  4320.     min
     Execute   1 times, every .0000     mins.
 14: Dump full profile file at  7473.     min
     Execute   1 times, every .0000     mins.
================================================================================
VERSE-LC finished in  1039 steps.  Average step size 9.721     minutes
End run:  09:21:30 on 04-22-2004
Integrated Areas in History Files:
case.$.h01                  3.69660
case.$.h02                  3.68830
case.$.h03                  1.31356
case.$.h04                  1.30538
```

Appendix D (Full-Scale Facility Input and Output Files)

VERSE-LC input and output files for the full-scale facility are provided in this appendix. Twenty-two simulations were run. The cases presented here correspond to the three nominal LAW feeds, three chemically degraded LAW feeds, and sixteen sensitivity runs for the chemically degraded Hot Commissioning Operations feed. The sensitivity runs include perturbations to cesium, potassium, sodium and hydroxide concentrations, liquid flowrate, bulk and pore diffusivities, particle radius and bed density.

D.1 Hot Commissioning Operations (Nominal Isotherm)

D.1.1 VERSE Datafile

```
SL644 3-column carousel, single component Cs isotherm, Criterion: lag

LAW feed: Hot Commissioning, CT: Nominal, Sensitivity: None
1, 150, 4, 6                        ncomp, nelem, ncol-bed, ncol-part
FCWNA                               isotherm,axial-disp,film-coef,surf-diff,BC-col
NNNNN                               input-only,perfusable,feed-equil,datafile.yio
M                                   comp-conc units
403.86, 121.92, 56781.2, 2214466.   Length(cm),Diam(cm),Q-flow(ml/min),CSTR-vol(ml)
192.49, 0.380, 0.668159, 0.0        part-rad(um), bed-void, part-void, sorb-cap()
0.0                                 initial concentration (M)
S                                   COMMAND - conc step change
1, 0.0, 2.7400d-5, 1, 0.0           spec id, time(min), conc(M), freq, dt(min)
V                                   COMMAND - viscosity/density change
0.025001, 1.2133                    fluid viscosity(poise), density(g/cm^3)
m                                         COMMAND - subcolumns
50, 100, 0, 1, 3.70d-8, 0.0, 1.0d+6       elem-shift,elem-watch,pp-watch,c-watch,c-thresh,t-e,t-ee
h                                         COMMAND - effluent history dump
0, 2.0, 50, 4.033d-4, 0.016               unit op#, ptscale(1-4) filtering
h                                         COMMAND - effluent history dump
2, 2.0, 50, 4.033d-4, 0.016               unit op#, ptscale(1-4) filtering
h                                         COMMAND - effluent history dump
4, 2.0, 50, 4.033d-4, 0.016               unit op#, ptscale(1-4) filtering
h                                         COMMAND - effluent history dump
6, 2.0, 50, 4.033d-4, 0.016               unit op#, ptscale(1-4) filtering
-                                   end of commands
120000.0, 1.0                       end time(min), max dt in B.V.s
1.0d-7, 1.0d-4                      abs-tol, rel-tol
-                                   non-negative conc constraint
1.0                                 size exclusion factor
1.1209d-4                           part-pore diffusivities(cm^2/min)
3.3628d-4                           Brownian diffusivities(cm^2/min)
1.5404d-1                           Freundlich/Langmuir Hybrid a (moles/L B.V.)
1.0                                 Freundlich/Langmuir Hybrid b     (1/M)
1.0                                 Freundlich/Langmuir Hybrid Ma    (-)
1.0                                 Freundlich/Langmuir Hybrid Mb    (-)
5.1474d-4                           Freundlich/Langmuir Hybrid beta (-)
```

D.1.2 VERSE Datafile.run

```
================================================================================

VERSE v7.80  by R. D. Whitley and N.-H. L. Wang, c1999 PRF
================================================================================
Input file: case01
SL644 3-column carousel, single component Cs isotherm, Criterion: lag
LAW feed: Hot Commissioning, CT: Nominal, Sensitivity: None
Begin Run:  10:21:20 on 04-05-2004   running under Windows 95/8
Finite elements    - axial:150  particle: 1
Collocation points - axial:  4  particle: 6 => Number of eqns:  6028
Inlet species at equilib.? N   Perfusable sorbent? N   Feed profile only? N
```

```
Use Profile File? N   Generate Profile File? N
Axial dispersion correlation:   Chung & Wen (1968)
Film mass transfer correlation: Wilson & Geankoplis (1966)
Sub-Column Boundary Conditions: Axial Dispersion and CSTR
================================================================================
SYSTEM PARAMETERS (at initial conditions):

t(stop)        = 120000.00000 min        dtheta max     =      1.00000 BV
abs. tol.      =       .10000E-06        rel. tol.      =       .10000E-03
Total Length   =    403.86000 cm         D              =    121.92000 cm
Tot. Capacity  =       .00000 eq/L solid Col. Vol.      =4714879.85299 mL
F              =  56781.20000 mL/min     Uo (linear)    =     12.79915 cm/min
R              =    192.49000 microns    L/R            =  20980.83017
Bed Void frac. =       .38000           Pcl. Porosity  =       .66816
Spec. Area     =     96.62840 1/cm       Time/BV        =     10.51788 min
Vol CSTRs      =2214466.00000 mL

Component no.  =      1
Ke  [-]        =  .10000E+01
Eb  [cm2/min]  =  .91585E+00
Dp  [cm2/min]  =  .11209E-03
Doo [cm2/min]  =  .33628E-03
kf  [cm/min]   =  .20613E+00
Ds  [cm2/min]  =  .00000E+00

Dimensionless Groups:
Re             =  .15145E+00
Sc(i)          =  .36765E+04
Peb(i)         =  .18813E+04
Bi(i)          =  .52979E+02
Nf(i)          =  .55130E+03
Np(i)          =  .21260E+01
Pep(i)         =  .32896E+04

Isotherm       =  Freundlich/Langmuir Hybrid
Iso. Const. 1  =  .15404E+00
Iso. Const. 2  =  .10000E+01
Iso. Const. 3  =  .10000E+01
Iso. Const. 4  =  .10000E+01
Iso. Const. 5  =  .51474E-03
Init. Conc.    =  .00000E+00
Conc. at eqb.  =  .00000E+00
Conc. units       M
================================================================================
COMMAND LIST:
  1: Step conc. of component 1 at .0000     min to .2740E-04 M
     Execute   1 times, every .0000     mins.
  2: User set viscosity to .2500E-01 poise and density to 1.213     g/cm3
  3: Carousel (conc.). Active between t = .0000     and .1000E+07 min.
     When comp.  1 reaches .3700E-07 M     at end of node 100,
     shift  50 axial elements out the feed end
  4: Monitor conc. history at stream  0.  Filename = case01.h01
     Output density adjustments:
     2.0    *default abs conc delta,       50.    *default rel conc delta,
     .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
  5: Monitor conc. history at stream  2.  Filename = case01.h02
     Output density adjustments:
     2.0    *default abs conc delta,       50.    *default rel conc delta,
     .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
  6: Monitor conc. history at stream  4.  Filename = case01.h03
     Output density adjustments:
     2.0    *default abs conc delta,       50.    *default rel conc delta,
     .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
  7: Monitor conc. history at stream  6.  Filename = case01.h04
     Output density adjustments:
     2.0    *default abs conc delta,       50.    *default rel conc delta,
     .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
================================================================================
Conc. Carousel caused bed shift at t = .1027E+05 min
Conc. Carousel caused bed shift at t = .1690E+05 min
Conc. Carousel caused bed shift at t = .2380E+05 min
Conc. Carousel caused bed shift at t = .3085E+05 min
Conc. Carousel caused bed shift at t = .3801E+05 min
Conc. Carousel caused bed shift at t = .4524E+05 min
```

```
Conc. Carousel caused bed shift at t = .5249E+05 min
Conc. Carousel caused bed shift at t = .5976E+05 min
Conc. Carousel caused bed shift at t = .6704E+05 min
Conc. Carousel caused bed shift at t = .7431E+05 min
Conc. Carousel caused bed shift at t = .8157E+05 min
Conc. Carousel caused bed shift at t = .8884E+05 min
Conc. Carousel caused bed shift at t = .9611E+05 min
Conc. Carousel caused bed shift at t = .1034E+06 min
Conc. Carousel caused bed shift at t = .1106E+06 min
Conc. Carousel caused bed shift at t = .1179E+06 min
VERSE-LC finished in 12240 steps.  Average step size 9.804     minutes
End run:  10:56:46 on 04-05-2004
Integrated Areas in History Files:
case01.h01                 3.28800
case01.h02                 .401227
case01.h03                 .579189E-03
case01.h04                 .241228E-06
```

D.2 Envelope B Operations (Nominal Isotherm)

D.2.1 VERSE Datafile

```
SL644 3-column carousel, single component Cs isotherm, Criterion: lag

LAW feed: Envelope B, CT: Nominal, Sensitivity: None
1, 150, 4, 6                        ncomp, nelem, ncol-bed, ncol-part
FCWNA                               isotherm,axial-disp,film-coef,surf-diff,BC-col
NNNNN                               input-only,perfusable,feed-equil,datafile.yio
M                                   comp-conc units
403.86, 121.92, 28390.6, 2214466. Length(cm),Diam(cm),Q-flow(ml/min),CSTR-vol(ml)
192.49, 0.380, 0.668159, 0.0        part-rad(um), bed-void, part-void, sorb-cap()
0.0                                 initial concentration (M)
S                                   COMMAND - conc step change
1, 0.0, 2.8300d-4, 1, 0.0           spec id, time(min), conc(M), freq, dt(min)
V                                   COMMAND - viscosity/density change
0.020010, 1.1793                    fluid viscosity(poise), density(g/cm^3)
m                                        COMMAND - subcolumns
50, 100, 0, 1, 3.40d-8, 0.0, 1.0d+6      elem-shift,elem-watch,pp-watch,c-watch,c-thresh,t-e,t-ee
h                                        COMMAND - effluent history dump
0, 2.0, 50, 4.033d-4, 0.016              unit op#, ptscale(1-4) filtering
h                                        COMMAND - effluent history dump
2, 2.0, 50, 4.033d-4, 0.016              unit op#, ptscale(1-4) filtering
h                                        COMMAND - effluent history dump
4, 2.0, 50, 4.033d-4, 0.016              unit op#, ptscale(1-4) filtering
h                                        COMMAND - effluent history dump
6, 2.0, 50, 4.033d-4, 0.016              unit op#, ptscale(1-4) filtering
-                                   end of commands
120000.0, 1.0                       end time(min), max dt in B.V.s 120000.

1.0d-7, 1.0d-4                      abs-tol, rel-tol
-                                   non-negative conc constraint
1.0                                 size exclusion factor
1.7409d-4                           part-pore diffusivities(cm^2/min)
5.2228d-4                           Brownian diffusivities(cm^2/min)
1.5159d-1                           Freundlich/Langmuir Hybrid a (moles/L B.V.)
1.0                                 Freundlich/Langmuir Hybrid b    (1/M)
1.0                                 Freundlich/Langmuir Hybrid Ma   (-)
1.0                                 Freundlich/Langmuir Hybrid Mb   (-)
1.4192d-4                           Freundlich/Langmuir Hybrid beta (-)
```

D.2.2 VERSE Datafile.run

```
================================================================================

VERSE v7.80  by R. D. Whitley and N.-H. L. Wang, c1999 PRF
================================================================================
Input file: case02
SL644 3-column carousel, single component Cs isotherm, Criterion: lag
LAW feed: Envelope B, CT: Nominal, Sensitivity: None
Begin Run:  10:59:33 on 04-05-2004   running under Windows 95/8
```

```
Finite elements    - axial:150  particle: 1
Collocation points - axial:  4  particle: 6 => Number of eqns:  6028
Inlet species at equilib.? N   Perfusable sorbent? N   Feed profile only? N
Use Profile File? N   Generate Profile File? N
Axial dispersion correlation:   Chung & Wen (1968)
Film mass transfer correlation: Wilson & Geankoplis (1966)
Sub-Column Boundary Conditions: Axial Dispersion and CSTR
================================================================================
SYSTEM PARAMETERS (at initial conditions):

t(stop)         = 120000.00000 min          dtheta max      =      1.00000 BV
abs. tol.       =       .10000E-06          rel. tol.       =       .10000E-03
Total Length    =    403.86000 cm           D               =    121.92000 cm
Tot. Capacity   =       .00000 eq/L solid   Col. Vol.       =4714879.85299 mL
F               =  28390.60000 mL/min       Uo (linear)     =      6.39958 cm/min
R               =    192.49000 microns      L/R             =  20980.83017
Bed Void frac.  =       .38000              Pcl. Porosity   =       .66816
Spec. Area      =     96.62840 1/cm         Time/BV         =     21.03577 min
Vol CSTRs       =2214466.00000 mL

Component no.   =       1
Ke   [-]        =  .10000E+01
Eb   [cm2/min]  =  .46006E+00
Dp   [cm2/min]  =  .17409E-03
Doo  [cm2/min]  =  .52228E-03
kf   [cm/min]   =  .21941E+00
Ds   [cm2/min]  =  .00000E+00

Dimensionless Groups:
Re              =  .91960E-01
Sc(i)           =  .19493E+04
Peb(i)          =  .18726E+04
Bi(i)           =  .36309E+02
Nf(i)           =  .11737E+04
Np(i)           =  .66038E+01
Pep(i)          =  .10590E+04

Isotherm        =  Freundlich/Langmuir Hybrid
Iso. Const. 1   =  .15159E+00
Iso. Const. 2   =  .10000E+01
Iso. Const. 3   =  .10000E+01
Iso. Const. 4   =  .10000E+01
Iso. Const. 5   =  .14192E-03
Init. Conc.     =  .00000E+00
Conc. at eqb.   =  .00000E+00
Conc. units          M
================================================================================
COMMAND LIST:
  1: Step conc. of component 1 at .0000     min to .2830E-03 M
     Execute   1 times, every .0000     mins.
  2: User set viscosity to .2001E-01 poise and density to 1.179     g/cm3
  3: Carousel (conc.). Active between t = .0000     and .1000E+07 min.
     When comp.  1 reaches .3400E-07 M     at end of node 100,
     shift  50 axial elements out the feed end
  4: Monitor conc. history at stream  0.  Filename = case02.h01
     Output density adjustments:
     2.0    *default abs conc delta,      50.    *default rel conc delta,
     .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
  5: Monitor conc. history at stream  2.  Filename = case02.h02
     Output density adjustments:
     2.0    *default abs conc delta,      50.    *default rel conc delta,
     .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
  6: Monitor conc. history at stream  4.  Filename = case02.h03
     Output density adjustments:
     2.0    *default abs conc delta,      50.    *default rel conc delta,
     .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
  7: Monitor conc. history at stream  6.  Filename = case02.h04
     Output density adjustments:
     2.0    *default abs conc delta,      50.    *default rel conc delta,
     .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
================================================================================
Conc. Carousel caused bed shift at t = .3838E+05 min
Conc. Carousel caused bed shift at t = .5825E+05 min
Conc. Carousel caused bed shift at t = .7812E+05 min
```

```
Conc. Carousel caused bed shift at t = .9799E+05 min
Conc. Carousel caused bed shift at t = .1179E+06 min
VERSE-LC finished in  6374 steps.  Average step size 18.83     minutes
End run:  11:30:36 on 04-05-2004
Integrated Areas in History Files:
case02.h01                33.9600
case02.h02                26.4426
case02.h03                .252390E-04
case02.h04                .202846E-22
```

D.3 Subsequent Operations (Nominal Isotherm)

D.3.1 VERSE Datafile

```
SL644 3-column carousel, single component Cs isotherm, Criterion: lag

LAW feed: Subsequent Operation, CT: Nominal, Sensitivity: None
1, 150, 4, 6                        ncomp, nelem, ncol-bed, ncol-part
FCWNA                               isotherm,axial-disp,film-coef,surf-diff,BC-col
NNNNN                               input-only,perfusable,feed-equil,datafile.yio
M                                   comp-conc units
403.86, 121.92, 56781.2, 2214466.   Length(cm),Diam(cm),Q-flow(ml/min),CSTR-vol(ml)
192.49, 0.380, 0.668159, 0.0        part-rad(um), bed-void, part-void, sorb-cap()
0.0                                 initial concentration (M)
S                                   COMMAND - conc step change
1, 0.0, 5.0000d-5, 1, 0.0           spec id, time(min), conc(M), freq, dt(min)
V                                   COMMAND - viscosity/density change
0.019792, 1.2093                    fluid viscosity(poise), density(g/cm^3)
m                                        COMMAND - subcolumns
50, 100, 0, 1, 3.40d-8, 0.0, 1.0d+6      elem-shift,elem-watch,pp-watch,c-watch,c-thresh,t-e,t-ee
h                                        COMMAND - effluent history dump
0, 2.0, 50, 4.033d-4, 0.016              unit op#, ptscale(1-4) filtering
h                                        COMMAND - effluent history dump
2, 2.0, 50, 4.033d-4, 0.016              unit op#, ptscale(1-4) filtering
h                                        COMMAND - effluent history dump
4, 2.0, 50, 4.033d-4, 0.016              unit op#, ptscale(1-4) filtering
h                                        COMMAND - effluent history dump
6, 2.0, 50, 4.033d-4, 0.016              unit op#, ptscale(1-4) filtering
-                                   end of commands
120000.0, 1.0                       end time(min), max dt in B.V.s
1.0d-7, 1.0d-4                      abs-tol, rel-tol
-                                   non-negative conc constraint
1.0                                 size exclusion factor
1.2936d-4                           part-pore diffusivities(cm^2/min)
3.8809d-4                           Brownian diffusivities(cm^2/min)
1.4706d-1                           Freundlich/Langmuir Hybrid a (moles/L B.V.)
1.0                                 Freundlich/Langmuir Hybrid b     (1/M)
1.0                                 Freundlich/Langmuir Hybrid Ma    (-)
1.0                                 Freundlich/Langmuir Hybrid Mb    (-)
2.4279d-4                           Freundlich/Langmuir Hybrid beta (-)
```

D.3.2 VERSE Datafile.run

```
================================================================================

VERSE v7.80  by R. D. Whitley and N.-H. L. Wang, c1999 PRF
================================================================================
Input file: case03
SL644 3-column carousel, single component Cs isotherm, Criterion: lag
LAW feed: Subsequent Operation, CT: Nominal, Sensitivity: None
Begin Run:  11:30:36 on 04-05-2004   running under Windows 95/8
Finite elements    - axial:150  particle: 1
Collocation points - axial:  4  particle: 6 => Number of eqns:  6028
Inlet species at equilib.? N   Perfusable sorbent? N   Feed profile only? N
Use Profile File? N   Generate Profile File? N
Axial dispersion correlation:   Chung & Wen (1968)
Film mass transfer correlation: Wilson & Geankoplis (1966)
Sub-Column Boundary Conditions: Axial Dispersion and CSTR
================================================================================
SYSTEM PARAMETERS (at initial conditions):
```

```
t(stop)         = 120000.00000 min        dtheta max      =      1.00000 BV
abs. tol.       =       .10000E-06        rel. tol.       =       .10000E-03
Total Length    =    403.86000 cm         D               =    121.92000 cm
Tot. Capacity   =       .00000 eq/L solid Col. Vol.       =4714879.85299 mL
F               =  56781.20000 mL/min     Uo (linear)     =     12.79915 cm/min
R               =    192.49000 microns    L/R             =  20980.83017
Bed Void frac.  =       .38000            Pcl. Porosity   =       .66816
Spec. Area      =     96.62840 1/cm       Time/BV         =     10.51788 min
Vol CSTRs       =2214466.00000 mL

Component no.   =      1
Ke   [-]        =  .10000E+01
Eb   [cm2/min]  =  .91353E+00
Dp   [cm2/min]  =  .12936E-03
Doo  [cm2/min]  =  .38809E-03
kf   [cm/min]   =  .22679E+00
Ds   [cm2/min]  =  .00000E+00

Dimensionless Groups:
Re              =  .19068E+00
Sc(i)           =  .25303E+04
Peb(i)          =  .18861E+04
Bi(i)           =  .50507E+02
Nf(i)           =  .60656E+03
Np(i)           =  .24535E+01
Pep(i)          =  .28504E+04

Isotherm        =  Freundlich/Langmuir Hybrid
Iso. Const. 1   =  .14706E+00
Iso. Const. 2   =  .10000E+01
Iso. Const. 3   =  .10000E+01
Iso. Const. 4   =  .10000E+01
Iso. Const. 5   =  .24279E-03
Init. Conc.     =  .00000E+00
Conc. at eqb.   =  .00000E+00
Conc. units          M
================================================================================
COMMAND LIST:
  1: Step conc. of component 1 at .0000     min to .5000E-04 M
     Execute   1 times, every .0000     mins.
  2: User set viscosity to .1979E-01 poise and density to 1.209     g/cm3
  3: Carousel (conc.). Active between t = .0000     and .1000E+07 min.
     When comp.  1 reaches .3400E-07 M     at end of node 100,
     shift  50 axial elements out the feed end
  4: Monitor conc. history at stream  0.  Filename = case03.h01
     Output density adjustments:
     2.0    *default abs conc delta,       50.    *default rel conc delta,
     .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
  5: Monitor conc. history at stream  2.  Filename = case03.h02
     Output density adjustments:
     2.0    *default abs conc delta,       50.    *default rel conc delta,
     .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
  6: Monitor conc. history at stream  4.  Filename = case03.h03
     Output density adjustments:
     2.0    *default abs conc delta,       50.    *default rel conc delta,
     .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
  7: Monitor conc. history at stream  6.  Filename = case03.h04
     Output density adjustments:
     2.0    *default abs conc delta,       50.    *default rel conc delta,
     .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
================================================================================
Conc. Carousel caused bed shift at t = .2018E+05 min
Conc. Carousel caused bed shift at t = .3312E+05 min
Conc. Carousel caused bed shift at t = .4647E+05 min
Conc. Carousel caused bed shift at t = .6005E+05 min
Conc. Carousel caused bed shift at t = .7377E+05 min
Conc. Carousel caused bed shift at t = .8757E+05 min
Conc. Carousel caused bed shift at t = .1014E+06 min
Conc. Carousel caused bed shift at t = .1153E+06 min
VERSE-LC finished in 11737 steps.  Average step size 10.22     minutes
End run:  11:48:17 on 04-05-2004
Integrated Areas in History Files:
case03.h01                  6.00000
```

```
case03.h02                1.81174
case03.h03                .313298E-03
case03.h04                .203611E-08
```

D.4 Hot Commissioning Operations (Degraded Isotherm)

D.4.1 VERSE Datafile

```
SL644 3-column carousel, single component Cs isotherm, Criterion: lag

LAW feed: Hot Commissioning, CT: Degraded, Sensitivity: None
1, 150, 4, 6                        ncomp, nelem, ncol-bed, ncol-part
FCWNA                               isotherm,axial-disp,film-coef,surf-diff,BC-col
NNNNN                               input-only,perfusable,feed-equil,datafile.yio
M                                   comp-conc units
403.86, 121.92, 56781.2, 2214466.   Length(cm),Diam(cm),Q-flow(ml/min),CSTR-vol(ml)
192.49, 0.380, 0.668159, 0.0        part-rad(um), bed-void, part-void, sorb-cap()
0.0                                 initial concentration (M)
S                                   COMMAND - conc step change
1, 0.0, 2.7400d-5, 1, 0.0           spec id, time(min), conc(M), freq, dt(min)
V                                   COMMAND - viscosity/density change
0.025001, 1.2133                    fluid viscosity(poise), density(g/cm^3)
m                                         COMMAND - subcolumns
50, 100, 0, 1, 3.70d-8, 0.0, 1.0d+6       elem-shift,elem-watch,pp-watch,c-watch,c-thresh,t-e,t-ee
h                                         COMMAND - effluent history dump
0, 2.0, 50, 4.033d-4, 0.016               unit op#, ptscale(1-4) filtering
h                                         COMMAND - effluent history dump
2, 2.0, 50, 4.033d-4, 0.016               unit op#, ptscale(1-4) filtering
h                                         COMMAND - effluent history dump
4, 2.0, 50, 4.033d-4, 0.016               unit op#, ptscale(1-4) filtering
h                                         COMMAND - effluent history dump
6, 2.0, 50, 4.033d-4, 0.016               unit op#, ptscale(1-4) filtering
-                                   end of commands
120000.0, 1.0                       end time(min), max dt in B.V.s

1.0d-7, 1.0d-4                      abs-tol, rel-tol
-                                   non-negative conc constraint
1.0                                 size exclusion factor
1.1209d-4                           part-pore diffusivities(cm^2/min)
3.3628d-4                           Brownian diffusivities(cm^2/min)
1.2323d-1                           Freundlich/Langmuir Hybrid a (moles/L B.V.)
1.0                                 Freundlich/Langmuir Hybrid b     (1/M)
1.0                                 Freundlich/Langmuir Hybrid Ma    (-)
1.0                                 Freundlich/Langmuir Hybrid Mb    (-)
5.1474d-4                           Freundlich/Langmuir Hybrid beta (-)
```

D.4.2 VERSE Datafile.run

```
================================================================================

VERSE v7.80  by R. D. Whitley and N.-H. L. Wang, c1999 PRF
================================================================================
Input file: case04
SL644 3-column carousel, single component Cs isotherm, Criterion: lag
LAW feed: Hot Commissioning, CT: Degraded, Sensitivity: None
Begin Run:  11:48:18 on 04-05-2004   running under Windows 95/8
Finite elements    - axial:150  particle: 1
Collocation points - axial:  4  particle: 6 => Number of eqns:  6028
Inlet species at equilib.? N   Perfusable sorbent? N   Feed profile only? N
Use Profile File? N   Generate Profile File? N
Axial dispersion correlation:   Chung & Wen (1968)
Film mass transfer correlation: Wilson & Geankoplis (1966)
Sub-Column Boundary Conditions: Axial Dispersion and CSTR
================================================================================
SYSTEM PARAMETERS (at initial conditions):

t(stop)        = 120000.00000 min        dtheta max     =      1.00000 BV
abs. tol.      =       .10000E-06        rel. tol.      =       .10000E-03
Total Length   =    403.86000 cm         D              =    121.92000 cm
Tot. Capacity  =       .00000 eq/L solid  Col. Vol.      =4714879.85299 mL
```

```
F              =  56781.20000 mL/min      Uo (linear)    =     12.79915 cm/min
R              =    192.49000 microns     L/R            =  20980.83017
Bed Void frac. =       .38000             Pcl. Porosity  =       .66816
Spec. Area     =     96.62840 1/cm        Time/BV        =     10.51788 min
Vol CSTRs      =2214466.00000 mL

Component no.  =      1
Ke  [-]        =  .10000E+01
Eb  [cm2/min]  =  .91585E+00
Dp  [cm2/min]  =  .11209E-03
Doo [cm2/min]  =  .33628E-03
kf  [cm/min]   =  .20613E+00
Ds  [cm2/min]  =  .00000E+00

Dimensionless Groups:
Re             =  .15145E+00
Sc(i)          =  .36765E+04
Peb(i)         =  .18813E+04
Bi(i)          =  .52979E+02
Nf(i)          =  .55130E+03
Np(i)          =  .21260E+01
Pep(i)         =  .32896E+04

Isotherm       =  Freundlich/Langmuir Hybrid
Iso. Const. 1  =  .12323E+00
Iso. Const. 2  =  .10000E+01
Iso. Const. 3  =  .10000E+01
Iso. Const. 4  =  .10000E+01
Iso. Const. 5  =  .51474E-03
Init. Conc.    =  .00000E+00
Conc. at eqb.  =  .00000E+00
Conc. units       M
================================================================================
COMMAND LIST:
  1: Step conc. of component 1 at .0000     min to .2740E-04 M
     Execute   1 times, every .0000     mins.
  2: User set viscosity to .2500E-01 poise and density to 1.213     g/cm3
  3: Carousel (conc.). Active between t = .0000     and .1000E+07 min.
     When comp.  1 reaches .3700E-07 M     at end of node 100,
     shift  50 axial elements out the feed end
  4: Monitor conc. history at stream  0.  Filename = case04.h01
     Output density adjustments:
     2.0    *default abs conc delta,       50.    *default rel conc delta,
     .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
  5: Monitor conc. history at stream  2.  Filename = case04.h02
     Output density adjustments:
     2.0    *default abs conc delta,       50.    *default rel conc delta,
     .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
  6: Monitor conc. history at stream  4.  Filename = case04.h03
     Output density adjustments:
     2.0    *default abs conc delta,       50.    *default rel conc delta,
     .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
  7: Monitor conc. history at stream  6.  Filename = case04.h04
     Output density adjustments:
     2.0    *default abs conc delta,       50.    *default rel conc delta,
     .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
================================================================================
Conc. Carousel caused bed shift at t = 8237.      min
Conc. Carousel caused bed shift at t = .1355E+05 min
Conc. Carousel caused bed shift at t = .1908E+05 min
Conc. Carousel caused bed shift at t = .2473E+05 min
Conc. Carousel caused bed shift at t = .3047E+05 min
Conc. Carousel caused bed shift at t = .3627E+05 min
Conc. Carousel caused bed shift at t = .4209E+05 min
Conc. Carousel caused bed shift at t = .4792E+05 min
Conc. Carousel caused bed shift at t = .5375E+05 min
Conc. Carousel caused bed shift at t = .5958E+05 min
Conc. Carousel caused bed shift at t = .6540E+05 min
Conc. Carousel caused bed shift at t = .7124E+05 min
Conc. Carousel caused bed shift at t = .7706E+05 min
Conc. Carousel caused bed shift at t = .8288E+05 min
Conc. Carousel caused bed shift at t = .8871E+05 min
Conc. Carousel caused bed shift at t = .9454E+05 min
Conc. Carousel caused bed shift at t = .1004E+06 min
```

```
Conc. Carousel caused bed shift at t = .1062E+06 min
Conc. Carousel caused bed shift at t = .1120E+06 min
Conc. Carousel caused bed shift at t = .1178E+06 min
VERSE-LC finished in 12373 steps.  Average step size 9.699     minutes
End run:  12:28:10 on 04-05-2004
Integrated Areas in History Files:
case04.h01                 3.28800
case04.h02                 .388347
case04.h03                 .600194E-03
case04.h04                 .290935E-06
```

D.5 Envelope B Operations (Degraded Isotherm)

D.5.1 VERSE Datafile

```
SL644 3-column carousel, single component Cs isotherm, Criterion: lag

LAW feed: Envelope B, CT: Degraded, Sensitivity: None
1, 150, 4, 6                       ncomp, nelem, ncol-bed, ncol-part
FCWNA                              isotherm,axial-disp,film-coef,surf-diff,BC-col
NNNNN                              input-only,perfusable,feed-equil,datafile.yio
M                                  comp-conc units
403.86, 121.92, 28390.6, 2214466.  Length(cm),Diam(cm),Q-flow(ml/min),CSTR-vol(ml)
192.49, 0.380, 0.668159, 0.0       part-rad(um), bed-void, part-void, sorb-cap()
0.0                                initial concentration (M)
S                                  COMMAND - conc step change
1, 0.0, 2.8300d-4, 1, 0.0          spec id, time(min), conc(M), freq, dt(min)
V                                  COMMAND - viscosity/density change
0.020010, 1.1793                   fluid viscosity(poise), density(g/cm^3)
m                                       COMMAND - subcolumns
50, 100, 0, 1, 3.40d-8, 0.0, 1.0d+6     elem-shift,elem-watch,pp-watch,c-watch,c-thresh,t-e,t-ee
h                                       COMMAND - effluent history dump
0, 2.0, 50, 4.033d-4, 0.016             unit op#, ptscale(1-4) filtering
h                                       COMMAND - effluent history dump
2, 2.0, 50, 4.033d-4, 0.016             unit op#, ptscale(1-4) filtering
h                                       COMMAND - effluent history dump
4, 2.0, 50, 4.033d-4, 0.016             unit op#, ptscale(1-4) filtering
h                                       COMMAND - effluent history dump
6, 2.0, 50, 4.033d-4, 0.016             unit op#, ptscale(1-4) filtering
-                                  end of commands
120000.0, 1.0                      end time(min), max dt in B.V.s 120000.
1.0d-7, 1.0d-4                     abs-tol, rel-tol
-                                  non-negative conc constraint
1.0                                size exclusion factor
1.7409d-4                          part-pore diffusivities(cm^2/min)
5.2228d-4                          Brownian diffusivities(cm^2/min)
1.2128d-1                          Freundlich/Langmuir Hybrid a (moles/L B.V.)
1.0                                Freundlich/Langmuir Hybrid b     (1/M)
1.0                                Freundlich/Langmuir Hybrid Ma    (-)
1.0                                Freundlich/Langmuir Hybrid Mb    (-)
1.4192d-4                          Freundlich/Langmuir Hybrid beta (-)
```

D.5.2 VERSE Datafile.run

```
================================================================================

VERSE v7.80  by R. D. Whitley and N.-H. L. Wang, c1999 PRF
================================================================================
Input file: case05
SL644 3-column carousel, single component Cs isotherm, Criterion: lag
LAW feed: Envelope B, CT: Degraded, Sensitivity: None
Begin Run:  12:28:10 on 04-05-2004   running under Windows 95/8
Finite elements     - axial:150  particle: 1
Collocation points - axial:  4  particle: 6 => Number of eqns:  6028
Inlet species at equilib.? N   Perfusable sorbent? N   Feed profile only? N
Use Profile File? N   Generate Profile File? N
Axial dispersion correlation:   Chung & Wen (1968)
Film mass transfer correlation: Wilson & Geankoplis (1966)
Sub-Column Boundary Conditions: Axial Dispersion and CSTR
================================================================================
```

```
SYSTEM PARAMETERS (at initial conditions):

t(stop)         = 120000.00000 min          dtheta max      =      1.00000 BV
abs. tol.       =       .10000E-06          rel. tol.       =       .10000E-03
Total Length    =    403.86000 cm           D               =    121.92000 cm
Tot. Capacity   =       .00000 eq/L solid   Col. Vol.       =4714879.85299 mL
F               =  28390.60000 mL/min       Uo (linear)     =      6.39958 cm/min
R               =    192.49000 microns      L/R             =  20980.83017
Bed Void frac.  =       .38000              Pcl. Porosity   =       .66816
Spec. Area      =     96.62840 1/cm         Time/BV         =     21.03577 min
Vol CSTRs       =2214466.00000 mL

Component no.   =      1
Ke   [-]        =  .10000E+01
Eb   [cm2/min]  =  .46006E+00
Dp   [cm2/min]  =  .17409E-03
Doo  [cm2/min]  =  .52228E-03
kf   [cm/min]   =  .21941E+00
Ds   [cm2/min]  =  .00000E+00

Dimensionless Groups:
Re              =  .91960E-01
Sc(i)           =  .19493E+04
Peb(i)          =  .18726E+04
Bi(i)           =  .36309E+02
Nf(i)           =  .11737E+04
Np(i)           =  .66038E+01
Pep(i)          =  .10590E+04

Isotherm        =  Freundlich/Langmuir Hybrid
Iso. Const. 1   =  .12128E+00
Iso. Const. 2   =  .10000E+01
Iso. Const. 3   =  .10000E+01
Iso. Const. 4   =  .10000E+01
Iso. Const. 5   =  .14192E-03
Init. Conc.     =  .00000E+00
Conc. at eqb.   =  .00000E+00
Conc. units           M
================================================================================
COMMAND LIST:
  1: Step conc. of component 1 at .0000     min to .2830E-03 M
     Execute   1 times, every .0000     mins.
  2: User set viscosity to .2001E-01 poise and density to 1.179     g/cm3
  3: Carousel (conc.). Active between t = .0000     and .1000E+07 min.
     When comp.  1 reaches .3400E-07 M     at end of node 100,
     shift  50 axial elements out the feed end
  4: Monitor conc. history at stream  0.  Filename = case05.h01
     Output density adjustments:
     2.0    *default abs conc delta,       50.    *default rel conc delta,
     .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
  5: Monitor conc. history at stream  2.  Filename = case05.h02
     Output density adjustments:
     2.0    *default abs conc delta,       50.    *default rel conc delta,
     .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
  6: Monitor conc. history at stream  4.  Filename = case05.h03
     Output density adjustments:
     2.0    *default abs conc delta,       50.    *default rel conc delta,
     .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
  7: Monitor conc. history at stream  6.  Filename = case05.h04
     Output density adjustments:
     2.0    *default abs conc delta,       50.    *default rel conc delta,
     .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
================================================================================
Conc. Carousel caused bed shift at t = .3077E+05 min
Conc. Carousel caused bed shift at t = .4667E+05 min
Conc. Carousel caused bed shift at t = .6259E+05 min
Conc. Carousel caused bed shift at t = .7852E+05 min
Conc. Carousel caused bed shift at t = .9443E+05 min
Conc. Carousel caused bed shift at t = .1104E+06 min
VERSE-LC finished in  6260 steps.  Average step size 19.17     minutes
End run:  12:55:54 on 04-05-2004
Integrated Areas in History Files:
case05.h01                  33.9600
case05.h02                  27.6338
```

```
case05.h03                .243974E-04
case05.h04               -.264398E-21
```

D.6 Subsequent Operations (Degraded Isotherm)

D.6.1 VERSE Datafile

```
SL644 3-column carousel, single component Cs isotherm, Criterion: lag

LAW feed: Subsequent Operation, CT: Degraded, Sensitivity: None
1, 150, 4, 6                        ncomp, nelem, ncol-bed, ncol-part
FCWNA                               isotherm,axial-disp,film-coef,surf-diff,BC-col
NNNNN                               input-only,perfusable,feed-equil,datafile.yio
M                                   comp-conc units
403.86, 121.92, 56781.2, 2214466.   Length(cm),Diam(cm),Q-flow(ml/min),CSTR-vol(ml)
192.49, 0.380, 0.668159, 0.0        part-rad(um), bed-void, part-void, sorb-cap()
0.0                                 initial concentration (M)
S                                   COMMAND - conc step change
1, 0.0, 5.0000d-5, 1, 0.0           spec id, time(min), conc(M), freq, dt(min)
V                                   COMMAND - viscosity/density change
0.019792, 1.2093                    fluid viscosity(poise), density(g/cm^3)
m                                         COMMAND - subcolumns
50, 100, 0, 1, 3.40d-8, 0.0, 1.0d+6       elem-shift,elem-watch,pp-watch,c-watch,c-thresh,t-e,t-ee
h                                         COMMAND - effluent history dump
0, 2.0, 50, 4.033d-4, 0.016               unit op#, ptscale(1-4) filtering
h                                         COMMAND - effluent history dump
2, 2.0, 50, 4.033d-4, 0.016               unit op#, ptscale(1-4) filtering
h                                         COMMAND - effluent history dump
4, 2.0, 50, 4.033d-4, 0.016               unit op#, ptscale(1-4) filtering
h                                         COMMAND - effluent history dump
6, 2.0, 50, 4.033d-4, 0.016               unit op#, ptscale(1-4) filtering
-                                   end of commands
120000.0, 1.0                       end time(min), max dt in B.V.s
1.0d-7, 1.0d-4                      abs-tol, rel-tol
-                                   non-negative conc constraint
1.0                                 size exclusion factor
1.2936d-4                           part-pore diffusivities(cm^2/min)
3.8809d-4                           Brownian diffusivities(cm^2/min)
1.1764d-1                           Freundlich/Langmuir Hybrid a (moles/L B.V.)
1.0                                 Freundlich/Langmuir Hybrid b    (1/M)
1.0                                 Freundlich/Langmuir Hybrid Ma   (-)
1.0                                 Freundlich/Langmuir Hybrid Mb   (-)
2.4279d-4                           Freundlich/Langmuir Hybrid beta (-)
```

D.6.2 VERSE Datafile.run

```
================================================================================

VERSE v7.80  by R. D. Whitley and N.-H. L. Wang, c1999 PRF
================================================================================
Input file: case06
SL644 3-column carousel, single component Cs isotherm, Criterion: lag
LAW feed: Subsequent Operation, CT: Degraded, Sensitivity: None
Begin Run:  12:55:54 on 04-05-2004   running under Windows 95/8
Finite elements     - axial:150  particle: 1
Collocation points - axial:  4  particle: 6 => Number of eqns:  6028
Inlet species at equilib.? N   Perfusable sorbent? N   Feed profile only? N
Use Profile File? N   Generate Profile File? N
Axial dispersion correlation:   Chung & Wen (1968)
Film mass transfer correlation: Wilson & Geankoplis (1966)
Sub-Column Boundary Conditions: Axial Dispersion and CSTR
================================================================================
SYSTEM PARAMETERS (at initial conditions):

t(stop)        = 120000.00000 min         dtheta max     =      1.00000 BV
abs. tol.      =       .10000E-06         rel. tol.      =       .10000E-03
Total Length   =    403.86000 cm          D              =    121.92000 cm
Tot. Capacity  =       .00000 eq/L solid  Col. Vol.      =4714879.85299 mL
F              =  56781.20000 mL/min      Uo (linear)    =     12.79915 cm/min
R              =    192.49000 microns     L/R            =  20980.83017
```

```
Bed Void frac. =       .38000          Pcl. Porosity  =       .66816
Spec. Area     =     96.62840 1/cm     Time/BV        =     10.51788 min
Vol CSTRs      =2214466.00000 mL

Component no.  =       1
Ke  [-]        =  .10000E+01
Eb  [cm2/min]  =  .91353E+00
Dp  [cm2/min]  =  .12936E-03
Doo [cm2/min]  =  .38809E-03
kf  [cm/min]   =  .22679E+00
Ds  [cm2/min]  =  .00000E+00

Dimensionless Groups:
Re             =  .19068E+00
Sc(i)          =  .25303E+04
Peb(i)         =  .18861E+04
Bi(i)          =  .50507E+02
Nf(i)          =  .60656E+03
Np(i)          =  .24535E+01
Pep(i)         =  .28504E+04

Isotherm       =  Freundlich/Langmuir Hybrid
Iso. Const. 1  =  .11764E+00
Iso. Const. 2  =  .10000E+01
Iso. Const. 3  =  .10000E+01
Iso. Const. 4  =  .10000E+01
Iso. Const. 5  =  .24279E-03
Init. Conc.    =  .00000E+00
Conc. at eqb.  =  .00000E+00
Conc. units          M
================================================================================
COMMAND LIST:
  1: Step conc. of component 1 at .0000     min to .5000E-04 M
     Execute   1 times, every .0000     mins.
  2: User set viscosity to .1979E-01 poise and density to 1.209     g/cm3
  3: Carousel (conc.). Active between t = .0000     and .1000E+07 min.
     When comp.  1 reaches .3400E-07 M     at end of node 100,
     shift  50 axial elements out the feed end
  4: Monitor conc. history at stream  0.  Filename = case06.h01
     Output density adjustments:
     2.0    *default abs conc delta,       50.    *default rel conc delta,
     .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
  5: Monitor conc. history at stream  2.  Filename = case06.h02
     Output density adjustments:
     2.0    *default abs conc delta,       50.    *default rel conc delta,
     .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
  6: Monitor conc. history at stream  4.  Filename = case06.h03
     Output density adjustments:
     2.0    *default abs conc delta,       50.    *default rel conc delta,
     .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
  7: Monitor conc. history at stream  6.  Filename = case06.h04
     Output density adjustments:
     2.0    *default abs conc delta,       50.    *default rel conc delta,
     .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
================================================================================
Conc. Carousel caused bed shift at t = .1617E+05 min
Conc. Carousel caused bed shift at t = .2653E+05 min
Conc. Carousel caused bed shift at t = .3722E+05 min
Conc. Carousel caused bed shift at t = .4810E+05 min
Conc. Carousel caused bed shift at t = .5908E+05 min
Conc. Carousel caused bed shift at t = .7013E+05 min
Conc. Carousel caused bed shift at t = .8123E+05 min
Conc. Carousel caused bed shift at t = .9235E+05 min
Conc. Carousel caused bed shift at t = .1035E+06 min
Conc. Carousel caused bed shift at t = .1146E+06 min
VERSE-LC finished in 11751 steps.  Average step size 10.21     minutes
End run:  13:14:24 on 04-05-2004
Integrated Areas in History Files:
case06.h01                6.00000
case06.h02                1.76740
case06.h03                .326742E-03
case06.h04                .334795E-08
```

D.7 Hot Commissioning Operations ([Cs^+] + 20%)

D.7.1 VERSE Datafile

```
SL644 3-column carousel, single component Cs isotherm, Criterion: lag

LAW feed: Hot Commissioning, CT: Degraded, Sensitivity: 1.2*[Cs+]
1, 150, 4, 6                        ncomp, nelem, ncol-bed, ncol-part
FCWNA                               isotherm,axial-disp,film-coef,surf-diff,BC-col
NNNNN                               input-only,perfusable,feed-equil,datafile.yio
M                                   comp-conc units
403.86, 121.92, 56781.2, 2214466.   Length(cm),Diam(cm),Q-flow(ml/min),CSTR-vol(ml)
192.49, 0.380, 0.668159, 0.0        part-rad(um), bed-void, part-void, sorb-cap()
0.0                                 initial concentration (M)
S                                   COMMAND - conc step change
1, 0.0, 3.2880d-5, 1, 0.0           spec id, time(min), conc(M), freq, dt(min)
V                                   COMMAND - viscosity/density change
0.025001, 1.2133                    fluid viscosity(poise), density(g/cm^3)
m                                         COMMAND - subcolumns
50, 100, 0, 1, 3.70d-8, 0.0, 1.0d+6       elem-shift,elem-watch,pp-watch,c-watch,c-thresh,t-e,t-ee
h                                         COMMAND - effluent history dump
0, 2.0, 50, 4.033d-4, 0.016               unit op#, ptscale(1-4) filtering
h                                         COMMAND - effluent history dump
2, 2.0, 50, 4.033d-4, 0.016               unit op#, ptscale(1-4) filtering
h                                         COMMAND - effluent history dump
4, 2.0, 50, 4.033d-4, 0.016               unit op#, ptscale(1-4) filtering
h                                         COMMAND - effluent history dump
6, 2.0, 50, 4.033d-4, 0.016               unit op#, ptscale(1-4) filtering
-                                   end of commands
120000.0, 1.0                       end time(min), max dt in B.V.s
1.0d-7, 1.0d-4                      abs-tol, rel-tol
-                                   non-negative conc constraint
1.0                                 size exclusion factor
1.1209d-4                           part-pore diffusivities(cm^2/min)
3.3628d-4                           Brownian diffusivities(cm^2/min)
1.2323d-1                           Freundlich/Langmuir Hybrid a (moles/L B.V.)
1.0                                 Freundlich/Langmuir Hybrid b    (1/M)
1.0                                 Freundlich/Langmuir Hybrid Ma   (-)
1.0                                 Freundlich/Langmuir Hybrid Mb   (-)
5.1474d-4                           Freundlich/Langmuir Hybrid beta (-)
```

D.7.2 VERSE Datafile.run

```
================================================================================

VERSE v7.80  by R. D. Whitley and N.-H. L. Wang, c1999 PRF
================================================================================
Input file: case07
SL644 3-column carousel, single component Cs isotherm, Criterion: lag
LAW feed: Hot Commissioning, CT: Degraded, Sensitivity: 1.2*[Cs+]
Begin Run:  13:14:24 on 04-05-2004   running under Windows 95/8
Finite elements    - axial:150  particle: 1
Collocation points - axial:  4  particle: 6 => Number of eqns:  6028
Inlet species at equilib.? N   Perfusable sorbent? N   Feed profile only? N
Use Profile File? N   Generate Profile File? N
Axial dispersion correlation:   Chung & Wen (1968)
Film mass transfer correlation: Wilson & Geankoplis (1966)
Sub-Column Boundary Conditions: Axial Dispersion and CSTR
================================================================================
SYSTEM PARAMETERS (at initial conditions):

t(stop)        = 120000.00000 min         dtheta max     =      1.00000 BV
abs. tol.      =       .10000E-06         rel. tol.      =       .10000E-03
Total Length   =    403.86000 cm          D              =    121.92000 cm
Tot. Capacity  =       .00000 eq/L solid  Col. Vol.      =4714879.85299 mL
F              =  56781.20000 mL/min      Uo (linear)    =     12.79915 cm/min
R              =    192.49000 microns     L/R            =  20980.83017
Bed Void frac. =       .38000            Pcl. Porosity  =       .66816
Spec. Area     =     96.62840 1/cm        Time/BV        =     10.51788 min
Vol CSTRs      =2214466.00000 mL
```

```
Component no.  =      1
Ke  [-]        =  .10000E+01
Eb  [cm2/min]  =  .91585E+00
Dp  [cm2/min]  =  .11209E-03
Doo [cm2/min]  =  .33628E-03
kf  [cm/min]   =  .20613E+00
Ds  [cm2/min]  =  .00000E+00

Dimensionless Groups:
Re             =  .15145E+00
Sc(i)          =  .36765E+04
Peb(i)         =  .18813E+04
Bi(i)          =  .52979E+02
Nf(i)          =  .55130E+03
Np(i)          =  .21260E+01
Pep(i)         =  .32896E+04

Isotherm       =  Freundlich/Langmuir Hybrid
Iso. Const. 1  =  .12323E+00
Iso. Const. 2  =  .10000E+01
Iso. Const. 3  =  .10000E+01
Iso. Const. 4  =  .10000E+01
Iso. Const. 5  =  .51474E-03
Init. Conc.    =  .00000E+00
Conc. at eqb.  =  .00000E+00
Conc. units          M
================================================================================
COMMAND LIST:
  1: Step conc. of component 1 at .0000     min to .3288E-04 M
     Execute   1 times, every .0000     mins.
  2: User set viscosity to .2500E-01 poise and density to 1.213     g/cm3
  3: Carousel (conc.). Active between t = .0000     and .1000E+07 min.
     When comp.  1 reaches .3700E-07 M     at end of node 100,
     shift  50 axial elements out the feed end
  4: Monitor conc. history at stream  0.  Filename = case07.h01
     Output density adjustments:
     2.0    *default abs conc delta,      50.    *default rel conc delta,
     .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
  5: Monitor conc. history at stream  2.  Filename = case07.h02
     Output density adjustments:
     2.0    *default abs conc delta,      50.    *default rel conc delta,
     .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
  6: Monitor conc. history at stream  4.  Filename = case07.h03
     Output density adjustments:
     2.0    *default abs conc delta,      50.    *default rel conc delta,
     .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
  7: Monitor conc. history at stream  6.  Filename = case07.h04
     Output density adjustments:
     2.0    *default abs conc delta,      50.    *default rel conc delta,
     .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
================================================================================
Conc. Carousel caused bed shift at t = 8143.     min
Conc. Carousel caused bed shift at t = .1344E+05 min
Conc. Carousel caused bed shift at t = .1893E+05 min
Conc. Carousel caused bed shift at t = .2456E+05 min
Conc. Carousel caused bed shift at t = .3027E+05 min
Conc. Carousel caused bed shift at t = .3604E+05 min
Conc. Carousel caused bed shift at t = .4183E+05 min
Conc. Carousel caused bed shift at t = .4763E+05 min
Conc. Carousel caused bed shift at t = .5342E+05 min
Conc. Carousel caused bed shift at t = .5922E+05 min
Conc. Carousel caused bed shift at t = .6501E+05 min
Conc. Carousel caused bed shift at t = .7082E+05 min
Conc. Carousel caused bed shift at t = .7661E+05 min
Conc. Carousel caused bed shift at t = .8241E+05 min
Conc. Carousel caused bed shift at t = .8820E+05 min
Conc. Carousel caused bed shift at t = .9399E+05 min
Conc. Carousel caused bed shift at t = .9979E+05 min
Conc. Carousel caused bed shift at t = .1056E+06 min
Conc. Carousel caused bed shift at t = .1114E+06 min
Conc. Carousel caused bed shift at t = .1172E+06 min
VERSE-LC finished in 12386 steps.  Average step size 9.688     minutes
End run:  13:54:38 on 04-05-2004
```

```
Integrated Areas in History Files:
case07.h01                3.94560
case07.h02                .461936
case07.h03                .579033E-03
case07.h04                .232016E-06
```

D.8 Hot Commissioning Operations ([Cs^+] – 20%)

D.8.1 VERSE Datafile

```
SL644 3-column carousel, single component Cs isotherm, Criterion: lag

LAW feed: Hot Commissioning, CT: Degraded, Sensitivity: 0.8*[Cs+]
1, 150, 4, 6                        ncomp, nelem, ncol-bed, ncol-part
FCWNA                               isotherm,axial-disp,film-coef,surf-diff,BC-col
NNNNN                               input-only,perfusable,feed-equil,datafile.yio
M                                   comp-conc units
403.86, 121.92, 56781.2, 2214466.   Length(cm),Diam(cm),Q-flow(ml/min),CSTR-vol(ml)
192.49, 0.380, 0.668159, 0.0        part-rad(um), bed-void, part-void, sorb-cap()
0.0                                 initial concentration (M)
S                                   COMMAND - conc step change
1, 0.0, 2.1920d-5, 1, 0.0           spec id, time(min), conc(M), freq, dt(min)
V                                   COMMAND - viscosity/density change
0.025001, 1.2133                    fluid viscosity(poise), density(g/cm^3)
m                                         COMMAND - subcolumns
50, 100, 0, 1, 3.70d-8, 0.0, 1.0d+6       elem-shift,elem-watch,pp-watch,c-watch,c-thresh,t-e,t-ee
h                                         COMMAND - effluent history dump
0, 2.0, 50, 4.033d-4, 0.016               unit op#, ptscale(1-4) filtering
h                                         COMMAND - effluent history dump
2, 2.0, 50, 4.033d-4, 0.016               unit op#, ptscale(1-4) filtering
h                                         COMMAND - effluent history dump
4, 2.0, 50, 4.033d-4, 0.016               unit op#, ptscale(1-4) filtering
h                                         COMMAND - effluent history dump
6, 2.0, 50, 4.033d-4, 0.016               unit op#, ptscale(1-4) filtering
-                                   end of commands
120000.0, 1.0                       end time(min), max dt in B.V.s
1.0d-7, 1.0d-4                      abs-tol, rel-tol
-                                   non-negative conc constraint
1.0                                 size exclusion factor
1.1209d-4                           part-pore diffusivities(cm^2/min)
3.3628d-4                           Brownian diffusivities(cm^2/min)
1.2323d-1                           Freundlich/Langmuir Hybrid a (moles/L B.V.)
1.0                                 Freundlich/Langmuir Hybrid b     (1/M)
1.0                                 Freundlich/Langmuir Hybrid Ma    (-)
1.0                                 Freundlich/Langmuir Hybrid Mb    (-)
5.1474d-4                           Freundlich/Langmuir Hybrid beta  (-)
```

D.8.2 VERSE Datafile.run

```
================================================================================

VERSE v7.80  by R. D. Whitley and N.-H. L. Wang, c1999 PRF
================================================================================
Input file: case08
SL644 3-column carousel, single component Cs isotherm, Criterion: lag
LAW feed: Hot Commissioning, CT: Degraded, Sensitivity: 0.8*[Cs+]
Begin Run:  13:54:38 on 04-05-2004   running under Windows 95/8
Finite elements     - axial:150  particle: 1
Collocation points - axial:  4  particle: 6 => Number of eqns:  6028
Inlet species at equilib.? N   Perfusable sorbent? N   Feed profile only? N
Use Profile File? N   Generate Profile File? N
Axial dispersion correlation:   Chung & Wen (1968)
Film mass transfer correlation: Wilson & Geankoplis (1966)
Sub-Column Boundary Conditions: Axial Dispersion and CSTR
================================================================================
SYSTEM PARAMETERS (at initial conditions):

t(stop)        = 120000.00000 min        dtheta max     =      1.00000 BV
abs. tol.      =       .10000E-06        rel. tol.      =       .10000E-03
Total Length   =    403.86000 cm         D              =    121.92000 cm
```

```
Tot. Capacity  =       .00000 eq/L solid  Col. Vol.      =4714879.85299 mL
F              =  56781.20000 mL/min      Uo (linear)    =     12.79915 cm/min
R              =    192.49000 microns     L/R            =  20980.83017
Bed Void frac. =       .38000             Pcl. Porosity  =       .66816
Spec. Area     =     96.62840 1/cm        Time/BV        =     10.51788 min
Vol CSTRs      =2214466.00000 mL

Component no.  =      1
Ke  [-]        =  .10000E+01
Eb  [cm2/min]  =  .91585E+00
Dp  [cm2/min]  =  .11209E-03
Doo [cm2/min]  =  .33628E-03
kf  [cm/min]   =  .20613E+00
Ds  [cm2/min]  =  .00000E+00

Dimensionless Groups:
Re             =  .15145E+00
Sc(i)          =  .36765E+04
Peb(i)         =  .18813E+04
Bi(i)          =  .52979E+02
Nf(i)          =  .55130E+03
Np(i)          =  .21260E+01
Pep(i)         =  .32896E+04

Isotherm       =  Freundlich/Langmuir Hybrid
Iso. Const. 1  =  .12323E+00
Iso. Const. 2  =  .10000E+01
Iso. Const. 3  =  .10000E+01
Iso. Const. 4  =  .10000E+01
Iso. Const. 5  =  .51474E-03
Init. Conc.    =  .00000E+00
Conc. at eqb.  =  .00000E+00
Conc. units          M
================================================================================
COMMAND LIST:
  1: Step conc. of component 1 at .0000     min to .2192E-04 M
     Execute   1 times, every .0000     mins.
  2: User set viscosity to .2500E-01 poise and density to 1.213     g/cm3
  3: Carousel (conc.). Active between t = .0000     and .1000E+07 min.
     When comp.  1 reaches .3700E-07 M     at end of node 100,
     shift  50 axial elements out the feed end
  4: Monitor conc. history at stream  0.  Filename = case08.h01
     Output density adjustments:
     2.0    *default abs conc delta,       50.    *default rel conc delta,
     .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
  5: Monitor conc. history at stream  2.  Filename = case08.h02
     Output density adjustments:
     2.0    *default abs conc delta,       50.    *default rel conc delta,
     .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
  6: Monitor conc. history at stream  4.  Filename = case08.h03
     Output density adjustments:
     2.0    *default abs conc delta,       50.    *default rel conc delta,
     .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
  7: Monitor conc. history at stream  6.  Filename = case08.h04
     Output density adjustments:
     2.0    *default abs conc delta,       50.    *default rel conc delta,
     .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
================================================================================
Conc. Carousel caused bed shift at t = 8342.     min
Conc. Carousel caused bed shift at t = .1370E+05 min
Conc. Carousel caused bed shift at t = .1926E+05 min
Conc. Carousel caused bed shift at t = .2494E+05 min
Conc. Carousel caused bed shift at t = .3071E+05 min
Conc. Carousel caused bed shift at t = .3654E+05 min
Conc. Carousel caused bed shift at t = .4240E+05 min
Conc. Carousel caused bed shift at t = .4826E+05 min
Conc. Carousel caused bed shift at t = .5413E+05 min
Conc. Carousel caused bed shift at t = .5999E+05 min
Conc. Carousel caused bed shift at t = .6585E+05 min
Conc. Carousel caused bed shift at t = .7172E+05 min
Conc. Carousel caused bed shift at t = .7757E+05 min
Conc. Carousel caused bed shift at t = .8344E+05 min
Conc. Carousel caused bed shift at t = .8930E+05 min
Conc. Carousel caused bed shift at t = .9516E+05 min
```

```
Conc. Carousel caused bed shift at t = .1010E+06 min
Conc. Carousel caused bed shift at t = .1069E+06 min
Conc. Carousel caused bed shift at t = .1127E+06 min
Conc. Carousel caused bed shift at t = .1186E+06 min
VERSE-LC finished in 12351 steps.  Average step size 9.716     minutes
End run:  14:34:09 on 04-05-2004
Integrated Areas in History Files:
case08.h01                 2.63040
case08.h02                 .317726
case08.h03                 .624774E-03
case08.h04                 .374912E-06
```

D.9 Hot Commissioning Operations ($[K^+]$ + 20%)

D.9.1 VERSE Datafile

```
SL644 3-column carousel, single component Cs isotherm, Criterion: lag

LAW feed: Hot Commissioning, CT: Degraded, Sensitivity: 1.2*[K+]
1, 150, 4, 6                        ncomp, nelem, ncol-bed, ncol-part
FCWNA                               isotherm,axial-disp,film-coef,surf-diff,BC-col
NNNNN                               input-only,perfusable,feed-equil,datafile.yio
M                                   comp-conc units
403.86, 121.92, 56781.2, 2214466.   Length(cm),Diam(cm),Q-flow(ml/min),CSTR-vol(ml)
192.49, 0.380, 0.668159, 0.0        part-rad(um), bed-void, part-void, sorb-cap()
0.0                                 initial concentration (M)
S                                   COMMAND - conc step change
1, 0.0, 2.7400d-5, 1, 0.0           spec id, time(min), conc(M), freq, dt(min)
V                                   COMMAND - viscosity/density change
0.025207, 1.2183                    fluid viscosity(poise), density(g/cm^3)
m                                         COMMAND - subcolumns
50, 100, 0, 1, 3.70d-8, 0.0, 1.0d+6       elem-shift,elem-watch,pp-watch,c-watch,c-thresh,t-e,t-ee
h                                         COMMAND - effluent history dump
0, 2.0, 50, 4.033d-4, 0.016               unit op#, ptscale(1-4) filtering
h                                         COMMAND - effluent history dump
2, 2.0, 50, 4.033d-4, 0.016               unit op#, ptscale(1-4) filtering
h                                         COMMAND - effluent history dump
4, 2.0, 50, 4.033d-4, 0.016               unit op#, ptscale(1-4) filtering
h                                         COMMAND - effluent history dump
6, 2.0, 50, 4.033d-4, 0.016               unit op#, ptscale(1-4) filtering
-                                   end of commands
120000.0, 1.0                       end time(min), max dt in B.V.s
1.0d-7, 1.0d-4                      abs-tol, rel-tol
-                                   non-negative conc constraint
1.0                                 size exclusion factor
9.7713d-5                           part-pore diffusivities(cm^2/min)
2.9314d-4                           Brownian diffusivities(cm^2/min)
1.2323d-1                           Freundlich/Langmuir Hybrid a (moles/L B.V.)
1.0                                 Freundlich/Langmuir Hybrid b     (1/M)
1.0                                 Freundlich/Langmuir Hybrid Ma    (-)
1.0                                 Freundlich/Langmuir Hybrid Mb    (-)
6.0329d-4                           Freundlich/Langmuir Hybrid beta (-)
```

D.9.2 VERSE Datafile.run

```
================================================================================

VERSE v7.80  by R. D. Whitley and N.-H. L. Wang, c1999 PRF
================================================================================
Input file: case09
SL644 3-column carousel, single component Cs isotherm, Criterion: lag
LAW feed: Hot Commissioning, CT: Degraded, Sensitivity: 1.2*[K+]
Begin Run:  14:34:09 on 04-05-2004   running under Windows 95/8
Finite elements    - axial:150  particle: 1
Collocation points - axial:  4  particle: 6 => Number of eqns:  6028
Inlet species at equilib.? N   Perfusable sorbent? N   Feed profile only? N
Use Profile File? N   Generate Profile File? N
Axial dispersion correlation:   Chung & Wen (1968)
Film mass transfer correlation: Wilson & Geankoplis (1966)
Sub-Column Boundary Conditions: Axial Dispersion and CSTR
```

```
================================================================================
SYSTEM PARAMETERS (at initial conditions):

t(stop)        = 120000.00000 min          dtheta max     =      1.00000 BV
abs. tol.      =       .10000E-06          rel. tol.      =       .10000E-03
Total Length   =    403.86000 cm           D              =    121.92000 cm
Tot. Capacity  =       .00000 eq/L solid   Col. Vol.      =4714879.85299 mL
F              =  56781.20000 mL/min       Uo (linear)    =     12.79915 cm/min
R              =    192.49000 microns      L/R            =  20980.83017
Bed Void frac. =       .38000              Pcl. Porosity  =       .66816
Spec. Area     =     96.62840 1/cm         Time/BV        =     10.51788 min
Vol CSTRs      =2214466.00000 mL

Component no.  =      1
Ke  [-]        =  .10000E+01
Eb  [cm2/min]  =  .91589E+00
Dp  [cm2/min]  =  .97713E-04
Doo [cm2/min]  =  .29314E-03
kf  [cm/min]   =  .18810E+00
Ds  [cm2/min]  =  .00000E+00

Dimensionless Groups:
Re             =  .15083E+00
Sc(i)          =  .42349E+04
Peb(i)         =  .18813E+04
Bi(i)          =  .55458E+02
Nf(i)          =  .50308E+03
Np(i)          =  .18533E+01
Pep(i)         =  .37736E+04

Isotherm       =  Freundlich/Langmuir Hybrid
Iso. Const. 1  =  .12323E+00
Iso. Const. 2  =  .10000E+01
Iso. Const. 3  =  .10000E+01
Iso. Const. 4  =  .10000E+01
Iso. Const. 5  =  .60329E-03
Init. Conc.    =  .00000E+00
Conc. at eqb.  =  .00000E+00
Conc. units        M
================================================================================
COMMAND LIST:
  1: Step conc. of component 1 at .0000     min to .2740E-04 M
     Execute   1 times, every .0000     mins.
  2: User set viscosity to .2521E-01 poise and density to 1.218     g/cm3
  3: Carousel (conc.). Active between t = .0000     and .1000E+07 min.
     When comp.  1 reaches .3700E-07 M     at end of node 100,
     shift  50 axial elements out the feed end
  4: Monitor conc. history at stream  0.  Filename = case09.h01
     Output density adjustments:
     2.0    *default abs conc delta,       50.    *default rel conc delta,
     .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
  5: Monitor conc. history at stream  2.  Filename = case09.h02
     Output density adjustments:
     2.0    *default abs conc delta,       50.    *default rel conc delta,
     .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
  6: Monitor conc. history at stream  4.  Filename = case09.h03
     Output density adjustments:
     2.0    *default abs conc delta,       50.    *default rel conc delta,
     .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
  7: Monitor conc. history at stream  6.  Filename = case09.h04
     Output density adjustments:
     2.0    *default abs conc delta,       50.    *default rel conc delta,
     .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
================================================================================
Conc. Carousel caused bed shift at t = 6805.     min
Conc. Carousel caused bed shift at t = .1129E+05 min
Conc. Carousel caused bed shift at t = .1596E+05 min
Conc. Carousel caused bed shift at t = .2074E+05 min
Conc. Carousel caused bed shift at t = .2560E+05 min
Conc. Carousel caused bed shift at t = .3049E+05 min
Conc. Carousel caused bed shift at t = .3539E+05 min
Conc. Carousel caused bed shift at t = .4030E+05 min
Conc. Carousel caused bed shift at t = .4520E+05 min
Conc. Carousel caused bed shift at t = .5011E+05 min
```

```
Conc. Carousel caused bed shift at t = .5502E+05 min
Conc. Carousel caused bed shift at t = .5991E+05 min
Conc. Carousel caused bed shift at t = .6482E+05 min
Conc. Carousel caused bed shift at t = .6972E+05 min
Conc. Carousel caused bed shift at t = .7462E+05 min
Conc. Carousel caused bed shift at t = .7952E+05 min
Conc. Carousel caused bed shift at t = .8443E+05 min
Conc. Carousel caused bed shift at t = .8934E+05 min
Conc. Carousel caused bed shift at t = .9423E+05 min
Conc. Carousel caused bed shift at t = .9914E+05 min
Conc. Carousel caused bed shift at t = .1040E+06 min
Conc. Carousel caused bed shift at t = .1089E+06 min
Conc. Carousel caused bed shift at t = .1138E+06 min
Conc. Carousel caused bed shift at t = .1187E+06 min
VERSE-LC finished in 12601 steps.  Average step size 9.523     minutes
End run:  15:22:01 on 04-05-2004
Integrated Areas in History Files:
case09.h01                 3.28800
case09.h02                 .341415
case09.h03                 .639293E-03
case09.h04                 .429365E-06
```

D.10 Hot Commissioning Operations ($[K^+]$ – 20%)

D.10.1 VERSE Datafile

```
SL644 3-column carousel, single component Cs isotherm, Criterion: lag

LAW feed: Hot Commissioning, CT: Degraded, Sensitivity: 0.8*[K+]
1, 150, 4, 6                        ncomp, nelem, ncol-bed, ncol-part
FCWNA                               isotherm,axial-disp,film-coef,surf-diff,BC-col
NNNNN                               input-only,perfusable,feed-equil,datafile.yio
M                                   comp-conc units
403.86, 121.92, 56781.2, 2214466.   Length(cm),Diam(cm),Q-flow(ml/min),CSTR-vol(ml)
192.49, 0.380, 0.668159, 0.0        part-rad(um), bed-void, part-void, sorb-cap()
0.0                                 initial concentration (M)
S                                   COMMAND - conc step change
1, 0.0, 2.7400d-5, 1, 0.0           spec id, time(min), conc(M), freq, dt(min)
V                                   COMMAND - viscosity/density change
0.024799, 1.2083                    fluid viscosity(poise), density(g/cm^3)
m                                         COMMAND - subcolumns
50, 100, 0, 1, 3.70d-8, 0.0, 1.0d+6       elem-shift,elem-watch,pp-watch,c-watch,c-thresh,t-e,t-ee
h                                         COMMAND - effluent history dump
0, 2.0, 50, 4.033d-4, 0.016               unit op#, ptscale(1-4) filtering
h                                         COMMAND - effluent history dump
2, 2.0, 50, 4.033d-4, 0.016               unit op#, ptscale(1-4) filtering
h                                         COMMAND - effluent history dump
4, 2.0, 50, 4.033d-4, 0.016               unit op#, ptscale(1-4) filtering
h                                         COMMAND - effluent history dump
6, 2.0, 50, 4.033d-4, 0.016               unit op#, ptscale(1-4) filtering
-                                   end of commands
120000.0, 1.0                       end time(min), max dt in B.V.s
1.0d-7, 1.0d-4                      abs-tol, rel-tol
-                                   non-negative conc constraint
1.0                                 size exclusion factor
1.2578d-4                           part-pore diffusivities(cm^2/min)
3.7734d-4                           Brownian diffusivities(cm^2/min)
1.2323d-1                           Freundlich/Langmuir Hybrid a (moles/L B.V.)
1.0                                 Freundlich/Langmuir Hybrid b     (1/M)
1.0                                 Freundlich/Langmuir Hybrid Ma    (-)
1.0                                 Freundlich/Langmuir Hybrid Mb    (-)
4.2670d-4                           Freundlich/Langmuir Hybrid beta  (-)
```

D.10.2 VERSE Datafile.run

```
================================================================================

VERSE v7.80  by R. D. Whitley and N.-H. L. Wang, c1999 PRF
================================================================================
Input file: case10
```

```
SL644 3-column carousel, single component Cs isotherm, Criterion: lag
LAW feed: Hot Commissioning, CT: Degraded, Sensitivity: 0.8*[K+]
Begin Run:  15:22:02 on 04-05-2004   running under Windows 95/8
Finite elements    - axial:150  particle: 1
Collocation points - axial:  4  particle: 6 => Number of eqns:  6028
Inlet species at equilib.? N   Perfusable sorbent? N   Feed profile only? N
Use Profile File? N   Generate Profile File? N
Axial dispersion correlation:   Chung & Wen (1968)
Film mass transfer correlation: Wilson & Geankoplis (1966)
Sub-Column Boundary Conditions: Axial Dispersion and CSTR
================================================================================
SYSTEM PARAMETERS (at initial conditions):

t(stop)        = 120000.00000 min          dtheta max     =      1.00000 BV
abs. tol.      =       .10000E-06         rel. tol.      =       .10000E-03
Total Length   =    403.86000 cm          D              =    121.92000 cm
Tot. Capacity  =       .00000 eq/L solid  Col. Vol.      =4714879.85299 mL
F              =  56781.20000 mL/min      Uo (linear)    =     12.79915 cm/min
R              =    192.49000 microns     L/R            =  20980.83017
Bed Void frac. =       .38000            Pcl. Porosity  =       .66816
Spec. Area     =     96.62840 1/cm        Time/BV        =     10.51788 min
Vol CSTRs      =2214466.00000 mL

Component no.  =      1
Ke  [-]        =  .10000E+01
Eb  [cm2/min]  =  .91581E+00
Dp  [cm2/min]  =  .12578E-03
Doo [cm2/min]  =  .37734E-03
kf  [cm/min]   =  .22258E+00
Ds  [cm2/min]  =  .00000E+00

Dimensionless Groups:
Re             =  .15205E+00
Sc(i)          =  .32635E+04
Peb(i)         =  .18814E+04
Bi(i)          =  .50981E+02
Nf(i)          =  .59531E+03
Np(i)          =  .23856E+01
Pep(i)         =  .29316E+04

Isotherm       =  Freundlich/Langmuir Hybrid
Iso. Const. 1  =  .12323E+00
Iso. Const. 2  =  .10000E+01
Iso. Const. 3  =  .10000E+01
Iso. Const. 4  =  .10000E+01
Iso. Const. 5  =  .42670E-03
Init. Conc.    =  .00000E+00
Conc. at eqb.  =  .00000E+00
Conc. units        M
================================================================================
COMMAND LIST:
  1: Step conc. of component 1 at .0000     min to .2740E-04 M
     Execute   1 times, every .0000     mins.
  2: User set viscosity to .2480E-01 poise and density to 1.208     g/cm3
  3: Carousel (conc.). Active between t = .0000     and .1000E+07 min.
     When comp.  1 reaches .3700E-07 M     at end of node 100,
     shift  50 axial elements out the feed end
  4: Monitor conc. history at stream  0.  Filename = case10.h01
     Output density adjustments:
     2.0    *default abs conc delta,      50.    *default rel conc delta,
     .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
  5: Monitor conc. history at stream  2.  Filename = case10.h02
     Output density adjustments:
     2.0    *default abs conc delta,      50.    *default rel conc delta,
     .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
  6: Monitor conc. history at stream  4.  Filename = case10.h03
     Output density adjustments:
     2.0    *default abs conc delta,      50.    *default rel conc delta,
     .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
  7: Monitor conc. history at stream  6.  Filename = case10.h04
     Output density adjustments:
     2.0    *default abs conc delta,      50.    *default rel conc delta,
     .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
================================================================================
```

```
Conc. Carousel caused bed shift at t = .1016E+05 min
Conc. Carousel caused bed shift at t = .1664E+05 min
Conc. Carousel caused bed shift at t = .2335E+05 min
Conc. Carousel caused bed shift at t = .3020E+05 min
Conc. Carousel caused bed shift at t = .3716E+05 min
Conc. Carousel caused bed shift at t = .4418E+05 min
Conc. Carousel caused bed shift at t = .5125E+05 min
Conc. Carousel caused bed shift at t = .5833E+05 min
Conc. Carousel caused bed shift at t = .6542E+05 min
Conc. Carousel caused bed shift at t = .7252E+05 min
Conc. Carousel caused bed shift at t = .7961E+05 min
Conc. Carousel caused bed shift at t = .8670E+05 min
Conc. Carousel caused bed shift at t = .9379E+05 min
Conc. Carousel caused bed shift at t = .1009E+06 min
Conc. Carousel caused bed shift at t = .1080E+06 min
Conc. Carousel caused bed shift at t = .1151E+06 min
VERSE-LC finished in 12170 steps.  Average step size 9.860     minutes
End run:  15:55:15 on 04-05-2004
Integrated Areas in History Files:
case10.h01                3.28800
case10.h02                .450910
case10.h03                .545082E-03
case10.h04                .164401E-06
```

D.11 Hot Commissioning Operations ([Na^+] + 20%)

D.11.1 VERSE Datafile

```
SL644 3-column carousel, single component Cs isotherm, Criterion: lag

LAW feed: Hot Commissioning, CT: Degraded, Sensitivity: 1.2*[Na+]
1, 150, 4, 6                        ncomp, nelem, ncol-bed, ncol-part
FCWNA                               isotherm,axial-disp,film-coef,surf-diff,BC-col
NNNNN                               input-only,perfusable,feed-equil,datafile.yio
M                                   comp-conc units
403.86, 121.92, 56781.2, 2214466.   Length(cm),Diam(cm),Q-flow(ml/min),CSTR-vol(ml)
192.49, 0.380, 0.668159, 0.0        part-rad(um), bed-void, part-void, sorb-cap()
0.0                                 initial concentration (M)
S                                   COMMAND - conc step change
1, 0.0, 2.7400d-5, 1, 0.0           spec id, time(min), conc(M), freq, dt(min)
V                                   COMMAND - viscosity/density change
0.029577, 1.2494                    fluid viscosity(poise), density(g/cm^3)
m                                        COMMAND - subcolumns
50, 100, 0, 1, 3.70d-8, 0.0, 1.0d+6      elem-shift,elem-watch,pp-watch,c-watch,c-thresh,t-e,t-ee
h                                        COMMAND - effluent history dump
0, 2.0, 50, 4.033d-4, 0.016              unit op#, ptscale(1-4) filtering
h                                        COMMAND - effluent history dump
2, 2.0, 50, 4.033d-4, 0.016              unit op#, ptscale(1-4) filtering
h                                        COMMAND - effluent history dump
4, 2.0, 50, 4.033d-4, 0.016              unit op#, ptscale(1-4) filtering
h                                        COMMAND - effluent history dump
6, 2.0, 50, 4.033d-4, 0.016              unit op#, ptscale(1-4) filtering
-                                   end of commands
120000.0, 1.0                       end time(min), max dt in B.V.s
1.0d-7, 1.0d-4                      abs-tol, rel-tol
-                                   non-negative conc constraint
1.0                                 size exclusion factor
5.2483d-6                           part-pore diffusivities(cm^2/min)
1.5745d-5                           Brownian diffusivities(cm^2/min)
1.2323d-1                           Freundlich/Langmuir Hybrid a (moles/L B.V.)
1.0                                 Freundlich/Langmuir Hybrid b     (1/M)
1.0                                 Freundlich/Langmuir Hybrid Ma    (-)
1.0                                 Freundlich/Langmuir Hybrid Mb    (-)
5.6334d-4                           Freundlich/Langmuir Hybrid beta (-)
```

D.11.2 VERSE Datafile.run

```
================================================================================

VERSE v7.80  by R. D. Whitley and N.-H. L. Wang, c1999 PRF
```

```
================================================================================
Input file: case11
SL644 3-column carousel, single component Cs isotherm, Criterion: lag
LAW feed: Hot Commissioning, CT: Degraded, Sensitivity: 1.2*[Na+]
Begin Run:  15:55:15 on 04-05-2004   running under Windows 95/8
Finite elements    - axial:150  particle: 1
Collocation points - axial:  4  particle: 6 => Number of eqns:  6028
Inlet species at equilib.? N   Perfusable sorbent? N   Feed profile only? N
Use Profile File? N   Generate Profile File? N
Axial dispersion correlation:   Chung & Wen (1968)
Film mass transfer correlation: Wilson & Geankoplis (1966)
Sub-Column Boundary Conditions: Axial Dispersion and CSTR
================================================================================
SYSTEM PARAMETERS (at initial conditions):

t(stop)        = 120000.00000 min          dtheta max     =      1.00000 BV
abs. tol.      =       .10000E-06         rel. tol.      =       .10000E-03
Total Length   =    403.86000 cm          D              =    121.92000 cm
Tot. Capacity  =       .00000 eq/L solid  Col. Vol.      =4714879.85299 mL
F              =  56781.20000 mL/min      Uo (linear)    =     12.79915 cm/min
R              =    192.49000 microns     L/R            =  20980.83017
Bed Void frac. =       .38000            Pcl. Porosity  =       .66816
Spec. Area     =     96.62840 1/cm        Time/BV        =     10.51788 min
Vol CSTRs      =2214466.00000 mL

Component no.  =      1
Ke  [-]        =  .10000E+01
Eb  [cm2/min]  =  .91714E+00
Dp  [cm2/min]  =  .52483E-05
Doo [cm2/min]  =  .15745E-04
kf  [cm/min]   =  .26777E-01
Ds  [cm2/min]  =  .00000E+00

Dimensionless Groups:
Re             =  .13183E+00
Sc(i)          =  .90211E+05
Peb(i)         =  .18787E+04
Bi(i)          =  .14699E+03
Nf(i)          =  .71617E+02
Np(i)          =  .99543E-01
Pep(i)         =  .70257E+05

Isotherm       =  Freundlich/Langmuir Hybrid
Iso. Const. 1  =  .12323E+00
Iso. Const. 2  =  .10000E+01
Iso. Const. 3  =  .10000E+01
Iso. Const. 4  =  .10000E+01
Iso. Const. 5  =  .56334E-03
Init. Conc.    =  .00000E+00
Conc. at eqb.  =  .00000E+00
Conc. units          M
================================================================================
COMMAND LIST:
  1: Step conc. of component 1 at .0000     min to .2740E-04 M
     Execute   1 times, every .0000     mins.
  2: User set viscosity to .2958E-01 poise and density to 1.249     g/cm3
  3: Carousel (conc.). Active between t = .0000     and .1000E+07 min.
     When comp.  1 reaches .3700E-07 M     at end of node 100,
     shift  50 axial elements out the feed end
  4: Monitor conc. history at stream  0.  Filename = case11.h01
     Output density adjustments:
     2.0    *default abs conc delta,       50.    *default rel conc delta,
     .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
  5: Monitor conc. history at stream  2.  Filename = case11.h02
     Output density adjustments:
     2.0    *default abs conc delta,       50.    *default rel conc delta,
     .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
  6: Monitor conc. history at stream  4.  Filename = case11.h03
     Output density adjustments:
     2.0    *default abs conc delta,       50.    *default rel conc delta,
     .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
  7: Monitor conc. history at stream  6.  Filename = case11.h04
     Output density adjustments:
     2.0    *default abs conc delta,       50.    *default rel conc delta,
```

.40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta

Conc. Carousel caused bed shift at t = 1352. min
Conc. Carousel caused bed shift at t = 2602. min
Conc. Carousel caused bed shift at t = 3861. min
Conc. Carousel caused bed shift at t = 5119. min
Conc. Carousel caused bed shift at t = 6381. min
Conc. Carousel caused bed shift at t = 7642. min
Conc. Carousel caused bed shift at t = 8903. min
Conc. Carousel caused bed shift at t = .1016E+05 min
Conc. Carousel caused bed shift at t = .1143E+05 min
Conc. Carousel caused bed shift at t = .1269E+05 min
Conc. Carousel caused bed shift at t = .1395E+05 min
Conc. Carousel caused bed shift at t = .1521E+05 min
Conc. Carousel caused bed shift at t = .1647E+05 min
Conc. Carousel caused bed shift at t = .1773E+05 min
Conc. Carousel caused bed shift at t = .1899E+05 min
Conc. Carousel caused bed shift at t = .2025E+05 min
Conc. Carousel caused bed shift at t = .2151E+05 min
Conc. Carousel caused bed shift at t = .2278E+05 min
Conc. Carousel caused bed shift at t = .2404E+05 min
Conc. Carousel caused bed shift at t = .2530E+05 min
Conc. Carousel caused bed shift at t = .2656E+05 min
Conc. Carousel caused bed shift at t = .2782E+05 min
Conc. Carousel caused bed shift at t = .2908E+05 min
Conc. Carousel caused bed shift at t = .3034E+05 min
Conc. Carousel caused bed shift at t = .3160E+05 min
Conc. Carousel caused bed shift at t = .3286E+05 min
Conc. Carousel caused bed shift at t = .3413E+05 min
Conc. Carousel caused bed shift at t = .3539E+05 min
Conc. Carousel caused bed shift at t = .3665E+05 min
Conc. Carousel caused bed shift at t = .3791E+05 min
Conc. Carousel caused bed shift at t = .3917E+05 min
Conc. Carousel caused bed shift at t = .4043E+05 min
Conc. Carousel caused bed shift at t = .4169E+05 min
Conc. Carousel caused bed shift at t = .4295E+05 min
Conc. Carousel caused bed shift at t = .4421E+05 min
Conc. Carousel caused bed shift at t = .4548E+05 min
Conc. Carousel caused bed shift at t = .4674E+05 min
Conc. Carousel caused bed shift at t = .4800E+05 min
Conc. Carousel caused bed shift at t = .4926E+05 min
Conc. Carousel caused bed shift at t = .5052E+05 min

Conc. Carousel caused bed shift at t = .5178E+05 min
Conc. Carousel caused bed shift at t = .5304E+05 min
Conc. Carousel caused bed shift at t = .5430E+05 min
Conc. Carousel caused bed shift at t = .5556E+05 min
Conc. Carousel caused bed shift at t = .5683E+05 min
Conc. Carousel caused bed shift at t = .5809E+05 min
Conc. Carousel caused bed shift at t = .5935E+05 min
Conc. Carousel caused bed shift at t = .6061E+05 min
Conc. Carousel caused bed shift at t = .6187E+05 min
Conc. Carousel caused bed shift at t = .6313E+05 min
Conc. Carousel caused bed shift at t = .6439E+05 min
Conc. Carousel caused bed shift at t = .6565E+05 min
Conc. Carousel caused bed shift at t = .6691E+05 min
Conc. Carousel caused bed shift at t = .6818E+05 min
Conc. Carousel caused bed shift at t = .6944E+05 min
Conc. Carousel caused bed shift at t = .7070E+05 min
Conc. Carousel caused bed shift at t = .7196E+05 min
Conc. Carousel caused bed shift at t = .7322E+05 min
Conc. Carousel caused bed shift at t = .7448E+05 min
Conc. Carousel caused bed shift at t = .7574E+05 min
Conc. Carousel caused bed shift at t = .7700E+05 min
Conc. Carousel caused bed shift at t = .7826E+05 min
Conc. Carousel caused bed shift at t = .7953E+05 min
Conc. Carousel caused bed shift at t = .8079E+05 min
Conc. Carousel caused bed shift at t = .8205E+05 min
Conc. Carousel caused bed shift at t = .8331E+05 min
Conc. Carousel caused bed shift at t = .8457E+05 min
Conc. Carousel caused bed shift at t = .8583E+05 min
Conc. Carousel caused bed shift at t = .8709E+05 min
Conc. Carousel caused bed shift at t = .8835E+05 min
Conc. Carousel caused bed shift at t = .8961E+05 min

```
Conc. Carousel caused bed shift at t = .9088E+05 min
Conc. Carousel caused bed shift at t = .9214E+05 min
Conc. Carousel caused bed shift at t = .9340E+05 min
Conc. Carousel caused bed shift at t = .9466E+05 min
Conc. Carousel caused bed shift at t = .9592E+05 min
Conc. Carousel caused bed shift at t = .9718E+05 min
Conc. Carousel caused bed shift at t = .9844E+05 min
Conc. Carousel caused bed shift at t = .9970E+05 min
Conc. Carousel caused bed shift at t = .1010E+06 min
Conc. Carousel caused bed shift at t = .1022E+06 min
Conc. Carousel caused bed shift at t = .1035E+06 min
Conc. Carousel caused bed shift at t = .1047E+06 min
Conc. Carousel caused bed shift at t = .1060E+06 min
Conc. Carousel caused bed shift at t = .1073E+06 min
Conc. Carousel caused bed shift at t = .1085E+06 min
Conc. Carousel caused bed shift at t = .1098E+06 min
Conc. Carousel caused bed shift at t = .1111E+06 min
Conc. Carousel caused bed shift at t = .1123E+06 min
Conc. Carousel caused bed shift at t = .1136E+06 min
Conc. Carousel caused bed shift at t = .1148E+06 min
Conc. Carousel caused bed shift at t = .1161E+06 min
Conc. Carousel caused bed shift at t = .1174E+06 min
Conc. Carousel caused bed shift at t = .1186E+06 min
Conc. Carousel caused bed shift at t = .1199E+06 min
VERSE-LC finished in 21862 steps.  Average step size 5.489     minutes
End run:  21:52:17 on 04-05-2004
Integrated Areas in History Files:
case11.h01                  3.28800
case11.h02                  .124002
case11.h03                  .844256E-03
case11.h04                  .304556E-05
```

D.12 Hot Commissioning Operations ([Na^+] – 20%)

D.12.1 VERSE Datafile

```
SL644 3-column carousel, single component Cs isotherm, Criterion: lag

LAW feed: Hot Commissioning, CT: Degraded, Sensitivity: 0.8*[Na+]
1, 150, 4, 6                        ncomp, nelem, ncol-bed, ncol-part
FCWNA                               isotherm,axial-disp,film-coef,surf-diff,BC-col
NNNNN                               input-only,perfusable,feed-equil,datafile.yio
M                                   comp-conc units
403.86, 121.92, 56781.2, 2214466. Length(cm),Diam(cm),Q-flow(ml/min),CSTR-vol(ml)
192.49, 0.380, 0.668159, 0.0        part-rad(um), bed-void, part-void, sorb-cap()
0.0                                 initial concentration (M)
S                                   COMMAND - conc step change
1, 0.0, 2.7400d-5, 1, 0.0           spec id, time(min), conc(M), freq, dt(min)
V                                   COMMAND - viscosity/density change
0.021256, 1.1750                    fluid viscosity(poise), density(g/cm^3)
m                                         COMMAND - subcolumns
50, 100, 0, 1, 3.70d-8, 0.0, 1.0d+6       elem-shift,elem-watch,pp-watch,c-watch,c-thresh,t-e,t-ee
h                                         COMMAND - effluent history dump
0, 2.0, 50, 4.033d-4, 0.016               unit op#, ptscale(1-4) filtering
h                                         COMMAND - effluent history dump
2, 2.0, 50, 4.033d-4, 0.016               unit op#, ptscale(1-4) filtering
h                                         COMMAND - effluent history dump
4, 2.0, 50, 4.033d-4, 0.016               unit op#, ptscale(1-4) filtering
h                                         COMMAND - effluent history dump
6, 2.0, 50, 4.033d-4, 0.016               unit op#, ptscale(1-4) filtering
-                                   end of commands
120000.0, 1.0                       end time(min), max dt in B.V.s
1.0d-7, 1.0d-4                      abs-tol, rel-tol
-                                   non-negative conc constraint
1.0                                 size exclusion factor
2.1078d-4                           part-pore diffusivities(cm^2/min)
6.3234d-4                           Brownian diffusivities(cm^2/min)
1.2323d-1                           Freundlich/Langmuir Hybrid a (moles/L B.V.)
1.0                                 Freundlich/Langmuir Hybrid b     (1/M)
1.0                                 Freundlich/Langmuir Hybrid Ma    (-)
1.0                                 Freundlich/Langmuir Hybrid Mb    (-)
```

4.8191d-4 Freundlich/Langmuir Hybrid beta (-)

D.12.2 VERSE Datafile.run

```
================================================================================

VERSE v7.80  by R. D. Whitley and N.-H. L. Wang, c1999 PRF
================================================================================
Input file: case12
SL644 3-column carousel, single component Cs isotherm, Criterion: lag
LAW feed: Hot Commissioning, CT: Degraded, Sensitivity: 0.8*[Na+]
Begin Run:  21:52:17 on 04-05-2004   running under Windows 95/8
Finite elements    - axial:150  particle: 1
Collocation points - axial:  4  particle: 6 => Number of eqns:  6028
Inlet species at equilib.? N   Perfusable sorbent? N   Feed profile only? N
Use Profile File? N   Generate Profile File? N
Axial dispersion correlation:   Chung & Wen (1968)
Film mass transfer correlation: Wilson & Geankoplis (1966)
Sub-Column Boundary Conditions: Axial Dispersion and CSTR
================================================================================
SYSTEM PARAMETERS (at initial conditions):

t(stop)        = 120000.00000 min         dtheta max     =      1.00000 BV
abs. tol.      =       .10000E-06         rel. tol.      =       .10000E-03
Total Length   =    403.86000 cm          D              =    121.92000 cm
Tot. Capacity  =       .00000 eq/L solid  Col. Vol.      =4714879.85299 mL
F              =  56781.20000 mL/min      Uo (linear)    =     12.79915 cm/min
R              =    192.49000 microns     L/R            =  20980.83017
Bed Void frac. =       .38000            Pcl. Porosity  =       .66816
Spec. Area     =     96.62840 1/cm        Time/BV        =     10.51788 min
Vol CSTRs      =2214466.00000 mL

Component no.  =      1
Ke   [-]       =  .10000E+01
Eb   [cm2/min] =  .91457E+00
Dp   [cm2/min] =  .21078E-03
Doo  [cm2/min] =  .63234E-03
kf   [cm/min]  =  .31403E+00
Ds   [cm2/min] =  .00000E+00

Dimensionless Groups:
Re             =  .17251E+00
Sc(i)          =  .17165E+04
Peb(i)         =  .18840E+04
Bi(i)          =  .42921E+02
Nf(i)          =  .83989E+03
Np(i)          =  .39978E+01
Pep(i)         =  .17494E+04

Isotherm       =  Freundlich/Langmuir Hybrid
Iso. Const. 1  =  .12323E+00
Iso. Const. 2  =  .10000E+01
Iso. Const. 3  =  .10000E+01
Iso. Const. 4  =  .10000E+01
Iso. Const. 5  =  .48191E-03
Init. Conc.    =  .00000E+00
Conc. at eqb.  =  .00000E+00
Conc. units          M
================================================================================
COMMAND LIST:
  1: Step conc. of component 1 at .0000     min to .2740E-04 M
     Execute   1 times, every .0000     mins.
  2: User set viscosity to .2126E-01 poise and density to 1.175     g/cm3
  3: Carousel (conc.). Active between t = .0000     and .1000E+07 min.
     When comp.  1 reaches .3700E-07 M     at end of node 100,
     shift  50 axial elements out the feed end
  4: Monitor conc. history at stream  0.  Filename = case12.h01
     Output density adjustments:
     2.0    *default abs conc delta,      50.    *default rel conc delta,
     .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
  5: Monitor conc. history at stream  2.  Filename = case12.h02
     Output density adjustments:
```

```
     2.0    *default abs conc delta,      50.    *default rel conc delta,
     .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
  6: Monitor conc. history at stream  4.  Filename = case12.h03
     Output density adjustments:
     2.0    *default abs conc delta,      50.    *default rel conc delta,
     .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
  7: Monitor conc. history at stream  6.  Filename = case12.h04
     Output density adjustments:
     2.0    *default abs conc delta,      50.    *default rel conc delta,
     .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
================================================================================
Conc. Carousel caused bed shift at t = 9983.     min
Conc. Carousel caused bed shift at t = .1601E+05 min
Conc. Carousel caused bed shift at t = .2220E+05 min
Conc. Carousel caused bed shift at t = .2850E+05 min
Conc. Carousel caused bed shift at t = .3485E+05 min
Conc. Carousel caused bed shift at t = .4127E+05 min
Conc. Carousel caused bed shift at t = .4773E+05 min
Conc. Carousel caused bed shift at t = .5421E+05 min
Conc. Carousel caused bed shift at t = .6073E+05 min
Conc. Carousel caused bed shift at t = .6727E+05 min
Conc. Carousel caused bed shift at t = .7382E+05 min
Conc. Carousel caused bed shift at t = .8037E+05 min
Conc. Carousel caused bed shift at t = .8692E+05 min
Conc. Carousel caused bed shift at t = .9350E+05 min
Conc. Carousel caused bed shift at t = .1001E+06 min
Conc. Carousel caused bed shift at t = .1066E+06 min
Conc. Carousel caused bed shift at t = .1132E+06 min
Conc. Carousel caused bed shift at t = .1197E+06 min
VERSE-LC finished in 12036 steps.  Average step size 9.970     minutes
End run:  22:20:32 on 04-05-2004
Integrated Areas in History Files:
case12.h01                 3.28800
case12.h02                 .653699
case12.h03                 .488532E-03
case12.h04                 .458593E-07
```

D.13 Hot Commissioning Operations ([OH⁻] + 20%)

D.13.1 VERSE Datafile

```
SL644 3-column carousel, single component Cs isotherm, Criterion: lag

LAW feed: Hot Commissioning, CT: Degraded, Sensitivity: 1.2*[OH-]
1, 150, 4, 6                        ncomp, nelem, ncol-bed, ncol-part
FCWNA                               isotherm,axial-disp,film-coef,surf-diff,BC-col
NNNNN                               input-only,perfusable,feed-equil,datafile.yio
M                                   comp-conc units
403.86, 121.92, 56781.2, 2214466.   Length(cm),Diam(cm),Q-flow(ml/min),CSTR-vol(ml)
192.49, 0.380, 0.668159, 0.0        part-rad(um), bed-void, part-void, sorb-cap()
0.0                                 initial concentration (M)
S                                   COMMAND - conc step change
1, 0.0, 2.7400d-5, 1, 0.0           spec id, time(min), conc(M), freq, dt(min)
V                                   COMMAND - viscosity/density change
0.025991, 1.2090                    fluid viscosity(poise), density(g/cm^3)
m                                        COMMAND - subcolumns
50, 100, 0, 1, 3.70d-8, 0.0, 1.0d+6      elem-shift,elem-watch,pp-watch,c-watch,c-thresh,t-e,t-ee
h                                        COMMAND - effluent history dump
0, 2.0, 50, 4.033d-4, 0.016              unit op#, ptscale(1-4) filtering
h                                        COMMAND - effluent history dump
2, 2.0, 50, 4.033d-4, 0.016              unit op#, ptscale(1-4) filtering
h                                        COMMAND - effluent history dump
4, 2.0, 50, 4.033d-4, 0.016              unit op#, ptscale(1-4) filtering
h                                        COMMAND - effluent history dump
6, 2.0, 50, 4.033d-4, 0.016              unit op#, ptscale(1-4) filtering
-                                   end of commands
120000.0, 1.0                       end time(min), max dt in B.V.s
1.0d-7, 1.0d-4                      abs-tol, rel-tol
-                                   non-negative conc constraint
1.0                                 size exclusion factor
1.2232d-4                           part-pore diffusivities(cm^2/min)
```

```
3.6697d-4                       Brownian diffusivities(cm^2/min)
1.2397d-1                       Freundlich/Langmuir Hybrid a (moles/L B.V.)
1.0                             Freundlich/Langmuir Hybrid b    (1/M)
1.0                             Freundlich/Langmuir Hybrid Ma   (-)
1.0                             Freundlich/Langmuir Hybrid Mb   (-)
4.9934d-4                       Freundlich/Langmuir Hybrid beta (-)
```

D.13.2 VERSE Datafile.run

```
================================================================================

VERSE v7.80  by R. D. Whitley and N.-H. L. Wang, c1999 PRF
================================================================================
Input file: case13
SL644 3-column carousel, single component Cs isotherm, Criterion: lag
LAW feed: Hot Commissioning, CT: Degraded, Sensitivity: 1.2*[OH-]
Begin Run:  22:20:32 on 04-05-2004   running under Windows 95/8
Finite elements    - axial:150  particle: 1
Collocation points - axial:  4  particle: 6 => Number of eqns:  6028
Inlet species at equilib.? N   Perfusable sorbent? N   Feed profile only? N
Use Profile File? N   Generate Profile File? N
Axial dispersion correlation:   Chung & Wen (1968)
Film mass transfer correlation: Wilson & Geankoplis (1966)
Sub-Column Boundary Conditions: Axial Dispersion and CSTR
================================================================================
SYSTEM PARAMETERS (at initial conditions):

t(stop)        = 120000.00000 min         dtheta max     =      1.00000 BV
abs. tol.      =       .10000E-06         rel. tol.      =       .10000E-03
Total Length   =    403.86000 cm          D              =    121.92000 cm
Tot. Capacity  =       .00000 eq/L solid  Col. Vol.      =4714879.85299 mL
F              =  56781.20000 mL/min      Uo (linear)    =     12.79915 cm/min
R              =    192.49000 microns     L/R            =  20980.83017
Bed Void frac. =       .38000            Pcl. Porosity  =       .66816
Spec. Area     =     96.62840 1/cm        Time/BV        =     10.51788 min
Vol CSTRs      =2214466.00000 mL

Component no.  =      1
Ke   [-]       =  .10000E+01
Eb   [cm2/min] =  .91625E+00
Dp   [cm2/min] =  .12232E-03
Doo  [cm2/min] =  .36697E-03
kf   [cm/min]  =  .21849E+00
Ds   [cm2/min] =  .00000E+00

Dimensionless Groups:
Re             =  .14516E+00
Sc(i)          =  .35149E+04
Peb(i)         =  .18805E+04
Bi(i)          =  .51458E+02
Nf(i)          =  .58435E+03
Np(i)          =  .23200E+01
Pep(i)         =  .30145E+04

Isotherm       =  Freundlich/Langmuir Hybrid
Iso. Const. 1  =  .12397E+00
Iso. Const. 2  =  .10000E+01
Iso. Const. 3  =  .10000E+01
Iso. Const. 4  =  .10000E+01
Iso. Const. 5  =  .49934E-03
Init. Conc.    =  .00000E+00
Conc. at eqb.  =  .00000E+00
Conc. units          M
================================================================================
COMMAND LIST:
  1: Step conc. of component 1 at .0000     min to .2740E-04 M
     Execute   1 times, every .0000     mins.
  2: User set viscosity to .2599E-01 poise and density to 1.209     g/cm3
  3: Carousel (conc.). Active between t = .0000     and .1000E+07 min.
     When comp.  1 reaches .3700E-07 M     at end of node 100,
     shift  50 axial elements out the feed end
  4: Monitor conc. history at stream  0.  Filename = case13.h01
```

```
     Output density adjustments:
     2.0    *default abs conc delta,       50.    *default rel conc delta,
     .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
  5: Monitor conc. history at stream  2.  Filename = case13.h02
     Output density adjustments:
     2.0    *default abs conc delta,       50.    *default rel conc delta,
     .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
  6: Monitor conc. history at stream  4.  Filename = case13.h03
     Output density adjustments:
     2.0    *default abs conc delta,       50.    *default rel conc delta,
     .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
  7: Monitor conc. history at stream  6.  Filename = case13.h04
     Output density adjustments:
     2.0    *default abs conc delta,       50.    *default rel conc delta,
     .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
================================================================================
Conc. Carousel caused bed shift at t = 8709.     min
Conc. Carousel caused bed shift at t = .1428E+05 min
Conc. Carousel caused bed shift at t = .2005E+05 min
Conc. Carousel caused bed shift at t = .2595E+05 min
Conc. Carousel caused bed shift at t = .3194E+05 min
Conc. Carousel caused bed shift at t = .3799E+05 min
Conc. Carousel caused bed shift at t = .4406E+05 min
Conc. Carousel caused bed shift at t = .5016E+05 min
Conc. Carousel caused bed shift at t = .5627E+05 min
Conc. Carousel caused bed shift at t = .6236E+05 min
Conc. Carousel caused bed shift at t = .6846E+05 min
Conc. Carousel caused bed shift at t = .7456E+05 min
Conc. Carousel caused bed shift at t = .8066E+05 min
Conc. Carousel caused bed shift at t = .8675E+05 min
Conc. Carousel caused bed shift at t = .9285E+05 min
Conc. Carousel caused bed shift at t = .9895E+05 min
Conc. Carousel caused bed shift at t = .1050E+06 min
Conc. Carousel caused bed shift at t = .1111E+06 min
Conc. Carousel caused bed shift at t = .1172E+06 min
VERSE-LC finished in 12293 steps.  Average step size 9.762     minutes
End run:  22:57:35 on 04-05-2004
Integrated Areas in History Files:
case13.h01                 3.28800
case13.h02                 .415559
case13.h03                 .579115E-03
case13.h04                 .231400E-06
```

D.14 Hot Commissioning Operations ([OH⁻] – 20%)

D.14.1 VERSE Datafile

```
SL644 3-column carousel, single component Cs isotherm, Criterion: lag

LAW feed: Hot Commissioning, CT: Degraded, Sensitivity: 0.8*[OH-]
1, 150, 4, 6                        ncomp, nelem, ncol-bed, ncol-part
FCWNA                               isotherm,axial-disp,film-coef,surf-diff,BC-col
NNNNN                               input-only,perfusable,feed-equil,datafile.yio
M                                   comp-conc units
403.86, 121.92, 56781.2, 2214466. Length(cm),Diam(cm),Q-flow(ml/min),CSTR-vol(ml)
192.49, 0.380, 0.668159, 0.0        part-rad(um), bed-void, part-void, sorb-cap()
0.0                                 initial concentration (M)
S                                   COMMAND - conc step change
1, 0.0, 2.7400d-5, 1, 0.0           spec id, time(min), conc(M), freq, dt(min)
V                                   COMMAND - viscosity/density change
0.023995, 1.2176                    fluid viscosity(poise), density(g/cm^3)
m                                        COMMAND - subcolumns
50, 100, 0, 1, 3.70d-8, 0.0, 1.0d+6      elem-shift,elem-watch,pp-watch,c-watch,c-thresh,t-e,t-ee
h                                        COMMAND - effluent history dump
0, 2.0, 50, 4.033d-4, 0.016              unit op#, ptscale(1-4) filtering
h                                        COMMAND - effluent history dump
2, 2.0, 50, 4.033d-4, 0.016              unit op#, ptscale(1-4) filtering
h                                        COMMAND - effluent history dump
4, 2.0, 50, 4.033d-4, 0.016              unit op#, ptscale(1-4) filtering
h                                        COMMAND - effluent history dump
6, 2.0, 50, 4.033d-4, 0.016              unit op#, ptscale(1-4) filtering
```

```
-                                   end of commands
120000.0, 1.0                       end time(min), max dt in B.V.s
1.0d-7, 1.0d-4                      abs-tol, rel-tol
-                                   non-negative conc constraint
1.0                                 size exclusion factor
1.0266d-4                           part-pore diffusivities(cm^2/min)
3.0799d-4                           Brownian diffusivities(cm^2/min)
1.2213d-1                           Freundlich/Langmuir Hybrid a (moles/L B.V.)
1.0                                 Freundlich/Langmuir Hybrid b    (1/M)
1.0                                 Freundlich/Langmuir Hybrid Ma   (-)
1.0                                 Freundlich/Langmuir Hybrid Mb   (-)
5.3147d-4                           Freundlich/Langmuir Hybrid beta (-)
```

D.14.2 VERSE Datafile.run

```
================================================================================

VERSE v7.80  by R. D. Whitley and N.-H. L. Wang, c1999 PRF
================================================================================
Input file: case14
SL644 3-column carousel, single component Cs isotherm, Criterion: lag
LAW feed: Hot Commissioning, CT: Degraded, Sensitivity: 0.8*[OH-]
Begin Run:  22:57:35 on 04-05-2004   running under Windows 95/8
Finite elements    - axial:150  particle: 1
Collocation points - axial:  4  particle: 6 => Number of eqns:  6028
Inlet species at equilib.? N   Perfusable sorbent? N   Feed profile only? N
Use Profile File? N   Generate Profile File? N
Axial dispersion correlation:   Chung & Wen (1968)
Film mass transfer correlation: Wilson & Geankoplis (1966)
Sub-Column Boundary Conditions: Axial Dispersion and CSTR
================================================================================
SYSTEM PARAMETERS (at initial conditions):

t(stop)        = 120000.00000 min        dtheta max     =      1.00000 BV
abs. tol.      =       .10000E-06        rel. tol.      =       .10000E-03
Total Length   =    403.86000 cm         D              =    121.92000 cm
Tot. Capacity  =       .00000 eq/L solid Col. Vol.      =4714879.85299 mL
F              =  56781.20000 mL/min     Uo (linear)    =     12.79915 cm/min
R              =    192.49000 microns    L/R            =  20980.83017
Bed Void frac. =       .38000           Pcl. Porosity  =       .66816
Spec. Area     =     96.62840 1/cm       Time/BV        =     10.51788 min
Vol CSTRs      =2214466.00000 mL

Component no.  =      1
Ke   [-]       =  .10000E+01
Eb   [cm2/min] =  .91542E+00
Dp   [cm2/min] =  .10266E-03
Doo  [cm2/min] =  .30799E-03
kf   [cm/min]  =  .19440E+00
Ds   [cm2/min] =  .00000E+00

Dimensionless Groups:
Re             =  .15836E+00
Sc(i)          =  .38391E+04
Peb(i)         =  .18822E+04
Bi(i)          =  .54554E+02
Nf(i)          =  .51993E+03
Np(i)          =  .19471E+01
Pep(i)         =  .35918E+04

Isotherm       =  Freundlich/Langmuir Hybrid
Iso. Const. 1  =  .12213E+00
Iso. Const. 2  =  .10000E+01
Iso. Const. 3  =  .10000E+01
Iso. Const. 4  =  .10000E+01
Iso. Const. 5  =  .53147E-03
Init. Conc.    =  .00000E+00
Conc. at eqb.  =  .00000E+00
Conc. units       M
================================================================================
COMMAND LIST:
  1: Step conc. of component 1 at .0000     min to .2740E-04 M
```

```
    Execute   1 times, every .0000     mins.
 2: User set viscosity to .2399E-01 poise and density to 1.218     g/cm3
 3: Carousel (conc.). Active between t = .0000     and .1000E+07 min.
    When comp.  1 reaches .3700E-07 M     at end of node 100,
    shift  50 axial elements out the feed end
 4: Monitor conc. history at stream  0.  Filename = case14.h01
    Output density adjustments:
    2.0    *default abs conc delta,       50.    *default rel conc delta,
    .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta

 5: Monitor conc. history at stream  2.  Filename = case14.h02
    Output density adjustments:
    2.0    *default abs conc delta,       50.    *default rel conc delta,
    .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
 6: Monitor conc. history at stream  4.  Filename = case14.h03
    Output density adjustments:
    2.0    *default abs conc delta,       50.    *default rel conc delta,
    .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
 7: Monitor conc. history at stream  6.  Filename = case14.h04
    Output density adjustments:
    2.0    *default abs conc delta,       50.    *default rel conc delta,
    .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
================================================================================
Conc. Carousel caused bed shift at t = 7741.     min
Conc. Carousel caused bed shift at t = .1280E+05 min
Conc. Carousel caused bed shift at t = .1806E+05 min
Conc. Carousel caused bed shift at t = .2345E+05 min
Conc. Carousel caused bed shift at t = .2893E+05 min
Conc. Carousel caused bed shift at t = .3444E+05 min
Conc. Carousel caused bed shift at t = .3998E+05 min
Conc. Carousel caused bed shift at t = .4552E+05 min
Conc. Carousel caused bed shift at t = .5106E+05 min
Conc. Carousel caused bed shift at t = .5660E+05 min
Conc. Carousel caused bed shift at t = .6215E+05 min
Conc. Carousel caused bed shift at t = .6768E+05 min
Conc. Carousel caused bed shift at t = .7322E+05 min
Conc. Carousel caused bed shift at t = .7876E+05 min
Conc. Carousel caused bed shift at t = .8429E+05 min
Conc. Carousel caused bed shift at t = .8983E+05 min
Conc. Carousel caused bed shift at t = .9537E+05 min
Conc. Carousel caused bed shift at t = .1009E+06 min
Conc. Carousel caused bed shift at t = .1064E+06 min
Conc. Carousel caused bed shift at t = .1120E+06 min
Conc. Carousel caused bed shift at t = .1175E+06 min
VERSE-LC finished in 12455 steps.  Average step size 9.635     minutes
End run:  23:40:08 on 04-05-2004
Integrated Areas in History Files:
case14.h01                 3.28800
case14.h02                 .361835
case14.h03                 .614906E-03
case14.h04                 .352970E-06
```

D.15 Hot Commissioning Operations (Q = 22 GPM)

D.15.1 VERSE Datafile

```
SL644 3-column carousel, single component Cs isotherm, Criterion: lag

LAW feed: Hot Commissioning, CT: Degraded, Sensitivity: Q=22gpm
1, 150, 4, 6                       ncomp, nelem, ncol-bed, ncol-part
FCWNA                              isotherm,axial-disp,film-coef,surf-diff,BC-col
NNNNN                              input-only,perfusable,feed-equil,datafile.yio
M                                  comp-conc units
403.86, 121.92, 83279.1, 2214466. Length(cm),Diam(cm),Q-flow(ml/min),CSTR-vol(ml)
192.49, 0.380, 0.668159, 0.0       part-rad(um), bed-void, part-void, sorb-cap()
0.0                                initial concentration (M)
S                                  COMMAND - conc step change
1, 0.0, 2.7400d-5, 1, 0.0          spec id, time(min), conc(M), freq, dt(min)
V                                  COMMAND - viscosity/density change
0.025001, 1.2133                   fluid viscosity(poise), density(g/cm^3)
m                                        COMMAND - subcolumns
```

```
50, 100, 0, 1, 3.70d-8, 0.0, 1.0d+6     elem-shift,elem-watch,pp-watch,c-watch,c-thresh,t-e,t-ee
h                                        COMMAND - effluent history dump
0, 2.0, 50, 4.033d-4, 0.016              unit op#, ptscale(1-4) filtering
h                                        COMMAND - effluent history dump
2, 2.0, 50, 4.033d-4, 0.016              unit op#, ptscale(1-4) filtering
h                                        COMMAND - effluent history dump
4, 2.0, 50, 4.033d-4, 0.016              unit op#, ptscale(1-4) filtering
h                                        COMMAND - effluent history dump
6, 2.0, 50, 4.033d-4, 0.016              unit op#, ptscale(1-4) filtering
-                                  end of commands
120000.0, 1.0                      end time(min), max dt in B.V.s
1.0d-7, 1.0d-4                     abs-tol, rel-tol
-                                  non-negative conc constraint
1.0                                size exclusion factor
1.1209d-4                          part-pore diffusivities(cm^2/min)
3.3628d-4                          Brownian diffusivities(cm^2/min)
1.2323d-1                          Freundlich/Langmuir Hybrid a (moles/L B.V.)
1.0                                Freundlich/Langmuir Hybrid b    (1/M)
1.0                                Freundlich/Langmuir Hybrid Ma   (-)
1.0                                Freundlich/Langmuir Hybrid Mb   (-)
5.1474d-4                          Freundlich/Langmuir Hybrid beta (-)
```

D.15.2 VERSE Datafile.run

```
================================================================================

VERSE v7.80  by R. D. Whitley and N.-H. L. Wang, c1999 PRF
================================================================================
Input file: case15
SL644 3-column carousel, single component Cs isotherm, Criterion: lag
LAW feed: Hot Commissioning, CT: Degraded, Sensitivity: Q=22gpm
Begin Run:  23:40:08 on 04-05-2004   running under Windows 95/8
Finite elements    - axial:150  particle: 1
Collocation points - axial:  4  particle: 6 => Number of eqns:  6028
Inlet species at equilib.? N   Perfusable sorbent? N   Feed profile only? N
Use Profile File? N   Generate Profile File? N
Axial dispersion correlation:   Chung & Wen (1968)
Film mass transfer correlation: Wilson & Geankoplis (1966)
Sub-Column Boundary Conditions: Axial Dispersion and CSTR
================================================================================
SYSTEM PARAMETERS (at initial conditions):

t(stop)        = 120000.00000 min         dtheta max     =      1.00000 BV
abs. tol.      =       .10000E-06         rel. tol.      =       .10000E-03
Total Length   =    403.86000 cm          D              =    121.92000 cm
Tot. Capacity  =       .00000 eq/L solid  Col. Vol.      =4714879.85299 mL
F              =  83279.10000 mL/min      Uo (linear)    =     18.77209 cm/min
R              =    192.49000 microns     L/R            =  20980.83017
Bed Void frac. =       .38000            Pcl. Porosity  =       .66816
Spec. Area     =     96.62840 1/cm        Time/BV        =      7.17128 min
Vol CSTRs      =2214466.00000 mL

Component no.  =      1
Ke   [-]       =  .10000E+01
Eb   [cm2/min] =  .13374E+01
Dp   [cm2/min] =  .11209E-03
Doo  [cm2/min] =  .33628E-03
kf   [cm/min]  =  .23420E+00
Ds   [cm2/min] =  .00000E+00

Dimensionless Groups:
Re             =  .22212E+00
Sc(i)          =  .36765E+04
Peb(i)         =  .18896E+04
Bi(i)          =  .60193E+02
Nf(i)          =  .42707E+03
Np(i)          =  .14495E+01
Pep(i)         =  .48247E+04

Isotherm       =  Freundlich/Langmuir Hybrid
Iso. Const. 1  =  .12323E+00
Iso. Const. 2  =  .10000E+01
```

```
Iso. Const. 3  =  .10000E+01
Iso. Const. 4  =  .10000E+01
Iso. Const. 5  =  .51474E-03
Init. Conc.    =  .00000E+00
Conc. at eqb.  =  .00000E+00
Conc. units           M
================================================================================
COMMAND LIST:
  1: Step conc. of component 1 at .0000     min to .2740E-04 M
     Execute   1 times, every .0000     mins.
  2: User set viscosity to .2500E-01 poise and density to 1.213     g/cm3
  3: Carousel (conc.). Active between t = .0000     and .1000E+07 min.
     When comp.  1 reaches .3700E-07 M     at end of node 100,
     shift  50 axial elements out the feed end
  4: Monitor conc. history at stream  0.  Filename = case15.h01
     Output density adjustments:
     2.0    *default abs conc delta,       50.    *default rel conc delta,
     .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
  5: Monitor conc. history at stream  2.  Filename = case15.h02
     Output density adjustments:
     2.0    *default abs conc delta,       50.    *default rel conc delta,
     .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
  6: Monitor conc. history at stream  4.  Filename = case15.h03
     Output density adjustments:
     2.0    *default abs conc delta,       50.    *default rel conc delta,
     .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
  7: Monitor conc. history at stream  6.  Filename = case15.h04
     Output density adjustments:
     2.0    *default abs conc delta,       50.    *default rel conc delta,
     .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
================================================================================
Conc. Carousel caused bed shift at t = 5064.     min
Conc. Carousel caused bed shift at t = 8516.     min
Conc. Carousel caused bed shift at t = .1213E+05 min
Conc. Carousel caused bed shift at t = .1584E+05 min
Conc. Carousel caused bed shift at t = .1959E+05 min
Conc. Carousel caused bed shift at t = .2337E+05 min
Conc. Carousel caused bed shift at t = .2713E+05 min
Conc. Carousel caused bed shift at t = .3089E+05 min
Conc. Carousel caused bed shift at t = .3466E+05 min
Conc. Carousel caused bed shift at t = .3843E+05 min
Conc. Carousel caused bed shift at t = .4219E+05 min
Conc. Carousel caused bed shift at t = .4595E+05 min
Conc. Carousel caused bed shift at t = .4971E+05 min
Conc. Carousel caused bed shift at t = .5348E+05 min
Conc. Carousel caused bed shift at t = .5724E+05 min
Conc. Carousel caused bed shift at t = .6101E+05 min
Conc. Carousel caused bed shift at t = .6477E+05 min
Conc. Carousel caused bed shift at t = .6853E+05 min
Conc. Carousel caused bed shift at t = .7230E+05 min
Conc. Carousel caused bed shift at t = .7606E+05 min
Conc. Carousel caused bed shift at t = .7983E+05 min
Conc. Carousel caused bed shift at t = .8359E+05 min
Conc. Carousel caused bed shift at t = .8736E+05 min
Conc. Carousel caused bed shift at t = .9112E+05 min
Conc. Carousel caused bed shift at t = .9488E+05 min
Conc. Carousel caused bed shift at t = .9865E+05 min
Conc. Carousel caused bed shift at t = .1024E+06 min
Conc. Carousel caused bed shift at t = .1062E+06 min
Conc. Carousel caused bed shift at t = .1099E+06 min
Conc. Carousel caused bed shift at t = .1137E+06 min
Conc. Carousel caused bed shift at t = .1175E+06 min
VERSE-LC finished in 18382 steps.  Average step size 6.528     minutes
End run:  00:47:15 on 04-06-2004
Integrated Areas in History Files:
case15.h01                 3.28800
case15.h02                 .298056
case15.h03                 .668084E-03
case15.h04                 .613186E-06
```

D.16 Hot Commissioning Operations (Q = 5 GPM)

D.16.1 VERSE Datafile

```
SL644 3-column carousel, single component Cs isotherm, Criterion: lag

LAW feed: Hot Commissioning, CT: Degraded, Sensitivity: Q=5gpm
1, 150, 4, 6                          ncomp, nelem, ncol-bed, ncol-part
FCWNA                                 isotherm,axial-disp,film-coef,surf-diff,BC-col
NNNNN                                 input-only,perfusable,feed-equil,datafile.yio
M                                     comp-conc units
403.86, 121.92, 18927.1, 2214466. Length(cm),Diam(cm),Q-flow(ml/min),CSTR-vol(ml)
192.49, 0.380, 0.668159, 0.0          part-rad(um), bed-void, part-void, sorb-cap()
0.0                                   initial concentration (M)
S                                     COMMAND - conc step change
1, 0.0, 2.7400d-5, 1, 0.0             spec id, time(min), conc(M), freq, dt(min)
V                                     COMMAND - viscosity/density change
0.025001, 1.2133                      fluid viscosity(poise), density(g/cm^3)
m                                           COMMAND - subcolumns
50, 100, 0, 1, 3.70d-8, 0.0, 1.0d+6        elem-shift,elem-watch,pp-watch,c-watch,c-thresh,t-e,t-ee
h                                           COMMAND - effluent history dump
0, 2.0, 50, 4.033d-4, 0.016                 unit op#, ptscale(1-4) filtering
h                                           COMMAND - effluent history dump
2, 2.0, 50, 4.033d-4, 0.016                 unit op#, ptscale(1-4) filtering
h                                           COMMAND - effluent history dump
4, 2.0, 50, 4.033d-4, 0.016                 unit op#, ptscale(1-4) filtering
h                                           COMMAND - effluent history dump
6, 2.0, 50, 4.033d-4, 0.016                 unit op#, ptscale(1-4) filtering
-                                     end of commands
120000.0, 1.0                         end time(min), max dt in B.V.s
1.0d-7, 1.0d-4                        abs-tol, rel-tol
-                                     non-negative conc constraint
1.0                                   size exclusion factor
1.1209d-4                             part-pore diffusivities(cm^2/min)
3.3628d-4                             Brownian diffusivities(cm^2/min)
1.2323d-1                             Freundlich/Langmuir Hybrid a (moles/L B.V.)
1.0                                   Freundlich/Langmuir Hybrid b    (1/M)
1.0                                   Freundlich/Langmuir Hybrid Ma   (-)
1.0                                   Freundlich/Langmuir Hybrid Mb   (-)
5.1474d-4                             Freundlich/Langmuir Hybrid beta (-)
```

D.16.2 VERSE Datafile.run

```
================================================================================

VERSE v7.80  by R. D. Whitley and N.-H. L. Wang, c1999 PRF
================================================================================
Input file: case16
SL644 3-column carousel, single component Cs isotherm, Criterion: lag
LAW feed: Hot Commissioning, CT: Degraded, Sensitivity: Q=5gpm
Begin Run:  00:47:15 on 04-06-2004   running under Windows 95/8
Finite elements    - axial:150  particle: 1
Collocation points - axial:  4  particle: 6 => Number of eqns:  6028
Inlet species at equilib.? N   Perfusable sorbent? N   Feed profile only? N
Use Profile File? N   Generate Profile File? N
Axial dispersion correlation:   Chung & Wen (1968)
Film mass transfer correlation: Wilson & Geankoplis (1966)
Sub-Column Boundary Conditions: Axial Dispersion and CSTR
================================================================================
SYSTEM PARAMETERS (at initial conditions):

t(stop)        = 120000.00000 min         dtheta max     =      1.00000 BV
abs. tol.      =       .10000E-06         rel. tol.      =       .10000E-03
Total Length   =    403.86000 cm          D              =    121.92000 cm
Tot. Capacity  =       .00000 eq/L solid  Col. Vol.      =4714879.85299 mL
F              =  18927.10000 mL/min      Uo (linear)    =      4.26639 cm/min
R              =    192.49000 microns     L/R            =  20980.83017
Bed Void frac. =       .38000            Pcl. Porosity  =       .66816
Spec. Area     =     96.62840 1/cm        Time/BV        =     31.55360 min
Vol CSTRs      =2214466.00000 mL
```

```
Component no.  =      1
Ke  [-]        =  .10000E+01
Eb  [cm2/min]  =  .30803E+00
Dp  [cm2/min]  =  .11209E-03
Doo [cm2/min]  =  .33628E-03
kf  [cm/min]   =  .14292E+00
Ds  [cm2/min]  =  .00000E+00

Dimensionless Groups:
Re             =  .50483E-01
Sc(i)          =  .36765E+04
Peb(i)         =  .18646E+04
Bi(i)          =  .36733E+02
Nf(i)          =  .11468E+04
Np(i)          =  .63779E+01
Pep(i)         =  .10965E+04

Isotherm       =  Freundlich/Langmuir Hybrid
Iso. Const. 1  =  .12323E+00
Iso. Const. 2  =  .10000E+01
Iso. Const. 3  =  .10000E+01
Iso. Const. 4  =  .10000E+01
Iso. Const. 5  =  .51474E-03
Init. Conc.    =  .00000E+00
Conc. at eqb.  =  .00000E+00
Conc. units       M
================================================================================
COMMAND LIST:
  1: Step conc. of component 1 at .0000     min to .2740E-04 M
     Execute   1 times, every .0000     mins.
  2: User set viscosity to .2500E-01 poise and density to 1.213     g/cm3
  3: Carousel (conc.). Active between t = .0000     and .1000E+07 min.
     When comp.  1 reaches .3700E-07 M     at end of node 100,
     shift  50 axial elements out the feed end
  4: Monitor conc. history at stream  0.  Filename = case16.h01
     Output density adjustments:
     2.0    *default abs conc delta,       50.    *default rel conc delta,
     .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
  5: Monitor conc. history at stream  2.  Filename = case16.h02
     Output density adjustments:
     2.0    *default abs conc delta,       50.    *default rel conc delta,
     .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
  6: Monitor conc. history at stream  4.  Filename = case16.h03
     Output density adjustments:
     2.0    *default abs conc delta,       50.    *default rel conc delta,
     .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
  7: Monitor conc. history at stream  6.  Filename = case16.h04
     Output density adjustments:
     2.0    *default abs conc delta,       50.    *default rel conc delta,
     .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
================================================================================
Conc. Carousel caused bed shift at t = .3010E+05 min
Conc. Carousel caused bed shift at t = .4761E+05 min
Conc. Carousel caused bed shift at t = .6547E+05 min
Conc. Carousel caused bed shift at t = .8354E+05 min
Conc. Carousel caused bed shift at t = .1018E+06 min
VERSE-LC finished in  3938 steps.  Average step size 30.47     minutes
End run:  00:53:47 on 04-06-2004
Integrated Areas in History Files:
case16.h01                 3.28800
case16.h02                 1.33275
case16.h03                 .257976E-03
case16.h04                 .666759E-11
```

D.17 Hot Commissioning Operations (D_p + 20%)

D.17.1 VERSE Datafile

```
SL644 3-column carousel, single component Cs isotherm, Criterion: lag

LAW feed: Hot Commissioning, CT: Degraded, Sensitivity: 1.2*Dp
1, 150, 4, 6                        ncomp, nelem, ncol-bed, ncol-part
FCWNA                               isotherm,axial-disp,film-coef,surf-diff,BC-col
NNNNN                               input-only,perfusable,feed-equil,datafile.yio
M                                   comp-conc units
403.86, 121.92, 56781.2, 2214466.   Length(cm),Diam(cm),Q-flow(ml/min),CSTR-vol(ml)
192.49, 0.380, 0.668159, 0.0        part-rad(um), bed-void, part-void, sorb-cap()
0.0                                 initial concentration (M)
S                                   COMMAND - conc step change
1, 0.0, 2.7400d-5, 1, 0.0           spec id, time(min), conc(M), freq, dt(min)
V                                   COMMAND - viscosity/density change
0.025001, 1.2133                    fluid viscosity(poise), density(g/cm^3)
m                                        COMMAND - subcolumns
50, 100, 0, 1, 3.70d-8, 0.0, 1.0d+6      elem-shift,elem-watch,pp-watch,c-watch,c-thresh,t-e,t-ee
h                                        COMMAND - effluent history dump
0, 2.0, 50, 4.033d-4, 0.016              unit op#, ptscale(1-4) filtering
h                                        COMMAND - effluent history dump
2, 2.0, 50, 4.033d-4, 0.016              unit op#, ptscale(1-4) filtering
h                                        COMMAND - effluent history dump
4, 2.0, 50, 4.033d-4, 0.016              unit op#, ptscale(1-4) filtering
h                                        COMMAND - effluent history dump
6, 2.0, 50, 4.033d-4, 0.016              unit op#, ptscale(1-4) filtering
-                                   end of commands
120000.0, 1.0                       end time(min), max dt in B.V.s
1.0d-7, 1.0d-4                      abs-tol, rel-tol
-                                   non-negative conc constraint
1.0                                 size exclusion factor
1.3451d-4                           part-pore diffusivities(cm^2/min)
4.0354d-4                           Brownian diffusivities(cm^2/min)
1.2323d-1                           Freundlich/Langmuir Hybrid a (moles/L B.V.)
1.0                                 Freundlich/Langmuir Hybrid b    (1/M)
1.0                                 Freundlich/Langmuir Hybrid Ma   (-)
1.0                                 Freundlich/Langmuir Hybrid Mb   (-)
5.1474d-4                           Freundlich/Langmuir Hybrid beta (-)
```

D.17.2 VERSE Datafile.run

```
================================================================================

VERSE v7.80  by R. D. Whitley and N.-H. L. Wang, c1999 PRF
================================================================================
Input file: case17
SL644 3-column carousel, single component Cs isotherm, Criterion: lag
LAW feed: Hot Commissioning, CT: Degraded, Sensitivity: 1.2*Dp
Begin Run:  00:53:47 on 04-06-2004   running under Windows 95/8
Finite elements    - axial:150  particle: 1
Collocation points - axial:  4  particle: 6 => Number of eqns:  6028
Inlet species at equilib.? N   Perfusable sorbent? N   Feed profile only? N
Use Profile File? N   Generate Profile File? N
Axial dispersion correlation:   Chung & Wen (1968)
Film mass transfer correlation: Wilson & Geankoplis (1966)
Sub-Column Boundary Conditions: Axial Dispersion and CSTR
================================================================================
SYSTEM PARAMETERS (at initial conditions):

t(stop)        = 120000.00000 min        dtheta max     =      1.00000 BV
abs. tol.      =       .10000E-06        rel. tol.      =       .10000E-03
Total Length   =    403.86000 cm         D              =    121.92000 cm
Tot. Capacity  =       .00000 eq/L solid Col. Vol.      =4714879.85299 mL
F              =  56781.20000 mL/min     Uo (linear)    =     12.79915 cm/min
R              =    192.49000 microns    L/R            =  20980.83017
Bed Void frac. =       .38000           Pcl. Porosity  =       .66816
Spec. Area     =     96.62840 1/cm       Time/BV        =     10.51788 min
Vol CSTRs      =2214466.00000 mL
```

```
Component no.  =      1
Ke  [-]        =  .10000E+01
Eb  [cm2/min]  =  .91585E+00
Dp  [cm2/min]  =  .13451E-03
Doo [cm2/min]  =  .40354E-03
kf  [cm/min]   =  .23277E+00
Ds  [cm2/min]  =  .00000E+00

Dimensionless Groups:
Re             =  .15145E+00
Sc(i)          =  .30638E+04
Peb(i)         =  .18813E+04
Bi(i)          =  .49854E+02
Nf(i)          =  .62256E+03
Np(i)          =  .25512E+01
Pep(i)         =  .27413E+04

Isotherm       =  Freundlich/Langmuir Hybrid
Iso. Const. 1  =  .12323E+00
Iso. Const. 2  =  .10000E+01
Iso. Const. 3  =  .10000E+01
Iso. Const. 4  =  .10000E+01
Iso. Const. 5  =  .51474E-03
Init. Conc.    =  .00000E+00
Conc. at eqb.  =  .00000E+00
Conc. units           M
-------------------------------------------------------------------------------
COMMAND LIST:
  1: Step conc. of component 1 at .0000     min to .2740E-04 M
     Execute   1 times, every .0000     mins.
  2: User set viscosity to .2500E-01 poise and density to 1.213     g/cm3
  3: Carousel (conc.). Active between t = .0000     and .1000E+07 min.
     When comp.  1 reaches .3700E-07 M     at end of node 100,
     shift  50 axial elements out the feed end
  4: Monitor conc. history at stream  0.  Filename = case17.h01
     Output density adjustments:
     2.0    *default abs conc delta,      50.    *default rel conc delta,
     .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
  5: Monitor conc. history at stream  2.  Filename = case17.h02
     Output density adjustments:
     2.0    *default abs conc delta,      50.    *default rel conc delta,
     .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
  6: Monitor conc. history at stream  4.  Filename = case17.h03
     Output density adjustments:
     2.0    *default abs conc delta,      50.    *default rel conc delta,
     .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
  7: Monitor conc. history at stream  6.  Filename = case17.h04
     Output density adjustments:
     2.0    *default abs conc delta,      50.    *default rel conc delta,
     .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
===============================================================================
Conc. Carousel caused bed shift at t = 8588.     min
Conc. Carousel caused bed shift at t = .1401E+05 min
Conc. Carousel caused bed shift at t = .1963E+05 min
Conc. Carousel caused bed shift at t = .2536E+05 min
Conc. Carousel caused bed shift at t = .3118E+05 min
Conc. Carousel caused bed shift at t = .3705E+05 min
Conc. Carousel caused bed shift at t = .4296E+05 min
Conc. Carousel caused bed shift at t = .4890E+05 min
Conc. Carousel caused bed shift at t = .5484E+05 min
Conc. Carousel caused bed shift at t = .6079E+05 min
Conc. Carousel caused bed shift at t = .6672E+05 min
Conc. Carousel caused bed shift at t = .7267E+05 min
Conc. Carousel caused bed shift at t = .7861E+05 min
Conc. Carousel caused bed shift at t = .8456E+05 min
Conc. Carousel caused bed shift at t = .9049E+05 min
Conc. Carousel caused bed shift at t = .9644E+05 min
Conc. Carousel caused bed shift at t = .1024E+06 min
Conc. Carousel caused bed shift at t = .1083E+06 min
Conc. Carousel caused bed shift at t = .1143E+06 min
VERSE-LC finished in 12270 steps.  Average step size 9.780     minutes
End run:  01:29:54 on 04-06-2004
Integrated Areas in History Files:
```

```
case17.h01                3.28800
case17.h02                .443592
case17.h03                .578462E-03
case17.h04                .200242E-06
```

D.18 Hot Commissioning Operations (D_p – 20%)

D.18.1 VERSE Datafile

```
SL644 3-column carousel, single component Cs isotherm, Criterion: lag

LAW feed: Hot Commissioning, CT: Degraded, Sensitivity: 0.8*Dp
1, 150, 4, 6                        ncomp, nelem, ncol-bed, ncol-part
FCWNA                               isotherm,axial-disp,film-coef,surf-diff,BC-col
NNNNN                               input-only,perfusable,feed-equil,datafile.yio
M                                   comp-conc units
403.86, 121.92, 56781.2, 2214466. Length(cm),Diam(cm),Q-flow(ml/min),CSTR-vol(ml)
192.49, 0.380, 0.668159, 0.0        part-rad(um), bed-void, part-void, sorb-cap()
0.0                                 initial concentration (M)
S                                   COMMAND - conc step change
1, 0.0, 2.7400d-5, 1, 0.0           spec id, time(min), conc(M), freq, dt(min)
V                                   COMMAND - viscosity/density change
0.025001, 1.2133                    fluid viscosity(poise), density(g/cm^3)
m                                         COMMAND - subcolumns
50, 100, 0, 1, 3.70d-8, 0.0, 1.0d+6       elem-shift,elem-watch,pp-watch,c-watch,c-thresh,t-e,t-ee
h                                         COMMAND - effluent history dump
0, 2.0, 50, 4.033d-4, 0.016               unit op#, ptscale(1-4) filtering
h                                         COMMAND - effluent history dump
2, 2.0, 50, 4.033d-4, 0.016               unit op#, ptscale(1-4) filtering
h                                         COMMAND - effluent history dump
4, 2.0, 50, 4.033d-4, 0.016               unit op#, ptscale(1-4) filtering
h                                         COMMAND - effluent history dump
6, 2.0, 50, 4.033d-4, 0.016               unit op#, ptscale(1-4) filtering
-                                   end of commands
120000.0, 1.0                       end time(min), max dt in B.V.s
1.0d-7, 1.0d-4                      abs-tol, rel-tol
-                                   non-negative conc constraint
1.0                                 size exclusion factor
8.9675d-5                           part-pore diffusivities(cm^2/min)
2.6902d-4                           Brownian diffusivities(cm^2/min)
1.2323d-1                           Freundlich/Langmuir Hybrid a (moles/L B.V.)
1.0                                 Freundlich/Langmuir Hybrid b     (1/M)
1.0                                 Freundlich/Langmuir Hybrid Ma    (-)
1.0                                 Freundlich/Langmuir Hybrid Mb    (-)
5.1474d-4                           Freundlich/Langmuir Hybrid beta (-)
```

D.18.2 VERSE Datafile.run

```
================================================================================

VERSE v7.80  by R. D. Whitley and N.-H. L. Wang, c1999 PRF
================================================================================
Input file: case18
SL644 3-column carousel, single component Cs isotherm, Criterion: lag
LAW feed: Hot Commissioning, CT: Degraded, Sensitivity: 0.8*Dp
Begin Run:  01:29:54 on 04-06-2004   running under Windows 95/8
Finite elements     - axial:150  particle: 1
Collocation points - axial:  4  particle: 6 => Number of eqns:  6028
Inlet species at equilib.? N   Perfusable sorbent? N   Feed profile only? N
Use Profile File? N   Generate Profile File? N
Axial dispersion correlation:   Chung & Wen (1968)
Film mass transfer correlation: Wilson & Geankoplis (1966)
Sub-Column Boundary Conditions: Axial Dispersion and CSTR
================================================================================
SYSTEM PARAMETERS (at initial conditions):

t(stop)        = 120000.00000 min        dtheta max     =      1.00000 BV
abs. tol.      =       .10000E-06        rel. tol.      =       .10000E-03
Total Length   =    403.86000 cm         D              =    121.92000 cm
```

```
Tot. Capacity  =       .00000 eq/L solid  Col. Vol.      =4714879.85299 mL
F              =  56781.20000 mL/min      Uo (linear)    =     12.79915 cm/min
R              =    192.49000 microns     L/R            =  20980.83017
Bed Void frac. =       .38000             Pcl. Porosity  =       .66816
Spec. Area     =     96.62840 1/cm        Time/BV        =     10.51788 min
Vol CSTRs      =2214466.00000 mL

Component no.  =      1
Ke  [-]        =  .10000E+01
Eb  [cm2/min]  =  .91585E+00
Dp  [cm2/min]  =  .89675E-04
Doo [cm2/min]  =  .26902E-03
kf  [cm/min]   =  .17764E+00
Ds  [cm2/min]  =  .00000E+00

Dimensionless Groups:
Re             =  .15145E+00
Sc(i)          =  .45957E+04
Peb(i)         =  .18813E+04
Bi(i)          =  .57067E+02
Nf(i)          =  .47509E+03
Np(i)          =  .17008E+01
Pep(i)         =  .41119E+04

Isotherm       =  Freundlich/Langmuir Hybrid
Iso. Const. 1  =  .12323E+00
Iso. Const. 2  =  .10000E+01
Iso. Const. 3  =  .10000E+01
Iso. Const. 4  =  .10000E+01
Iso. Const. 5  =  .51474E-03
Init. Conc.    =  .00000E+00
Conc. at eqb.  =  .00000E+00
Conc. units        M
================================================================================
COMMAND LIST:
  1: Step conc. of component 1 at .0000     min to .2740E-04 M
     Execute   1 times, every .0000     mins.
  2: User set viscosity to .2500E-01 poise and density to 1.213     g/cm3
  3: Carousel (conc.). Active between t = .0000     and .1000E+07 min.
     When comp.  1 reaches .3700E-07 M     at end of node 100,
     shift  50 axial elements out the feed end
  4: Monitor conc. history at stream  0.  Filename = case18.h01
     Output density adjustments:
     2.0    *default abs conc delta,       50.    *default rel conc delta,
     .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
  5: Monitor conc. history at stream  2.  Filename = case18.h02
     Output density adjustments:
     2.0    *default abs conc delta,       50.    *default rel conc delta,
     .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
  6: Monitor conc. history at stream  4.  Filename = case18.h03
     Output density adjustments:
     2.0    *default abs conc delta,       50.    *default rel conc delta,
     .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
  7: Monitor conc. history at stream  6.  Filename = case18.h04
     Output density adjustments:
     2.0    *default abs conc delta,       50.    *default rel conc delta,
     .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
================================================================================
Conc. Carousel caused bed shift at t = 7773.     min
Conc. Carousel caused bed shift at t = .1295E+05 min
Conc. Carousel caused bed shift at t = .1835E+05 min
Conc. Carousel caused bed shift at t = .2389E+05 min
Conc. Carousel caused bed shift at t = .2951E+05 min
Conc. Carousel caused bed shift at t = .3517E+05 min
Conc. Carousel caused bed shift at t = .4084E+05 min
Conc. Carousel caused bed shift at t = .4650E+05 min
Conc. Carousel caused bed shift at t = .5216E+05 min
Conc. Carousel caused bed shift at t = .5782E+05 min
Conc. Carousel caused bed shift at t = .6348E+05 min
Conc. Carousel caused bed shift at t = .6914E+05 min
Conc. Carousel caused bed shift at t = .7480E+05 min
Conc. Carousel caused bed shift at t = .8046E+05 min
Conc. Carousel caused bed shift at t = .8612E+05 min
Conc. Carousel caused bed shift at t = .9178E+05 min
```

```
Conc. Carousel caused bed shift at t = .9744E+05 min
Conc. Carousel caused bed shift at t = .1031E+06 min
Conc. Carousel caused bed shift at t = .1088E+06 min
Conc. Carousel caused bed shift at t = .1144E+06 min
VERSE-LC finished in 12473 steps.  Average step size 9.621     minutes
End run:  02:13:24 on 04-06-2004
Integrated Areas in History Files:
case18.h01                 3.28800
case18.h02                 .341346
case18.h03                 .640181E-03
case18.h04                 .437296E-06
```

D.19 Hot Commissioning Operations (R_p + 20%)

D.19.1 VERSE Datafile

```
SL644 3-column carousel, single component Cs isotherm, Criterion: lag

LAW feed: Hot Commissioning, CT: Degraded, Sensitivity: 1.2*R
1, 150, 4, 6                        ncomp, nelem, ncol-bed, ncol-part
FCWNA                               isotherm,axial-disp,film-coef,surf-diff,BC-col
NNNNN                               input-only,perfusable,feed-equil,datafile.yio
M                                   comp-conc units
403.86, 121.92, 56781.2, 2214466.   Length(cm),Diam(cm),Q-flow(ml/min),CSTR-vol(ml)
230.99, 0.380, 0.668159, 0.0        part-rad(um), bed-void, part-void, sorb-cap()
0.0                                 initial concentration (M)
S                                   COMMAND - conc step change
1, 0.0, 2.7400d-5, 1, 0.0           spec id, time(min), conc(M), freq, dt(min)
V                                   COMMAND - viscosity/density change
0.025001, 1.2133                    fluid viscosity(poise), density(g/cm^3)
m                                        COMMAND - subcolumns
50, 100, 0, 1, 3.70d-8, 0.0, 1.0d+6      elem-shift,elem-watch,pp-watch,c-watch,c-thresh,t-e,t-ee
h                                        COMMAND - effluent history dump
0, 2.0, 50, 4.033d-4, 0.016              unit op#, ptscale(1-4) filtering
h                                        COMMAND - effluent history dump
2, 2.0, 50, 4.033d-4, 0.016              unit op#, ptscale(1-4) filtering
h                                        COMMAND - effluent history dump
4, 2.0, 50, 4.033d-4, 0.016              unit op#, ptscale(1-4) filtering
h                                        COMMAND - effluent history dump
6, 2.0, 50, 4.033d-4, 0.016              unit op#, ptscale(1-4) filtering
-                                   end of commands
120000.0, 1.0                       end time(min), max dt in B.V.s
1.0d-7, 1.0d-4                      abs-tol, rel-tol
-                                   non-negative conc constraint
1.0                                 size exclusion factor
1.1209d-4                           part-pore diffusivities(cm^2/min)
3.3628d-4                           Brownian diffusivities(cm^2/min)
1.2323d-1                           Freundlich/Langmuir Hybrid a (moles/L B.V.)
1.0                                 Freundlich/Langmuir Hybrid b     (1/M)
1.0                                 Freundlich/Langmuir Hybrid Ma    (-)
1.0                                 Freundlich/Langmuir Hybrid Mb    (-)
5.1474d-4                           Freundlich/Langmuir Hybrid beta (-)
```

D.19.2 VERSE Datafile.run

```
================================================================================

VERSE v7.80  by R. D. Whitley and N.-H. L. Wang, c1999 PRF
================================================================================
Input file: case19
SL644 3-column carousel, single component Cs isotherm, Criterion: lag
LAW feed: Hot Commissioning, CT: Degraded, Sensitivity: 1.2*R
Begin Run:  02:13:24 on 04-06-2004   running under Windows 95/8
Finite elements    - axial:150  particle: 1
Collocation points - axial:  4  particle: 6 => Number of eqns:  6028
Inlet species at equilib.? N   Perfusable sorbent? N   Feed profile only? N
Use Profile File? N   Generate Profile File? N
Axial dispersion correlation:   Chung & Wen (1968)
Film mass transfer correlation: Wilson & Geankoplis (1966)
```

```
Sub-Column Boundary Conditions: Axial Dispersion and CSTR
================================================================================
SYSTEM PARAMETERS (at initial conditions):

t(stop)        = 120000.00000 min          dtheta max     =      1.00000 BV
abs. tol.      =       .10000E-06          rel. tol.      =       .10000E-03
Total Length   =    403.86000 cm           D              =    121.92000 cm
Tot. Capacity  =       .00000 eq/L solid   Col. Vol.      =4714879.85299 mL
F              =  56781.20000 mL/min       Uo (linear)    =     12.79915 cm/min
R              =    230.99000 microns      L/R            =  17483.87376
Bed Void frac. =       .38000             Pcl. Porosity  =       .66816
Spec. Area     =     80.52297 1/cm         Time/BV        =     10.51788 min
Vol CSTRs      =2214466.00000 mL

Component no.  =      1
Ke  [-]        =  .10000E+01
Eb  [cm2/min]  =  .10969E+01
Dp  [cm2/min]  =  .11209E-03
Doo [cm2/min]  =  .33628E-03
kf  [cm/min]   =  .18254E+00
Ds  [cm2/min]  =  .00000E+00

Dimensionless Groups:
Re             =  .18174E+00
Sc(i)          =  .36765E+04
Peb(i)         =  .15709E+04
Bi(i)          =  .56298E+02
Nf(i)          =  .40683E+03
Np(i)          =  .14763E+01
Pep(i)         =  .39476E+04

Isotherm       =  Freundlich/Langmuir Hybrid
Iso. Const. 1  =  .12323E+00
Iso. Const. 2  =  .10000E+01
Iso. Const. 3  =  .10000E+01
Iso. Const. 4  =  .10000E+01
Iso. Const. 5  =  .51474E-03
Init. Conc.    =  .00000E+00
Conc. at eqb.  =  .00000E+00
Conc. units          M
================================================================================
COMMAND LIST:
  1: Step conc. of component 1 at .0000     min to .2740E-04 M
     Execute   1 times, every .0000     mins.
  2: User set viscosity to .2500E-01 poise and density to 1.213     g/cm3
  3: Carousel (conc.). Active between t = .0000     and .1000E+07 min.
     When comp.  1 reaches .3700E-07 M     at end of node 100,
     shift  50 axial elements out the feed end
  4: Monitor conc. history at stream  0.  Filename = case19.h01
     Output density adjustments:
     2.0    *default abs conc delta,      50.    *default rel conc delta,
     .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
  5: Monitor conc. history at stream  2.  Filename = case19.h02
     Output density adjustments:
     2.0    *default abs conc delta,      50.    *default rel conc delta,
     .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
  6: Monitor conc. history at stream  4.  Filename = case19.h03
     Output density adjustments:
     2.0    *default abs conc delta,      50.    *default rel conc delta,
     .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
  7: Monitor conc. history at stream  6.  Filename = case19.h04
     Output density adjustments:
     2.0    *default abs conc delta,      50.    *default rel conc delta,
     .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
================================================================================
Conc. Carousel caused bed shift at t = 7443.     min
Conc. Carousel caused bed shift at t = .1251E+05 min
Conc. Carousel caused bed shift at t = .1782E+05 min
Conc. Carousel caused bed shift at t = .2327E+05 min
Conc. Carousel caused bed shift at t = .2879E+05 min
Conc. Carousel caused bed shift at t = .3431E+05 min
Conc. Carousel caused bed shift at t = .3985E+05 min
Conc. Carousel caused bed shift at t = .4538E+05 min
Conc. Carousel caused bed shift at t = .5091E+05 min
```

```
Conc. Carousel caused bed shift at t = .5644E+05 min
Conc. Carousel caused bed shift at t = .6196E+05 min
Conc. Carousel caused bed shift at t = .6750E+05 min
Conc. Carousel caused bed shift at t = .7302E+05 min
Conc. Carousel caused bed shift at t = .7855E+05 min
Conc. Carousel caused bed shift at t = .8408E+05 min
Conc. Carousel caused bed shift at t = .8961E+05 min
Conc. Carousel caused bed shift at t = .9513E+05 min
Conc. Carousel caused bed shift at t = .1007E+06 min
Conc. Carousel caused bed shift at t = .1062E+06 min
Conc. Carousel caused bed shift at t = .1117E+06 min
Conc. Carousel caused bed shift at t = .1173E+06 min
VERSE-LC finished in 12560 steps.  Average step size 9.554     minutes
End run:  03:00:01 on 04-06-2004
Integrated Areas in History Files:
case19.h01                 3.28800
case19.h02                 .306371
case19.h03                 .645538E-03
case19.h04                 .537808E-06
```

D.20 Hot Commissioning Operations (R_p – 20%)

D.20.1 VERSE Datafile

```
SL644 3-column carousel, single component Cs isotherm, Criterion: lag

LAW feed: Hot Commissioning, CT: Degraded, Sensitivity: 0.8*R
1, 150, 4, 6                        ncomp, nelem, ncol-bed, ncol-part
FCWNA                               isotherm,axial-disp,film-coef,surf-diff,BC-col
NNNNN                               input-only,perfusable,feed-equil,datafile.yio
M                                   comp-conc units
403.86, 121.92, 56781.2, 2214466.   Length(cm),Diam(cm),Q-flow(ml/min),CSTR-vol(ml)
153.99, 0.380, 0.668159, 0.0        part-rad(um), bed-void, part-void, sorb-cap()
0.0                                 initial concentration (M)
S                                   COMMAND - conc step change
1, 0.0, 2.7400d-5, 1, 0.0           spec id, time(min), conc(M), freq, dt(min)
V                                   COMMAND - viscosity/density change
0.025001, 1.2133                    fluid viscosity(poise), density(g/cm^3)
m                                        COMMAND - subcolumns
50, 100, 0, 1, 3.70d-8, 0.0, 1.0d+6      elem-shift,elem-watch,pp-watch,c-watch,c-thresh,t-e,t-ee
h                                        COMMAND - effluent history dump
0, 2.0, 50, 4.033d-4, 0.016              unit op#, ptscale(1-4) filtering
h                                        COMMAND - effluent history dump
2, 2.0, 50, 4.033d-4, 0.016              unit op#, ptscale(1-4) filtering
h                                        COMMAND - effluent history dump
4, 2.0, 50, 4.033d-4, 0.016              unit op#, ptscale(1-4) filtering
h                                        COMMAND - effluent history dump
6, 2.0, 50, 4.033d-4, 0.016              unit op#, ptscale(1-4) filtering
-                                   end of commands
120000.0, 1.0                       end time(min), max dt in B.V.s
1.0d-7, 1.0d-4                      abs-tol, rel-tol
-                                   non-negative conc constraint
1.0                                 size exclusion factor
1.1209d-4                           part-pore diffusivities(cm^2/min)
3.3628d-4                           Brownian diffusivities(cm^2/min)
1.2323d-1                           Freundlich/Langmuir Hybrid a (moles/L B.V.)
1.0                                 Freundlich/Langmuir Hybrid b     (1/M)
1.0                                 Freundlich/Langmuir Hybrid Ma    (-)
1.0                                 Freundlich/Langmuir Hybrid Mb    (-)
5.1474d-4                           Freundlich/Langmuir Hybrid beta  (-)
```

D.20.2 VERSE Datafile.run

```
================================================================================

VERSE v7.80  by R. D. Whitley and N.-H. L. Wang, c1999 PRF
================================================================================
Input file: case20
SL644 3-column carousel, single component Cs isotherm, Criterion: lag
LAW feed: Hot Commissioning, CT: Degraded, Sensitivity: 0.8*R
```

```
Begin Run:  03:00:01 on 04-06-2004   running under Windows 95/8
Finite elements    - axial:150  particle: 1
Collocation points - axial:  4  particle: 6 => Number of eqns:  6028
Inlet species at equilib.? N   Perfusable sorbent? N   Feed profile only? N
Use Profile File? N   Generate Profile File? N
Axial dispersion correlation:   Chung & Wen (1968)
Film mass transfer correlation: Wilson & Geankoplis (1966)
Sub-Column Boundary Conditions: Axial Dispersion and CSTR
================================================================================
SYSTEM PARAMETERS (at initial conditions):

t(stop)         = 120000.00000 min          dtheta max      =      1.00000 BV
abs. tol.       =       .10000E-06          rel. tol.       =       .10000E-03
Total Length    =    403.86000 cm           D               =    121.92000 cm
Tot. Capacity   =       .00000 eq/L solid   Col. Vol.       =4714879.85299 mL
F               =  56781.20000 mL/min       Uo (linear)     =     12.79915 cm/min
R               =    153.99000 microns      L/R             =  26226.37834
Bed Void frac.  =       .38000              Pcl. Porosity   =       .66816
Spec. Area      =    120.78706 1/cm         Time/BV         =     10.51788 min
Vol CSTRs       =2214466.00000 mL

Component no.   =      1
Ke   [-]        =  .10000E+01
Eb   [cm2/min]  =  .73429E+00
Dp   [cm2/min]  =  .11209E-03
Doo  [cm2/min]  =  .33628E-03
kf   [cm/min]   =  .23919E+00
Ds   [cm2/min]  =  .00000E+00

Dimensionless Groups:
Re              =  .12116E+00
Sc(i)           =  .36765E+04
Peb(i)          =  .23465E+04
Bi(i)           =  .49181E+02
Nf(i)           =  .79968E+03
Np(i)           =  .33219E+01
Pep(i)          =  .26316E+04

Isotherm        =  Freundlich/Langmuir Hybrid
Iso. Const. 1   =  .12323E+00
Iso. Const. 2   =  .10000E+01
Iso. Const. 3   =  .10000E+01
Iso. Const. 4   =  .10000E+01
Iso. Const. 5   =  .51474E-03
Init. Conc.     =  .00000E+00
Conc. at eqb.   =  .00000E+00
Conc. units           M
================================================================================
COMMAND LIST:
  1: Step conc. of component 1 at .0000     min to .2740E-04 M
     Execute   1 times, every .0000     mins.
  2: User set viscosity to .2500E-01 poise and density to 1.213     g/cm3
  3: Carousel (conc.). Active between t = .0000     and .1000E+07 min.
     When comp.  1 reaches .3700E-07 M     at end of node 100,
     shift  50 axial elements out the feed end
  4: Monitor conc. history at stream  0.  Filename = case20.h01
     Output density adjustments:
     2.0    *default abs conc delta,       50.    *default rel conc delta,
     .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
  5: Monitor conc. history at stream  2.  Filename = case20.h02
     Output density adjustments:
     2.0    *default abs conc delta,       50.    *default rel conc delta,
     .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
  6: Monitor conc. history at stream  4.  Filename = case20.h03
     Output density adjustments:
     2.0    *default abs conc delta,       50.    *default rel conc delta,
     .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
  7: Monitor conc. history at stream  6.  Filename = case20.h04
     Output density adjustments:
     2.0    *default abs conc delta,       50.    *default rel conc delta,
     .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
================================================================================
Conc. Carousel caused bed shift at t = 9081.     min
Conc. Carousel caused bed shift at t = .1466E+05 min
```

```
Conc. Carousel caused bed shift at t = .2040E+05 min
Conc. Carousel caused bed shift at t = .2624E+05 min
Conc. Carousel caused bed shift at t = .3215E+05 min
Conc. Carousel caused bed shift at t = .3812E+05 min
Conc. Carousel caused bed shift at t = .4413E+05 min
Conc. Carousel caused bed shift at t = .5017E+05 min
Conc. Carousel caused bed shift at t = .5623E+05 min
Conc. Carousel caused bed shift at t = .6230E+05 min
Conc. Carousel caused bed shift at t = .6838E+05 min
Conc. Carousel caused bed shift at t = .7448E+05 min
Conc. Carousel caused bed shift at t = .8056E+05 min
Conc. Carousel caused bed shift at t = .8665E+05 min
Conc. Carousel caused bed shift at t = .9274E+05 min
Conc. Carousel caused bed shift at t = .9882E+05 min
Conc. Carousel caused bed shift at t = .1049E+06 min
Conc. Carousel caused bed shift at t = .1110E+06 min
Conc. Carousel caused bed shift at t = .1171E+06 min
VERSE-LC finished in 12150 steps.  Average step size 9.877     minutes
End run:  03:31:53 on 04-06-2004
Integrated Areas in History Files:
case20.h01                 3.28800
case20.h02                 .538337
case20.h03                 .519510E-03
case20.h04                 .933905E-07
```

D.21 Hot Commissioning Operations (ρ_b + 20%)

D.21.1 VERSE Datafile

```
SL644 3-column carousel, single component Cs isotherm, Criterion: lag

LAW feed: Hot Commissioning, CT: Degraded, Sensitivity: 1.2*rhob
1, 150, 4, 6                        ncomp, nelem, ncol-bed, ncol-part
FCWNA                               isotherm,axial-disp,film-coef,surf-diff,BC-col
NNNNN                               input-only,perfusable,feed-equil,datafile.yio
M                                   comp-conc units
403.86, 121.92, 56781.2, 2214466.   Length(cm),Diam(cm),Q-flow(ml/min),CSTR-vol(ml)
192.49, 0.380, 0.668159, 0.0        part-rad(um), bed-void, part-void, sorb-cap()
0.0                                 initial concentration (M)
S                                   COMMAND - conc step change
1, 0.0, 2.7400d-5, 1, 0.0           spec id, time(min), conc(M), freq, dt(min)
V                                   COMMAND - viscosity/density change
0.025001, 1.2133                    fluid viscosity(poise), density(g/cm^3)
m                                        COMMAND - subcolumns
50, 100, 0, 1, 3.70d-8, 0.0, 1.0d+6      elem-shift,elem-watch,pp-watch,c-watch,c-thresh,t-e,t-ee
h                                        COMMAND - effluent history dump
0, 2.0, 50, 4.033d-4, 0.016              unit op#, ptscale(1-4) filtering
h                                        COMMAND - effluent history dump
2, 2.0, 50, 4.033d-4, 0.016              unit op#, ptscale(1-4) filtering
h                                        COMMAND - effluent history dump
4, 2.0, 50, 4.033d-4, 0.016              unit op#, ptscale(1-4) filtering
h                                        COMMAND - effluent history dump
6, 2.0, 50, 4.033d-4, 0.016              unit op#, ptscale(1-4) filtering
-                                   end of commands
120000.0, 1.0                       end time(min), max dt in B.V.s
1.0d-7, 1.0d-4                      abs-tol, rel-tol
-                                   non-negative conc constraint
1.0                                 size exclusion factor
1.1209d-4                           part-pore diffusivities(cm^2/min)
3.3628d-4                           Brownian diffusivities(cm^2/min)
1.4788d-1                           Freundlich/Langmuir Hybrid a (moles/L B.V.)
1.0                                 Freundlich/Langmuir Hybrid b    (1/M)
1.0                                 Freundlich/Langmuir Hybrid Ma   (-)
1.0                                 Freundlich/Langmuir Hybrid Mb   (-)
5.1474d-4                           Freundlich/Langmuir Hybrid beta (-)
```

D.21.2 VERSE Datafile.run

```
================================================================================

VERSE v7.80  by R. D. Whitley and N.-H. L. Wang, c1999 PRF
================================================================================
Input file: case21
SL644 3-column carousel, single component Cs isotherm, Criterion: lag
LAW feed: Hot Commissioning, CT: Degraded, Sensitivity: 1.2*rhob
Begin Run:  03:31:54 on 04-06-2004   running under Windows 95/8
Finite elements    - axial:150  particle: 1
Collocation points - axial:  4  particle: 6 => Number of eqns:  6028
Inlet species at equilib.? N   Perfusable sorbent? N   Feed profile only? N
Use Profile File? N   Generate Profile File? N
Axial dispersion correlation:   Chung & Wen (1968)
Film mass transfer correlation: Wilson & Geankoplis (1966)
Sub-Column Boundary Conditions: Axial Dispersion and CSTR
================================================================================
SYSTEM PARAMETERS (at initial conditions):

t(stop)        = 120000.00000 min         dtheta max     =      1.00000 BV
abs. tol.      =       .10000E-06         rel. tol.      =       .10000E-03
Total Length   =    403.86000 cm          D              =    121.92000 cm
Tot. Capacity  =       .00000 eq/L solid  Col. Vol.      =4714879.85299 mL
F              =  56781.20000 mL/min      Uo (linear)    =     12.79915 cm/min
R              =    192.49000 microns     L/R            =  20980.83017
Bed Void frac. =       .38000            Pcl. Porosity  =       .66816
Spec. Area     =     96.62840 1/cm        Time/BV        =     10.51788 min
Vol CSTRs      =2214466.00000 mL

Component no.  =      1
Ke  [-]        =  .10000E+01
Eb  [cm2/min]  =  .91585E+00
Dp  [cm2/min]  =  .11209E-03
Doo [cm2/min]  =  .33628E-03
kf  [cm/min]   =  .20613E+00
Ds  [cm2/min]  =  .00000E+00

Dimensionless Groups:
Re             =  .15145E+00
Sc(i)          =  .36765E+04
Peb(i)         =  .18813E+04
Bi(i)          =  .52979E+02
Nf(i)          =  .55130E+03
Np(i)          =  .21260E+01
Pep(i)         =  .32896E+04

Isotherm       =  Freundlich/Langmuir Hybrid
Iso. Const. 1  =  .14788E+00
Iso. Const. 2  =  .10000E+01
Iso. Const. 3  =  .10000E+01
Iso. Const. 4  =  .10000E+01
Iso. Const. 5  =  .51474E-03
Init. Conc.    =  .00000E+00
Conc. at eqb.  =  .00000E+00
Conc. units       M
================================================================================
COMMAND LIST:
  1: Step conc. of component 1 at .0000     min to .2740E-04 M
     Execute   1 times, every .0000     mins.
  2: User set viscosity to .2500E-01 poise and density to 1.213     g/cm3
  3: Carousel (conc.). Active between t = .0000     and .1000E+07 min.
     When comp.  1 reaches .3700E-07 M     at end of node 100,
     shift  50 axial elements out the feed end
  4: Monitor conc. history at stream  0.  Filename = case21.h01
     Output density adjustments:
     2.0    *default abs conc delta,      50.    *default rel conc delta,
     .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
  5: Monitor conc. history at stream  2.  Filename = case21.h02
     Output density adjustments:
     2.0    *default abs conc delta,      50.    *default rel conc delta,
     .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
  6: Monitor conc. history at stream  4.  Filename = case21.h03
```

```
     Output density adjustments:
     2.0    *default abs conc delta,       50.    *default rel conc delta,
     .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
  7: Monitor conc. history at stream  6.  Filename = case21.h04
     Output density adjustments:
     2.0    *default abs conc delta,       50.    *default rel conc delta,
     .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
================================================================================
Conc. Carousel caused bed shift at t = 9855.     min
Conc. Carousel caused bed shift at t = .1624E+05 min
Conc. Carousel caused bed shift at t = .2285E+05 min
Conc. Carousel caused bed shift at t = .2963E+05 min
Conc. Carousel caused bed shift at t = .3650E+05 min
Conc. Carousel caused bed shift at t = .4345E+05 min
Conc. Carousel caused bed shift at t = .5042E+05 min
Conc. Carousel caused bed shift at t = .5740E+05 min
Conc. Carousel caused bed shift at t = .6438E+05 min
Conc. Carousel caused bed shift at t = .7136E+05 min
Conc. Carousel caused bed shift at t = .7834E+05 min
Conc. Carousel caused bed shift at t = .8532E+05 min
Conc. Carousel caused bed shift at t = .9230E+05 min
Conc. Carousel caused bed shift at t = .9929E+05 min
Conc. Carousel caused bed shift at t = .1063E+06 min
Conc. Carousel caused bed shift at t = .1132E+06 min
VERSE-LC finished in 12236 steps.  Average step size 9.807     minutes
End run:  04:06:57 on 04-06-2004
Integrated Areas in History Files:
case21.h01                 3.28800
case21.h02                 .401983
case21.h03                 .589262E-03
case21.h04                 .251797E-06
```

D.22 Hot Commissioning Operations (ρ_b – 20%)

D.22.1 VERSE Datafile

```
SL644 3-column carousel, single component Cs isotherm, Criterion: lag

LAW feed: Hot Commissioning, CT: Degraded, Sensitivity: 0.8*rhob
1, 150, 4, 6                        ncomp, nelem, ncol-bed, ncol-part
FCWNA                               isotherm,axial-disp,film-coef,surf-diff,BC-col
NNNNN                               input-only,perfusable,feed-equil,datafile.yio
M                                   comp-conc units
403.86, 121.92, 56781.2, 2214466.   Length(cm),Diam(cm),Q-flow(ml/min),CSTR-vol(ml)
192.49, 0.380, 0.668159, 0.0        part-rad(um), bed-void, part-void, sorb-cap()
0.0                                 initial concentration (M)
S                                   COMMAND - conc step change
1, 0.0, 2.7400d-5, 1, 0.0           spec id, time(min), conc(M), freq, dt(min)
V                                   COMMAND - viscosity/density change
0.025001, 1.2133                    fluid viscosity(poise), density(g/cm^3)
m                                         COMMAND - subcolumns
50, 100, 0, 1, 3.70d-8, 0.0, 1.0d+6       elem-shift,elem-watch,pp-watch,c-watch,c-thresh,t-e,t-ee
h                                         COMMAND - effluent history dump
0, 2.0, 50, 4.033d-4, 0.016               unit op#, ptscale(1-4) filtering
h                                         COMMAND - effluent history dump
2, 2.0, 50, 4.033d-4, 0.016               unit op#, ptscale(1-4) filtering
h                                         COMMAND - effluent history dump
4, 2.0, 50, 4.033d-4, 0.016               unit op#, ptscale(1-4) filtering
h                                         COMMAND - effluent history dump
6, 2.0, 50, 4.033d-4, 0.016               unit op#, ptscale(1-4) filtering
-                                   end of commands
120000.0, 1.0                       end time(min), max dt in B.V.s
1.0d-7, 1.0d-4                      abs-tol, rel-tol
-                                   non-negative conc constraint
1.0                                 size exclusion factor
1.1209d-4                           part-pore diffusivities(cm^2/min)
3.3628d-4                           Brownian diffusivities(cm^2/min)
9.8587d-2                           Freundlich/Langmuir Hybrid a (moles/L B.V.)
1.0                                 Freundlich/Langmuir Hybrid b     (1/M)
1.0                                 Freundlich/Langmuir Hybrid Ma    (-)
1.0                                 Freundlich/Langmuir Hybrid Mb    (-)
```

5.1474d-4 Freundlich/Langmuir Hybrid beta (-)

D.22.2 VERSE Datafile.run

```
================================================================================

VERSE v7.80  by R. D. Whitley and N.-H. L. Wang, c1999 PRF
================================================================================
Input file: case22
SL644 3-column carousel, single component Cs isotherm, Criterion: lag
LAW feed: Hot Commissioning, CT: Degraded, Sensitivity: 0.8*rhob
Begin Run:  04:06:57 on 04-06-2004   running under Windows 95/8
Finite elements    - axial:150  particle: 1
Collocation points - axial:  4  particle: 6 => Number of eqns:  6028
Inlet species at equilib.? N   Perfusable sorbent? N   Feed profile only? N
Use Profile File? N   Generate Profile File? N
Axial dispersion correlation:   Chung & Wen (1968)
Film mass transfer correlation: Wilson & Geankoplis (1966)
Sub-Column Boundary Conditions: Axial Dispersion and CSTR
================================================================================
SYSTEM PARAMETERS (at initial conditions):

t(stop)        = 120000.00000 min         dtheta max     =      1.00000 BV
abs. tol.      =       .10000E-06         rel. tol.      =       .10000E-03
Total Length   =    403.86000 cm          D              =    121.92000 cm
Tot. Capacity  =       .00000 eq/L solid  Col. Vol.      =4714879.85299 mL
F              =  56781.20000 mL/min      Uo (linear)    =     12.79915 cm/min
R              =    192.49000 microns     L/R            =  20980.83017
Bed Void frac. =       .38000            Pcl. Porosity  =       .66816
Spec. Area     =     96.62840 1/cm        Time/BV        =     10.51788 min
Vol CSTRs      =2214466.00000 mL

Component no.  =      1
Ke  [-]        =  .10000E+01
Eb  [cm2/min]  =  .91585E+00
Dp  [cm2/min]  =  .11209E-03
Doo [cm2/min]  =  .33628E-03
kf  [cm/min]   =  .20613E+00
Ds  [cm2/min]  =  .00000E+00

Dimensionless Groups:
Re             =  .15145E+00
Sc(i)          =  .36765E+04
Peb(i)         =  .18813E+04
Bi(i)          =  .52979E+02
Nf(i)          =  .55130E+03
Np(i)          =  .21260E+01
Pep(i)         =  .32896E+04

Isotherm       =  Freundlich/Langmuir Hybrid
Iso. Const. 1  =  .98587E-01
Iso. Const. 2  =  .10000E+01
Iso. Const. 3  =  .10000E+01
Iso. Const. 4  =  .10000E+01
Iso. Const. 5  =  .51474E-03
Init. Conc.    =  .00000E+00
Conc. at eqb.  =  .00000E+00
Conc. units          M
================================================================================
COMMAND LIST:
  1: Step conc. of component 1 at .0000     min to .2740E-04 M
     Execute   1 times, every .0000     mins.
  2: User set viscosity to .2500E-01 poise and density to 1.213     g/cm3
  3: Carousel (conc.). Active between t = .0000     and .1000E+07 min.
     When comp.  1 reaches .3700E-07 M     at end of node 100,
     shift  50 axial elements out the feed end
  4: Monitor conc. history at stream  0.  Filename = case22.h01
     Output density adjustments:
     2.0    *default abs conc delta,       50.    *default rel conc delta,
     .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
  5: Monitor conc. history at stream  2.  Filename = case22.h02
     Output density adjustments:
```

```
     2.0    *default abs conc delta,      50.    *default rel conc delta,
     .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
  6: Monitor conc. history at stream  4.  Filename = case22.h03
     Output density adjustments:
     2.0    *default abs conc delta,      50.    *default rel conc delta,
     .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
  7: Monitor conc. history at stream  6.  Filename = case22.h04
     Output density adjustments:
     2.0    *default abs conc delta,      50.    *default rel conc delta,
     .40E-03*default force w/ conc delta, .16E-01*default force w/o conc delta
================================================================================
Conc. Carousel caused bed shift at t = 6607.     min
Conc. Carousel caused bed shift at t = .1087E+05 min
Conc. Carousel caused bed shift at t = .1531E+05 min
Conc. Carousel caused bed shift at t = .1984E+05 min
Conc. Carousel caused bed shift at t = .2445E+05 min
Conc. Carousel caused bed shift at t = .2910E+05 min
Conc. Carousel caused bed shift at t = .3376E+05 min
Conc. Carousel caused bed shift at t = .3844E+05 min
Conc. Carousel caused bed shift at t = .4312E+05 min
Conc. Carousel caused bed shift at t = .4779E+05 min
Conc. Carousel caused bed shift at t = .5247E+05 min
Conc. Carousel caused bed shift at t = .5714E+05 min
Conc. Carousel caused bed shift at t = .6182E+05 min
Conc. Carousel caused bed shift at t = .6649E+05 min
Conc. Carousel caused bed shift at t = .7117E+05 min
Conc. Carousel caused bed shift at t = .7583E+05 min
Conc. Carousel caused bed shift at t = .8051E+05 min
Conc. Carousel caused bed shift at t = .8518E+05 min
Conc. Carousel caused bed shift at t = .8986E+05 min
Conc. Carousel caused bed shift at t = .9453E+05 min
Conc. Carousel caused bed shift at t = .9921E+05 min
Conc. Carousel caused bed shift at t = .1039E+06 min
Conc. Carousel caused bed shift at t = .1086E+06 min
Conc. Carousel caused bed shift at t = .1132E+06 min
Conc. Carousel caused bed shift at t = .1179E+06 min
VERSE-LC finished in 12505 steps.  Average step size 9.596     minutes
End run:  04:51:15 on 04-06-2004
Integrated Areas in History Files:
case22.h01                 3.28800
case22.h02                 .378181
case22.h03                 .616541E-03
case22.h04                 .332029E-06
```

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Appendix E (Cesium Column Inventory)

During the loading cycle, cesium is continually being adsorbed onto the SuperLig® 644 resin. At any point in time the total column inventory of cesium is made up of: absorbed cesium on the solid resin typically referred to as the cesium loading, cesium contained within the interstitial voids of the bed, and cesium contained within the pores of the resin particles. Due to the high affinity SuperLig® 644 resin has for cesium, after several column volumes of feed has past through the column, the majority of cesium column inventory will reside on the resin.

In order to compute the cumulative cesium inventories along the column, breakthrough curves at various axial locations are used. The molar balance of total cesium for a specified section of the lead column (i.e., from its inlet to a given axial location z) can be expressed as:

$$\frac{dn_{oz}}{dt} = \dot{n}_o - \dot{n}_z(t) \ . \tag{E-1}$$

Integration of Eq. (E-1) from an initial condition (i.e., assuming a fresh lead column and a fixed rate of feed input) up to some specified point in time, t, yields:

$$n_{oz}(t) = \dot{n}_o t - \int_0^t \dot{n}_z(t')dt' \ . \tag{E-2}$$

Given the definition of a breakthrough curve, Eq. (E-2) can be rearranged to:

$$n_{oz}(t) = Qc_o t - Q\int_0^t c_b(z,t')dt' \ . \tag{E-3}$$

Equation (E-3) can be further simplified by making use of the normalized time quantity expressed in terms of column volume (sometimes referred to as bed volume):

$$n_{oz}(t) \equiv n_{oz}(\tau) = c_o V_{CV} \int_0^\tau \left[1 - \frac{c_b(z,\tau')}{c_o}\right] d\tau' \ , \tag{E-4}$$

where

$$\tau = \frac{tQ}{V_{CV}} \ .$$

The integral in Eq. (E-4) represents the area above the normalized breakthrough curve up to the specified point in time.

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