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

by

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DOE Contract No. **DE-AC09-96SR18500**

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BNF-003-98-0220

Revision 0

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A, B	Binding constants for Langmuir isotherm, M^{-1} .
CV, BV	Active column (bed) volume, ml.
c_{bi}	Species i conc. in bed fluid, M.
c_{pi}	Species i conc. in pore fluid, M.
$\bar{c}_{pi}$	Species i solid surface conc., M.
$\bar{C}_T$	Total ion-exchange capacity of resin, M.
$\bar{C}_{Ti}$	Species i ion-exchange capacity of resin, M.
C_T	Total cationic strength of solution, M.
cdf(x)	Cumulative distribution function for the variable x.
D	Column diameter, cm.
D.F.	Decontamination factor.
D_{pi}	Species i pore diffusion coefficient, cm^2/min .
$\tilde{D}_{pi}$	Species i "overall" pore diffusion coefficient, cm^2/min .
$D_{\pm}^{\infty}$	Binary diffusion coefficient at infinite dilution, cm^2/s .
D_{AB}	Binary diffusion coefficient for A diffusing through solvent B, cm^2/s .
$D_{\infty i}$	Species i diffusion coefficient, cm^2/min .
E_{bi}	Species i axial dispersivity, cm^2/min .
F	Ratio of dry-to-"as received" resin mass
F	Faraday constant, 96,500 C/g-equiv.
J	"J factor" analogy dimensionless number.
k_f	Liquid film mass transfer coefficient, cm/min .
K_{di}	Species i distribution coefficient, M^{-1} or ml/g .
K_{ji}	Equilibrium constant between species j and i.
$\tilde{K}_{ji}$	Selectivity coefficient between species j and i.
L	Axial length of active bed of column, cm.
m_i	Mass of species i, g.
m_{resin}	Mass of resin, g.
M_i	Species i molecular weight, g/gmole.
M_{ai}, M_{bi}	Freundlich/Langmuir Hybrid model exponents for species i.
N_s	Total number of cations of interest.

N_c	Total number of chemical reactions.
$\text{pdf}(x)$	Probability distribution function for the variable x .
Q	Column volumetric flow rate, ml/min.
q_i	Species i fractional surface site loading.
r	Radial coordinate within avg. size particle, cm.
R	Ideal gas constant, 8.314 J/gmole-K.
R_i	Isotherm model residual for i^{th} data point.
R_A	Radius of diffusing particle, cm.
Re	Reynolds Number.
$\langle R_p \rangle$	Average particle radius, μm .
Sc_i	Species i Schmidt Number.
t	Time.
T	Absolute temperature, K.
u	Linear interstitial velocity, cm/min.
u'	Retarded linear interstitial velocity, cm/min.
u_{peak}	Peak radial velocity, cm/min.
u_{CL}	Column centerline velocity, cm/min.
U	Superficial (Darcy) velocity, cm/min.
V_{bed}	Total volume of active 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.
V_{CSTR}	Volume of inlet/outlet headspaces, ml.
z	Axial coordinate, cm.
z_+, z_-	valences of cation and anion, respectively.

Greek

β	Isotherm parameter constant.
$\hat{\beta}_i$	Langmuir "effective" single isotherm model constant.
β_i, a_i, b_i	Freundlich/Langmuir Hybrid model coefficients for species i .
κ	Boltzmann's constant.
τ_p	Particle tortuosity.

λ	Lambda value ($\equiv K_d \rho_b$), ml _{resin} /ml _{BV} .
v_j	Species j stoichiometric coefficient.
ϵ_b	Bed porosity.
ϵ_p	Particle porosity.
ϵ_T	Total porosity within column bed.
σ_q	Isotherm model standard deviation.
$\sigma_{K_{ji}}$	Selectivity coefficient standard deviation.
μ_B	Dynamic viscosity of solvent mixture.
μ_w	Dynamic viscosity of feed solution, centi-poise.
ρ_w	Density of feed solution, g/ml.
ρ_b	Bed density of active column, g/ml.
ρ_s	Solid (particle) density of resin, g/ml.
λ_+^o, λ_-^o	Limiting ionic conductance for cation and anion, mhos/equiv.

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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 status report on our current 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. Existing bench-scale column tests (eleven in total) and batch equilibrium experiments (~133 data points) are addressed. The methodology employed and sensitivity analyses are also included. Ongoing bench-scale testing and future pilot-scale testing will be assessed in a future report. Future analysis efforts will also address the elution phase of the process cycle. The sensitivity analyses provide guidance on what experimental areas of support will potentially have the biggest impact on column performance and design predictions. The sensitivity analyses also help to identify key parameters that aid in resin procurement acceptance criteria.

The major accomplishments and conclusions are:

- An approach to correlating the batch equilibrium data has been devised based on a simple algebraic isotherm model derived assuming average values for the various selectivity coefficients. Ternary (i.e., cesium, potassium, and sodium) and 4-component (i.e., ternary plus hydrogen) cation exchange isotherm models were created. The adequacy of this approach is tested by comparison to the available database and through their use in column simulations.
- Significant variability exists between the various series of batch equilibrium " K_d " test data considered. A variety of isotherm models and statistical techniques were attempted, all of which demonstrated essentially the same response of significant variability. Resin batch differences (perhaps resulting in variable total ionic exchange capacity) may be the dominant factor. However, insufficient experimental data addressing the ion-exchange mechanisms at the active resin sites are available to directly pin down the true reasons.
- Both multi-component and "effective" single-component column transport simulations were performed. For the cesium loading-phase only, justification is made that the simpler "effective" single-component column model is adequate for design purposes. Most likely, for future elution-phase modeling, the multi-component column transport model will be necessary along with the 4-component cation exchange isotherm model.
- The use of the Lambda value for estimating 50% cesium breakthrough for the Cesium-SuperLig[®] 644 system is questionable. Measured Lambda values based on available column tests ranged from 14% to 37% of their computed values. These discrepancies can be explained due to the occurrence of various mass transfer limitations, as well as, the non-linear aspect of the adsorption isotherm.
- For the majority of modeling parameters required to perform an ion-exchange transport simulation, a methodology was developed that can be reused/updated as future test data

become available. With few alterations this methodology can also be applied to the other ion-resin systems of interest (e.g., the Pertechmetate-SuperLig[®] 639 system).

- In the order of estimated affinity, the four cations competing for surface sites on SuperLig[®] 644 resin considered are: hydronium, cesium, potassium, and sodium. Based on limited analytical analysis of column eluate constituents, other cations are probably competing at levels of affinity equal to or greater than some of the above cations (e.g., uranyl appears to have a high affinity for this resin). For the above cations SuperLig[®] 644 resin is most selective for H^+ , then Cs^+ , followed by K^+ , and then Na^+ , with UO_2^{+2} somewhat less than H^+ . Chromium has also been observed in the eluate, and further testing to check for the possibility of precipitation versus ion-exchange is needed.
- A total cesium ion-exchange capacity of 0.3333 mmole/g was assumed based on vendor input. By assuming that each adsorption site is independent from its neighbors, the ion-exchange capacities for K^+ and Na^+ were set equal to the above Cs^+ value. A high level of sensitivity exists (similar to the sensitivity associated with a bed density variation) between breakthrough curve prediction and variation in ion-exchange capacities.
- 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.
- Based on this methodology full-scale facility "best estimate" simulations were run for two different lag (guard) column exit cesium concentration criteria. For a lag column exit cesium concentration of $<1 \mu Ci/ml$, ~305 column volumes per cycle can be processed where the lead column loads to ~97% or greater for each cycle and a cycle average decontamination factor $>1,700$ is achieved. For a lag column exit cesium concentration of $<0.0874 \mu Ci/ml$, ~287 column volumes per cycle can be processed where the lead column loads to ~91% or greater for each cycle and a cycle average decontamination factor $>21,000$ is achieved. A 100% loading refers to the maximum cesium loading achievable by the resin for the specified feed conditions.
- The number of column volumes required to reach 50% breakthrough in the lead column is somewhat insensitive to flow rate. On the other hand, the slower the flow rate the sharper the concentration profile remains leading to progressively higher cesium loadings on the lead column prior to reaching a fixed exit criterion for the lag column. For example, the number of column volumes required to reach a lag column exit cesium concentration of $<1 \mu Ci/ml$ were estimated to be 334, 423, and 493 for volumetric flow rates of 6.0, 3.0, and 1.5 CV/hr, respectively.
- Quantified uncertainties resulting in operational margins have not yet been computed; however, full-scale facility model sensitivities were computed. Uncertainties in the adsorption isotherms and the total amount of resin by mass contained within the columns (due to resin swelling) have the dominant impact on column performance. A prioritization of model parameters is provided and discussed. Future experimental efforts should focus on the high impact parameter needs.

- Based on sensitivity simulations we see that liquid film resistance is having a negligible impact on the cesium breakthrough curves, while mass transfer resistance due to pore diffusion has a significant impact on the shape of the breakthrough curve. However, the number of column volumes required to reach the 50% cesium breakthrough point is predominately set by the adsorption isotherm (~314 column volumes).
- Since the adsorption isotherm model for cesium is nonlinear, the performance on the ion-exchange columns is dependent upon the cesium inlet feed concentration. Sensitivity results indicate that this dependence can be significant over the expected operating range of inlet feed conditions.
- Since potassium competes with cesium (with a lesser selectivity) for available adsorption sites, the performance on the ion-exchange columns is dependent upon the potassium inlet feed concentration. Sensitivity results indicate that this dependence can be significant over the expected operating range of inlet feed conditions.

The current design and operational strategy appear sufficient to achieve the desired decontamination factors. However, significant uncertainty exists in understanding the causes of column performance variability. The numerical model presented in this report can be used to gain insight into these uncertainties and optimize system performance, while pilot-scale testing is needed to confirm these predictions. The current model appears to be adequate for predicting column behavior for Envelope A waste, but further work with respect to competitors is necessary for Envelope B and C wastes.

For preliminary design needs, computed "best estimate" decontamination factors (D.F.) on a cumulative basis are provided in Figure 1-1 for the Cesium-SuperLig[®] 644 system and in Figure 1-2 on a per cycle basis. These data are best applied to Envelope A, which the model predicts with the highest level of confidence, assuming similar levels of cesium, potassium, and sodium feed concentrations. Results for two different lag-column exit criteria are shown, where the exit cesium concentration is expressed in activity levels of ¹³⁷Cs (assuming on a mole basis 25% ¹³⁷Cs and the remainder ¹³³Cs). These results apply to a characteristic inlet feed consistent with an Envelope A waste. Each curve identifies (with symbols) where a cycle ends and a new one begins. At the end of a cycle, the lead-column is eluted and the lead-lag positions are reversed. Because some cesium passes the lead-column and loads onto the lag-column, the level of cesium loading on the lag-column initially varies at the start of cycle, until a pseudo-equilibrium is reached after several cycles. The columns with the lower exit criteria process a lower volume of decontaminated product, but the impact on throughput is partially offset because less cesium passes from the lead to the lag in each cycle. Experiments with full-length pilot-scale columns are planned which will confirm the results from these simulations.

The D.F.s presented in Figure 1-1 represent D.F. values on a cumulative basis computed from initial operation up to the end of each cycle shown. For example, D.F. values for operating three cycles represents the cumulative D.F. value obtained by integration over the entire time period (i.e., includes cycles 1, 2, and 3). D.F. values for individual cycles (such as, operation during cycle 3 alone) are presented in Figure 1-2.

Figure 1-1. Computed “best estimate” decontamination factors on a cumulative basis for the Cesium-SuperLig® 644 system ion exchange column for two different lag column exit criteria (under feed conditions of $[Cs^+]_o = 6.089 \times 10^{-5} \text{ M}$, $[K^+]_o = 0.090 \text{ M}$, $[Na^+]_o = 5.001 \text{ M}$).

Figure 1-2. Computed “best estimate” decontamination factors on a per cycle basis for the Cesium-SuperLig® 644 system ion exchange column for two different lag column exit criteria (under feed conditions of $[Cs^+]_o = 6.089 \times 10^{-5} \text{ M}$, $[K^+]_o = 0.090 \text{ M}$, $[Na^+]_o = 5.001 \text{ M}$).

2.0 Introduction and Background

A proposed facility is being designed for the immobilization of Hanford 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 two sets of two packed columns placed in series (i.e., a lead column followed by a lag (guard) column configuration). During operation, upon reaching a specified cesium concentration criterion at the exit of the lag column, operation is switched to the second set of lead and lag columns. The cesium-loaded lead column is processed (i.e., washed and eluted) and switched to the lag position. The previous lag column is then placed in the lead position (without eluting) 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.

[Note: Subsequent to preparation of this model, the BNFL Inc. design for the cesium ion exchange system was revised to include a single third column located after the two sets of lead and lag columns. The third column provides additional assurance that the target cesium concentration in the treated waste solution. For future updates, this model will be revised to reflect the current BNFL Inc. design for separating cesium.]

2.1 Ion Exchange Modeling

This ion-exchange system is one of many unit operations within a larger process flowsheet. Experimental efforts are currently underway 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. The decontamination factors presented in this report represent cumulative averages over the specified time interval of interest.

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 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 with "mean" particle (i.e., diameter) sizes measured through 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 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 the current SuperLig[®] 644 resin to be approximately 0.3333 mmole_{Cs}/g (on a dried resin basis). However, based on available batch distribution studies cesium capacity may have been as high as ~1 mmole_{Cs}/g in earlier batches (i.e., as shown in Figure A-1 several measured cesium loadings exceeded 0.3333 mmole_{Cs}/g).

Based on limited analytical data of the eluate retrieved from elution cycles during various column tests, the following five cations appear to be species competing for active surface sites: Cesium [Cs⁺], Potassium [K⁺], Sodium [Na⁺], Hydronium [H₃O⁺, sometimes referred to as H⁺], Uranyl [UO₂⁺²]. The above list is not comprehensive and further studies to determine all significant cations should be considered. Our current estimate for the relative affinities of SuperLig[®] 644 resin for ion-exchange are H⁺ >> Cs⁺ >> K⁺ > Na⁺, while the relative affinity for UO₂⁺² has not yet been determined. 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. An analysis methodology is developed where as much of the available and pertinent data on the Cesium-SuperLig[®] 644 system is incorporated. Many of the model parameters are not currently defined by direct experimentation. Therefore, these parameters have been estimated through indirect assessments (e.g., column test exit breakthrough curves). The methodology can easily be updated as new information becomes available (e.g., measured bed and particle porosities).

This document represents a status report on our current knowledge and capability to model the ion-exchange process for the Cesium-SuperLig[®] 644 system under Hanford feed conditions. The methodology, its justification, assessment, and application to the proposed facility is 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 is 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. 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. Potential future improvements to this isotherm model (e.g., to handle the elution phase of the complete cycle) are mentioned in Appendix A. The basis behind the use of a Lambda value for estimating column performance is discussed in Appendix B where it is shown that for the Cesium-SuperLig[®] 644 system its use should be limited. 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 feed conditions is 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 (11 in total). One set of column tests were used in initial parameter setup, while the remaining column tests were purely predicted cases. 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 two exit cesium concentration criteria, 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 E.

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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.

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 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

$$\underbrace{\epsilon_b \frac{\partial c_{bi}}{\partial t}}_{\text{storage}} + \underbrace{\epsilon_b u \frac{\partial c_{bi}}{\partial z}}_{\text{advection}} = \underbrace{\epsilon_b E_{bi} \frac{\partial^2 c_{bi}}{\partial z^2}}_{\text{axial dispersion}} - \underbrace{\left(\frac{3}{\langle R_p \rangle} \right) (1 - \epsilon_b) k_f \left(c_{bi} - c_{pi} \right) \Big|_{r=R_p}}_{\text{liquid film diffusion (mass transfer)}}, \quad (3-1a)$$

with boundary and initial conditions

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

$$z = 1, \quad \epsilon_b E_{bi} \frac{\partial c_{bi}}{\partial z} = 0, \quad (3-1c)$$

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

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

$$\underbrace{\epsilon_p \frac{\partial c_{pi}}{\partial t}}_{\text{storage}} + \underbrace{(1 - \epsilon_p) \bar{C}_T \sum_{j=1}^{N_s} \left[\left(\frac{\partial q_i}{\partial c_{pj}} \right) \frac{\partial c_{pj}}{\partial t} \right]}_{\text{surface adsorption}} = \underbrace{\epsilon_p D_{pi} \frac{1}{r^2} \frac{\partial}{\partial r} \left[r^2 \frac{\partial c_{pi}}{\partial r} \right]}_{\text{Fickian pore diffusion}}, \quad (3-2a)$$

with boundary and initial conditions

$$r = 0, \quad \epsilon_p D_{pi} \frac{\partial c_{pi}}{\partial r} = 0, \quad (3-2b)$$

$$r = \langle R_p \rangle, \quad \epsilon_p D_p \frac{\partial c_{bi}}{\partial r} = k_f (c_{bi} - c_{pi}), \quad (3-2c)$$

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

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:

$$q_i = F_i(\bar{C}_T, c_{p1}, c_{p2}, \dots, c_{pN_s}), \quad i = 1, N_s, \quad (3-3)$$

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. (1999). 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.).

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

$$\underbrace{\epsilon_b \frac{\partial c_b}{\partial t}}_{\text{storage}} + \underbrace{\epsilon_b u \frac{\partial c_b}{\partial z}}_{\text{advection}} = \underbrace{\epsilon_b E_b \frac{\partial^2 c_b}{\partial z^2}}_{\text{axial dispersion}} - \underbrace{\left(\frac{3}{\langle R_p \rangle} \right) (1 - \epsilon_b) k_f \left(c_b - c_p \Big|_{r=R_p} \right)}_{\text{liquid film diffusion (mass transfer)}}, \quad (3-4)$$

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

$$\underbrace{\epsilon_p \frac{\partial c_p}{\partial t}}_{\text{storage}} + \underbrace{(1 - \epsilon_p) \bar{C}_T \left(\frac{\partial q}{\partial c_p} \right) \frac{\partial c_p}{\partial t}}_{\text{surface adsorption}} = \underbrace{\epsilon_p D_p \frac{1}{r^2} \frac{\partial}{\partial r} \left[r^2 \frac{\partial c_p}{\partial r} \right]}_{\text{Fickian pore diffusion}}, \quad (3-5)$$

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 and solid phases becomes:

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

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 $\text{Cs}^+ \gg \text{K}^+ > \text{Na}^+$).

Given the above information, early column performance (say the first 5 to 10 column volumes or so) probably will require 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 (e.g., compare the cesium breakthrough curve in Figure 3-3 to the single-component result provided in Figure 9-4), the cesium breakthrough curve is only slightly altered. For example, 50% cesium breakthrough is estimated to be ~142 column volumes based on the multi-component simulation, while the estimate is ~135 column volumes for the single-component simulation (i.e., a 5% difference and well within overall uncertainties).

Since significant CPU savings are achieved when the single-component model is used and the differences are well within our current predictive capabilities, the majority of 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 the WK2 column experiment based on the porous particle multi-component ion exchange column model (data from King et al., 2000).

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4.0 Equilibrium Adsorption Isotherm

In our column modeling efforts 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 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 concentrations between the pore fluid and the solid 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 resin contains homogeneous adsorption sites whose concentration (sites per gram of resin) is independent of total ionic strength or solution composition. For varying material batches this assumption is suspect; however, currently only one ion-exchange capacity number has been provided.

In deriving an appropriate isotherm model the following items were considered:

- To keep reasonable runtimes an algebraic form of an isotherm model was desired that would be compatible/consistent with standard column models;
- The form of the isotherm model was to be thermodynamically consistent with the local mass-action equations;
- The effects of competing cations within possible feed solutions needed to be easily addressed (i.e., able to handle the expected range of Hanford waste feeds without major alterations required); and
- A large amount of the available batch equilibrium " K_d " data needed to be considered to statistically reduce any unwanted biases that may be present.

Based on these considerations a ternary homovalent isotherm model was developed and is presented below. Overall the model meets all of the above items; however, the confidence intervals for the model are higher than originally expected. In Appendix C further discussion of the isotherm model is given, where additional K_d data and the effect of pH on cesium loading are investigated. Also in Appendix C, preliminary attempts to create a 4-component (Cs^+ , K^+ , Na^+ and H^+) isotherm model are presented. In order to adequately model the elution cycle the impact of hydrogen ion H^+ (or hydronium ion H_3O^+) on cesium loadings is required. No attempt to incorporate the variation of liquid-phase activity coefficients or the uranyl cation is made in this report. Future updates to this model will address these issues.

4.1 The Isotherm Model

The total concentration of pore fluid cations is defined as

$$C_T = \sum_{i=1}^{N_c} c_{pi} , \quad (4-1)$$

while the total cation-exchange capacity of the resin is defined as

$$\bar{C}_T = \sum_{i=1}^{N_c} \bar{c}_{pi} \quad (4-2)$$

The fraction of surface sites occupied by the i^{th} cation is defined as

$$q_i \equiv \frac{\bar{c}_{pi}}{\bar{C}_T} = \frac{\bar{c}_{pi}}{\bar{C}_{Ti}} \quad (4-3)$$

where it is assumed that each ionic species exchange capacity is equivalent to the total exchange capacity.

As mentioned above we are making the important assumption of local chemical equilibrium. Hence, among the N_c exchanging ions in the system, there are N_c-1 independent equilibrium mass-action expressions of the form

$$\tilde{K}_{ji} \equiv \frac{1}{\tilde{K}_{ij}} = \left(\frac{q_j}{c_{pj}} \right)^{v_i} \left(\frac{c_{pi}}{q_i} \right)^{v_j} \quad \text{and} \quad \tilde{K}_{ii} \equiv 1, \quad (4-4)$$

where v_j is the stoichiometric coefficient for species j and $\tilde{K}_{ji}$ is the ion selectivity coefficient between species j and i . Equations (4-4) correspond to the stoichiometric ion-exchange for phase equilibrium:

where K_{ji} is the equilibrium constant. Even though the equilibrium constant is a true constant for a given temperature, the selectivity coefficients are compositionally dependent since non-unity activity coefficients will exist. This variation can be addressed in a thermodynamically consistent manner using the approach presented by Polzer et al. (1992). An application of this technique is presented in Zheng et al. (1995) for cesium ion exchange using crystalline silicotitanates (CSTs). However, in the development that follows average values for the selectivity coefficients are assumed. If accuracy requires it, in future work this functional dependence will be addressed. Also, reaction Eq. (4-5) implicitly assumes that a single surface site represents an ionic exchange unit. For some exchange systems multiple surface sites constitute an ionic exchange unit (Zheng et al., 1995) which can have profound effects on certain ionic species.

As originally demonstrated in the classical work by Rubin and James (1973) and later by Valocchi et al. (1981), if we consider only monovalent or divalent cations, the N_c chemical equations (i.e., Eqs. (4-2, 3, and 4)) can be combined to yield the explicit multi-component exchange isotherms:

$$q_i \equiv \frac{\bar{c}_{pi}}{\bar{C}_T} = \bar{C}_T \cdot F_i(c_{p1}, c_{p2}, \dots, c_{pN_c}, \tilde{K}_{ji}) \quad \text{for } i = 1, 2, \dots, N_c. \quad (4-6)$$

Making use of the above equations, the two adsorption isotherms for a binary homovalent exchange process (i.e., $N_c = 2$, $v_1 = v_2 = 1$) can be expressed in the form:

$$q_i = \frac{\tilde{K}_{il}c_{pi}}{c_{p1} + \tilde{K}_{2l}c_{p2}} \quad \text{for } i = 1, 2. \quad (4-7)$$

where use is made of the identities given by Eq. (4-4). In the case where the feed solution has the same total normality as the native solution (i.e., $C_T = \text{constant}$), Eq. (4-7) reduces from the binary exchange problem to the well-known single-species adsorption isotherm that has been studied extensively in the literature. Thereby, the multi-component ionic transport problem also reduces down to uncoupled single-component transport problems for each species as discussed in Section 3. Under the limitation of constant total normality, Eq. (4-7) takes the familiar form known as the Langmuir isotherm:

$$q_i = \frac{\tilde{K}_{12}c_{p1}}{1 + \left[\frac{(\tilde{K}_{21} - 1)}{C_T} \right] c_{p1}} \Rightarrow \frac{Ac_{p1}}{1 + Bc_{p1}}. \quad (4-8)$$

where the "binding constants" A and B are usually derived from adsorption data.

Following the same approach as for the binary case, the three adsorption isotherms for a ternary homovalent exchange process (i.e., $N_c = 3$, $v_1 = v_2 = v_3 = 1$) can be expressed as:

$$q_i \equiv \frac{\bar{c}_{pi}}{\bar{C}_T} = \frac{\tilde{K}_{il}c_{pi}}{c_{p1} + \tilde{K}_{2l}c_{p2} + \tilde{K}_{3l}c_{p3}} \quad \text{for } i = 1, 2, 3. \quad (4-9)$$

Equations (4-9) represent our chosen adsorption isotherm model that contains three physically based parameters that must be determined based on available adsorption data. Furthermore, only data for one species on the solid surface is required. For larger numbers of competing cations (>3) in a homovalent exchange process additional terms are added to the denominator of Eq. (4-9). The isotherm derivations for heterovalent exchange processes become increasingly more complicated beyond two species.

A distribution coefficient (i.e., a "chord" of the isotherm) for each species can be expressed as

$$K_{di} \equiv \frac{q_i}{c_{pi}} = \frac{\tilde{K}_{il}}{c_{p1} + \tilde{K}_{2l}c_{p2} + \tilde{K}_{3l}c_{p3}} \quad \text{for } i = 1, 2, 3. \quad (4-10)$$

The distribution coefficient (typically referred to as a " K_d " value) generally varies with composition where for favorable isotherms its value diminishes with increasing concentrations. The K_d value represents the chord (not the tangential) slope of the isotherm as illustrated in Figure B-1 of Appendix B. Under favorable isotherm conditions concentration profiles down a column tend to approach an asymptote resulting from the balancing of axial dispersion versus the self-sharpening tendency of the non-linear (convex) isotherm. Given the fixed and finite number

of available adsorption sites the isotherms of interest have the typical favorable (e.g., Langmuir like) shape. Generally, for very low fluid concentrations the isotherms are reasonably linear with approximate constant K_d values.

4.2 The Cesium-SuperLig[®] 644 System

For the expected pretreated waste feeds to the SuperLig[®] 644 ion exchange columns, the following three competing cations must be considered:

Cs^+	(0 to 3.5×10^{-3} M)	(component 1)
K^+	(0.024 to 1.0 M)	(component 2)
Na^+	(3.57 to 5.71 M)	(component 3)

Note that the presence of uranium in the column feed introduces an additional competing cation. However, it is assumed that all uranium present is taken out of the feed during a pretreatment phase. For Envelope C equilibrium contact test and column data shown herein, uranium was present as evident from the analytical results performed on the eluate. Also monovalent metal cations are generally too weak as proton donors to display significant acidic properties in water (Peters et al., 1997), and so very little effect on local pH variations within the particle pores is expected. Chromium is evident in some eluate samples, but its effect on performance cannot yet be quantified and has been ignored for this analysis.

Also during pretreatment sodium concentrations are adjusted to ~5 M, and the feed cesium and potassium levels are affected. The range of concentrations provided above corresponds to the range of available batch contact tests performed to measure point "effective" K_d values. As shown in Figure B-1 of Appendix B these "effective" K_d values correspond to chords along the non-linear isotherm.

The use of a Lambda value for estimating the number of column volumes required to reach 50% exit breakthrough has been a poor estimator for the Cesium-SuperLig[®] 644 system. A detailed discussion of what a Lambda value represents for these types of systems (i.e., favorable isotherms) is provided in Appendix B. Measured Lambda values (i.e., 50% breakthrough values) based on the available column tests range from 14% to 37% of their computed values as listed in Table B-1 of Appendix B. Care should be taken in its general use for the Cesium-SuperLig[®] 644 system, since several of the underlying assumptions made in deriving a Lambda value become invalid.

For the cations cesium, potassium, and sodium competing for surface sites during the loading phase of a cycle, the following mass-action expressions apply based on Eq. (4-5):

where the bars imply the solid surface phase and the three selectivity coefficients are related through

$$K_{13} = K_{12}K_{23}. \quad (4-12)$$

For the above ternary homovalent system the three isotherms (expressed by Eq. (4-9) become:

$$q_{\text{Cs}^+} = \frac{c_{\text{pCs}^+}}{c_{\text{pCs}^+} + \tilde{K}_{21}c_{\text{pK}^+} + \tilde{K}_{31}c_{\text{pNa}^+}}. \quad (4-13a)$$

$$q_{\text{K}^+} = \frac{\tilde{K}_{21}c_{\text{pK}^+}}{c_{\text{pCs}^+} + \tilde{K}_{21}c_{\text{pK}^+} + \tilde{K}_{31}c_{\text{pNa}^+}}. \quad (4-13b)$$

$$q_{\text{Na}^+} = \frac{\tilde{K}_{31}c_{\text{pNa}^+}}{c_{\text{pCs}^+} + \tilde{K}_{21}c_{\text{pK}^+} + \tilde{K}_{31}c_{\text{pNa}^+}}. \quad (4-13c)$$

Equations (4-13) have only two unique parameters (i.e., avg. selectivity coefficients) that must be obtained through a fitting procedure. Note that measured surface concentrations for only one of the species are required. The third parameter is the total cation exchange capacity of the resin that is required to convert from surface concentrations into fractional loadings. With these three parameters, ion adsorption for all three cations can be calculated.

The vendor (IBC Advanced Technologies) provided a total cesium exchange capacity of 0.3 mmole_{Cs}/g_{resin} for “as received” resin. For both batches measured (i.e., 644BZ and 981020MB48-563), F factors defined as the ratio of dry-to-“as received” mass of resin were 0.900 and 0.904, respectively (see, Hassan et al., 1999a). For both the adsorption isotherm development and then column assessments, the total exchange capacity of SuperLig[®] 644 was assumed to be a constant and on a “dry mass of resin basis” it was set to 0.3333 mmole/g_{resin}. We further assume that the ionic exchange capacities for cesium, potassium, and sodium are equivalent and are the same as the above stated value for the total exchange capacity. The impact associated with the assumptions made with regard to ionic exchange capacities are discussed in Section 10 where sensitivity studies are presented. An impact resulting in a variation in total ionic exchange capacity is similar to an impact resulting from a variation in bed density.

As discussed in Appendix A, when all available batch distribution data are considered, for certain batches a total cesium exchange capacity as high as ~1 mmole_{Cs}/g_{resin} appears more consistent. Brown et al. (1995b) using simulated neutralized current acid waste, NCAW (Envelope B with 5 M Na⁺ and 5.0x10⁻⁴ M Cs⁺), nearly completely loaded their column to 0.2 mmole_{Cs}/gram_{resin} (dry weight basis). For increasing cesium feed concentrations (i.e., decreasing Na/Cs ratio) the cesium loading on a column will rise ultimately approaching its total ionic exchange capacity. Brown et al. (1995b, page 5.2) also indicated that the total exchange capacity of their resin was

~3 mmole/g (no basis for this value was provided). However, their resin represented earlier batches of SuperLig[®] 644 whose bed density was estimated to be ~0.22 g/ml. Given the observed physical appearance and adsorption characteristics for differing batches of resin, the total cation exchange capacities probably does vary. However, since no conclusive information on the variations are available, the stated value of 0.3333 mmole/g for current batches is used for the analyses presented in this report.

Equilibrium contact test data from all available data sources for the Cesium-SuperLig[®] 644 system of interest was gathered. Table 4-1 defines the nomenclature used to reference the data and their sources. Table 4-2 provides a brief overview of the various data sources and their unique features. As indicated in Table 4-2:

- several batches of SuperLig[®] 644 resin were tested;
- both actual "hot" waste tank samples and "cold" simulated waste was considered;
- all three waste envelopes (A, B, and C) were tested;
- a modest range of solutions with varying K^+ and Na^+ concentration were tested; and
- cesium loadings as high as 61% of the assumed maximum value were achieved.

The database (i.e., 59 data points) considered for developing the ternary homovalent isotherm model is listed in Table 4-3. The measured total cesium loadings as a function of liquid-phase cesium concentration are plotted in Figure 4-1. The dashed lines represent the IBC data source while the solid lines represent the remaining data sources. Loadings as high as ~60% of the capacity value were measured. Liquid-phase cesium concentration varied over six orders of magnitude. Measured "effective" K_d values for the same database are plotted in Figures 4-2 and 4-3 versus liquid-phase cesium concentration and Cs^+ -to- ($K^+ + Na^+$) ratio, respectively. The majority of K_d value measurements assumed an adequate approach to equilibrium had occurred within 24 hours. Batch kinetics timing is discussed with respect to pore diffusion in Section 7.

As illustrated in Figures (4-1, 2, and 3), the systematic differences observed between data sets (e.g., IBC, PNNL, and SRTC) can not be explained due to variations in potassium and sodium concentration levels alone. The variations observed perhaps also result from batch variability and other competing cations such as the hydronium ion (H_3O^+) or uranyl ion (UO_2^{+2}). Uncertainties associated with the stated (in some cases assumed) waste sample concentrations for all competing cations probably greatly exceed the errors in experimental techniques and analytical measurements.

4.3 Isotherm Parameter Estimations

To establish the adsorption isotherms for the three (assumed) dominant cations, two independent selectivity coefficients must be determined based on the equilibrium contact test data. Based on the functional form chosen these two parameters can be obtained from equilibrium contact tests where only one of the cations solid-phase concentration is known. For the Cesium-SuperLig[®] 644 system the isotherm model to be considered takes the form

$$q_{Cs^+} = \frac{c_{pCs^+}}{c_{pCs^+} + \tilde{K}_{21}c_{pK^+} + \tilde{K}_{31}c_{pNa^+}}. \quad (4-14)$$

A non-linear regression analysis based on the maximum likelihood principle (see Anderson et al., 1978) was performed on Eq. (4-14) along with the Cs loading database provided in Table 4-2. Due to the broad range of cesium concentrations contained within the database several weighting schemes were tried. The criterion for parameter estimation is the minimization of the sum of squares of the residuals. The cost function being minimized is

$$\Phi(\tilde{K}_{21}, \tilde{K}_{31}) = \sum_{i=1}^{57} (R_i)^2, \quad (4-15)$$

where the various weighted residual functions considered were

$$R_i = q_{Cs^+}^{exp} - q_{Cs^+}^{mod}, \quad (4-16a)$$

$$R_i = \frac{1}{q_{Cs^+}^{exp}} - \frac{1}{q_{Cs^+}^{mod}}, \quad (4-16b)$$

$$R_i = \ln(q_{Cs^+}^{exp}) - \ln(q_{Cs^+}^{mod}). \quad (4-16c)$$

Equation (4-16a) results in uniform weighting among all of the measured data points. For the very large domain in cesium concentration too much weighting resulted for the higher cesium loading data. Using reciprocal weighting based on Eq. (4-16b), too much weighting was given to the low cesium loading data. The logarithmic weighting given by Eq. (4-16c) gave superior results when compared to results from Eq. (4-16a) or (4-16b). Application of the maximum likelihood algorithm (using logarithmic weighting) resulted in the estimated values for the two selectivity coefficients tabulated in Table 4-4. The other selectivity coefficients listed are computed based on the reciprocity identities given by Eq. (4-4). The upper/lower confidence levels and relative errors for the fitted selectivity coefficients are also provided in Table 4-4.

4.4 Assessment of Ternary Homovalent Isotherm Model

In Table 4-4 the best estimate values for the selectivity coefficients are listed along with additional information on the confidence levels of the fitting algorithm. The fitting results for these selectivity coefficients ("binding" constants) tabulated in Table 4-4 suggest the selectivity order to be $Cs^+ \gg K^+ > Na^+$; that is, the SuperLig[®] 644 resin is most selective for Cs^+ , followed by K^+ , and then Na^+ . Even at their lower and upper confidence levels, the order of selectivity remains the same. An appreciable amount of uncertainty exists for these selectivity coefficients as indicated by their % relative errors of 29.9% for Cs^+ -to- K^+ and 17.5% for Cs^+ -to- Na^+ .

A direct comparison of predicted versus measured total cesium loadings on SuperLig[®] 644 resin is shown in Figure 4-4. These are fractional loadings on the active sites whose values range from zero to one. Due to the extremely small values of fractional loadings the comparison is made on

a log-log plot. The location of a perfect match is represented by the 45° line provided in Figure 4-4. A slight trend to the residuals can be seen where the model tends to under-predict the data for low loadings and to over-predict the data at high loadings. This observed trend is probably a result of assuming compositionally independent selectivity coefficients. If the ionic activity coefficients for the cations (e.g., using Bromley's model in Bromley [1973]) were introduced into the model these systematic trends should be greatly reduced. A solution thermodynamic model is needed to better predict the adsorption by incorporating the aqueous-phase ionic activity coefficients and resin-ion bond energies.

Test data taken from several ion exchange column studies are assessed in a later section. To assess the adequacy of the above general isotherm model when used for specific column studies, a comparison is made between the general isotherm model and the appropriate Cs^+ loading equilibrium contact test data. For six of the column tests considered, Table 4-5 compares the best estimate values from the isotherm model to Cs^+ loading data. For each of the columns, inlet K^+ and Na^+ ionic concentrations were fixed at the molarities listed in Table 4-5. The best estimate results tabulated in Table 4-5 are shown as solid lines for comparison in Figures 4-5 through 4-11. In Figures 4-5 through 4-11 the upper and lower 95% confidence levels are shown as dashed and dot-dashed lines, respectively. These are confidence levels in the correlation fit and not in the data points. Also shown in Figures 4-5 through 4-11, are the ranges of inlet Cs^+ ionic concentrations to the columns that were tested.

Figure 4-5 presents the comparison for a simulated (no ^{137}Cs present) Envelope A waste (King et al., 2000). The isotherm model clearly demonstrates the residual trends mentioned above where it under-predicts loadings at low fluid Cs^+ concentrations and then over-predicts loadings at high values. However, given the fact that the isotherm model spans a broad range of ionic component concentrations and batch variabilities, the prediction is considered to be adequate. The inlet Cs^+ concentrations for the follow-on column tests fall within the tested range for K_d values. The WK series of equilibrium contact tests appear to be very consistent and also cover the entire range of expected inlet Cs^+ concentration values. As such, the corresponding WK column tests were chosen to set the best estimate values of various column model parameters discussed in a later section.

Figure 4-6 presents the comparison for a sample (25% by mole ^{137}Cs present) of Envelope A waste (Hassan et al., 1999b). For this different set of K^+ and Na^+ concentrations the isotherm model has excellent agreement with the available loading data. The inlet Cs^+ concentration for the follow-on column test fall within the tested range for K_d values.

Figure 4-7 presents the comparison for a simulated (no ^{137}Cs present) waste (IBC Advanced Technologies, 1996). The K^+ and Na^+ concentrations consistent with several follow-on columns test were chosen for comparison. The isotherm model significantly over-predicts the data and no batch ID for the resin was provided in their report. One of the two inlet Cs^+ concentrations for the follow-on column tests falls outside the tested range for K_d values. The higher inlet concentration value corresponds to the series of chemical stability studies (i.e., loading cycles 2 through 10) reported. Given the very poor agreement between the model and data, the column test data was not used in establishing any of the column model parameter settings. Note that the

IBC equilibrium data as shown in Figure 4-3 indicates that systematic differences between their data and the other data sets exist.

Figure 4-8 presents the comparison for a sample (25% by mole ^{137}Cs present) of Envelope A waste (Hassan and McCabe, 1997c). For this different set of K^+ and Na^+ concentrations only two equilibrium tests (one a repeat of the other) were performed and the expected range of column operation greatly exceeds these values. Since the data points are fairly close to the origin, little assessment of the isotherm model's predictive capability can be drawn.

Figure 4-9 presents the comparison for a sample (3.45% by mole ^{137}Cs present) of Envelope B waste (Hassan and McCabe, 1997d). This sample was actually an Envelope A sample, spiked with non-radioactive cesium to mimic a type B waste. For this different set of K^+ and Na^+ concentrations only two equilibrium tests (one a repeat of the other) were performed and the expected range of column operation greatly exceeds these values. The isotherm model performs a reasonable prediction of this data.

Figure 4-10 presents the comparison for a sample (25% by mole ^{137}Cs present) of Envelope C waste (Hassan and McCabe, 1997b). For this different set of K^+ and Na^+ concentrations only two equilibrium tests (one a repeat of the other) were performed and the expected range of column operation greatly exceeds these values. Since the data points are fairly close to the origin little assessment of the isotherm model's predictive capability can be drawn. However, this waste sample contained a modest amount of uranium (i.e., based on analytical assay of the eluate) which apparently is a competitor of cesium for adsorption sites.

Figure 4-11 presents the comparison for a sample (25% by mole ^{137}Cs present) and a simulant of Envelope A waste (Brown et al., 1995b). For this different set of K^+ and Na^+ concentrations several equilibrium tests were performed and the expected range of column operation was within these values. The isotherm model predictions fall in between the simulant and sample data. The resin used in these tests was a lower bed density material and may not be directly comparable to the latest resin materials (which may result in lower cesium loadings as seen in Figure 4-11).

For specific applications to an individual column the isotherm model could be fitted to the most appropriate subset of available equilibrium data. However, based on the potentially wide range of feed conditions and resin properties that may be encountered, the entire database was fitted and the above assessments illustrate the strengths and weaknesses in this approach.

4.5 Uncertainty Analysis

Uncertainties associated with the analytical measurements of liquid phase ionic concentrations were generally reported to be within 10% of the measured value. In several cases repeated tests and measurements were performed to check for repeatability. Uncertainty associated with resin batch variability appears to be a dominant factor with regard to error analysis. For example, as shown in Figures 4-1 through 4-3, the IBC measured cesium loadings (dashed lines) show systematic differences when compared to the remaining database (solid lines). No batch ID's were provided for these early equilibrium contact tests, while the remaining tests were taken based on two identified batch IDs. However, only the two IBC data points questioned (with

regard to their measurement accuracy) in the report (see IBC Advanced Technologies, 1996) were omitted from our maximum likelihood fit of the database. Total cesium ionic capacity was assumed to be the same for all data sets. The possible shifts between data sets may be the result of different capacity values.

The correlation coefficient matrix for the maximum likelihood fit of the database is provided in Table 4-6. Non-zero off-diagonal values indicate that a certain degree of dependence exists between the two selectivity coefficients. As indicated by Table 4-6, a fair degree of cross-correlation exists between the two selectivity coefficients. The high cross-correlation between the two estimated selectivity coefficients, as evident from the statistical results of the maximum likelihood output, can be partially explained. The cesium isotherm model can be rearranged by dividing through by the liquid-phase cesium concentration (pore-phase when using VERSE-LC) to obtained:

$$q_{Cs^+} = \frac{1}{1 + \tilde{K}_{21} \left(\frac{c_{pK^+}}{c_{pCs^+}} \right) + \tilde{K}_{31} \left(\frac{c_{pNa^+}}{c_{pCs^+}} \right)}. \quad (4-17)$$

As Eq. (4-17) illustrates only two independent variables actually exists (i.e., two concentration ratios). A plot of the sample space provided by the database is shown in Figure 4-12. Based on the technique used to generate a series of K_d measurements by means of re-contact testing, a series of measurements generally fall parallel to the line drawn in Figure 4-12. To better-defined unique values (i.e., lower cross-correlation uncertainty) for the two selectivity coefficients, test conditions along a line rotated 90° from the line shown should be considered. It should also be pointed out that resin batch variability may contribute to the low level of confidence in the two selectivity coefficients.

The upper and lower 95% confidence bounds for predicted fractional Cs^+ loadings were plotted in Figure 4-5 through 4-11. These bounds were computed by adding and subtracting off from the best estimate predictions the error term

$$E_{95\%} = \pm 2.0\sigma_q, \quad (4-18)$$

where the variance of the predicted fractional Cs^+ loadings was computed by

$$\sigma_q^2 \cong \left(\frac{\partial q}{\partial \tilde{K}_{21}} \right)^2 \sigma_{\tilde{K}_{21}}^2 + \left(\frac{\partial q}{\partial \tilde{K}_{31}} \right)^2 \sigma_{\tilde{K}_{31}}^2 + 2R\sigma_{\tilde{K}_{21}}\sigma_{\tilde{K}_{31}} \left(\frac{\partial q}{\partial \tilde{K}_{21}} \right) \left(\frac{\partial q}{\partial \tilde{K}_{31}} \right). \quad (4-19)$$

Equation (4-19) assumes that the contributions due to uncertainties in the measured ionic concentrations are small.

4.6 Application Using VERSE-LC

VERSE-LC has several equilibrium adsorption isotherm models to choose from (see user manual by Whitley and Wang, 1996). For our set of equilibrium isotherms as defined by Eq. (4-9) the VERSE-LC option of a Freundlich/Langmuir Hybrid (option F) can conform to its functional form. The Freundlich/Langmuir Hybrid model is expressed as:

$$\bar{c}_{pi} = \frac{a_i c_{pi}^{M_{ai}}}{\beta_i + b_1 c_{pi}^{M_{bi}} + b_2 c_{p2}^{M_{b2}} + b_3 c_{p3}^{M_{b3}}} \quad \text{for } i = 1, 2, 3, \quad (4-20)$$

where the model parameters (a_i , b_i , M_{ai} , M_{bi} , and β_i for $i=1,2,3$) can be determined from the parameter values associated with the ternary homovalent model above. The computed parameter values for Eq. (4-20) are listed in Table 4-7.

The Freundlich/Langmuir Hybrid model can also be used for the effective single component case as well. Here the concentrations for potassium and sodium throughout the column are assumed to be at their feed concentration levels. For an effective single-component cesium isotherm, Eq. (4-20) under these conditions becomes:

$$\bar{c}_{pl} = \frac{a_1 c_{pl}^{M_{ai}}}{[\beta_i + b_2 c_{p2}^{M_{b2}} + b_3 c_{p3}^{M_{b3}}] + b_1 c_{pl}^{M_{bi}}} \Rightarrow \frac{a_1 c_{pl}^{M_{ai}}}{\hat{\beta}_i + b_1 c_{pl}^{M_{bi}}}, \quad (4-21)$$

where the beta parameter for cesium becomes dependent upon the potassium and sodium feed concentrations.

Table 4-1. Nomenclature used to identify various batch equilibrium tests and column experiments discussed throughout this report.

Test ID	Type of data	Specific test case	Test Temperature (°C)	Reference report
WK	Batch equilibrium tests	All tests	22–23 °C	King et al., 2000
WK1	Column experiments	Exp. 1	22–23 °C	King et al., 2000
WK2	Column experiments	Exp. 2	22–23 °C	King et al., 2000
WK3	Column experiments	Exp. 3	22–23 °C	King et al., 2000
WK4	Column experiments	Exp. 4	22–23 °C	King et al., 2000
IBC	Batch equilibrium tests	All tests	25 °C	IBC Advanced Technologies, 1996
IBC1	Column experiments	Cycle 1	25 °C	IBC Advanced Technologies, 1996
IBC2	Column experiments	Cycles 2-10	25 °C	IBC Advanced Technologies, 1996
PNNL	Batch equilibrium tests	All tests	~21 °C	Kurath et al., 1999
NH	Batch equilibrium tests	All tests	25–27 °C	Hassan et al., 1999b
NH	Column experiments	All tests	~26 °C	Hassan et al., 1999b
DM-A	Batch equilibrium tests	All tests	~26 °C	Hassan and McCabe, 1997c
DM-A	Column experiments	All tests	~26 °C	Hassan and McCabe, 1997a
DM-B	Batch equilibrium tests	All tests	~26 °C	McCabe, 1997
DM-B	Column experiments	All tests	~26 °C	Hassan and McCabe, 1997d
DM-C	Batch equilibrium tests	All tests	~26 °C	Hassan and McCabe, 1998
DM-C	Column experiments	All tests	~26 °C	Hassan and McCabe, 1997b
BN-SIM	Batch equilibrium tests	All tests	25 °C	Brown et al., 1996
BN-ACT	Batch equilibrium tests	All tests	25 °C	Brown et al., 1996
BN-SIM-A	Batch equilibrium tests	All tests	25 °C	Brown et al., 1995b
BN-SIM-A	Column experiments	Exp. 1	25 °C	Brown et al., 1995b
BN-SIM-RAD	Batch equilibrium tests	All tests	25 °C	Brown et al., 1995a
BN-SIM-pH	Batch equilibrium tests	All tests	25 °C	Bray et al., 1995

Table 4-2. Adsorption isotherm “K_d” database summary for Cesium-SuperLig[®] 644 system (batch contact tests typically assume equilibrium reached in ~24 hrs).

Test ID	SL644 batch ID	Simulated waste envelope & tank #	Mole % ¹³⁷ Cs	Range of Cs ⁺ [M]	K ⁺ [M]	Na ⁺ [M]	Maximum % Cs loading on resin	Comments
PNNL	644BZ	Sample A AW-101	0.4% to 25%	1.10x10 ⁻⁵ to 3.27x10 ⁻³ M	0.610	6.59	60.6%	72 hr contact time used
PNNL	644BZ	Sample C AN-107	0.3% to 25%	5.53x10 ⁻⁶ to 3.44x10 ⁻³ M	0.024	5.61	55.6%	72 hr contact time used
WK	981020MB48-563	Simulant A 241-AN-105	0%	1.58x10 ⁻⁷ to 2.08x10 ⁻⁴ M	0.0908	5.00	30.2%	Good repeatability
WK	644BZ	Simulant A 241-AN-105	0%	2.98x10 ⁻⁶ to 3.11x10 ⁻⁶ M	0.0908	5.00	1.9%	Batch variability study
WK	981020MB48-563	Simulant A 241-AN-105	0%	2.01x10 ⁻⁶ to 2.07x10 ⁻⁶ M	0.06481	3.57	1.3%	Original simulant diluted with water
DMA	-na-	Sample A AW-101	25%	8.00x10 ⁻⁶ to 8.13x10 ⁻⁶ M	0.448	5.07	2.3%	-
DMB	-na-	Sample B ^a AN-105	3.45%	7.73x10 ⁻⁵ to 7.97x10 ⁻⁵ M	0.140	5.70	20.8%	Spiked with additional ¹³³ Cs
DMC	-na-	Sample C AN-107	25%	7.62x10 ⁻⁶ to 7.73x10 ⁻⁶ M	0.026	5.71	2.4%	Organic in simulant
NH	981020MB48-563	Sample A 241-AN-103	25%	1.35x10 ⁻⁸ to 1.40x10 ⁻⁴ M	0.121	5.25	29.0%	-
IBC	-na-	Simulant range	0%	2.47x10 ⁻⁷ to 8.30x10 ⁻⁴ M	0.050 to 1.000	5.19	33.2%	Investigated competition of K ⁺ with Cs ⁺ on resin

^a Originally an Envelope A sample that was modified to fall into the Envelope B category.

Table 4-3. Equilibrium data for Cesium on SuperLig® 644 based on batch contact tests.

Sample Description	Liquid Na ⁺ [M]	Liquid K ⁺ [M]	Liquid Cs ⁺ [M]	K _d [ml/g]	Solid Cs ⁺ [mmole/g]	Cs ⁺ loading ^a [-]
WK-563	5.00	0.0908	1.58E-07	2070	3.27E-04	9.81E-04
WK-563	5.00	0.0908	1.65E-07	1935	3.20E-04	9.61E-04
WK-563	5.00	0.0908	3.01E-06	2042	6.14E-03	1.84E-02
WK-563	5.00	0.0908	3.02E-06	2066	6.23E-03	1.87E-02
WK-563	5.00	0.0908	1.20E-05	1631	1.96E-02	5.89E-02
WK-563	5.00	0.0908	1.26E-05	1567	1.97E-02	5.90E-02
WK-563	5.00	0.0908	5.18E-05	916	4.74E-02	1.42E-01
WK-563	5.00	0.0908	5.20E-05	916	4.77E-02	1.43E-01
WK-563	5.00	0.0908	1.05E-04	702	7.34E-02	2.20E-01
WK-563	5.00	0.0908	1.13E-04	635	7.17E-02	2.15E-01
WK-563	5.00	0.0908	2.06E-04	486	1.00E-01	3.01E-01
WK-563	5.00	0.0908	2.08E-04	483	1.01E-01	3.02E-01
WK-644BZ	5.00	0.0908	2.98E-06	2089	6.22E-03	1.87E-02
WK-644BZ	5.00	0.0908	3.11E-06	1996	6.21E-03	1.86E-02
WK-563	3.57	0.0648	2.01E-06	2193	4.40E-03	1.32E-02
WK-563	3.57	0.0648	2.02E-06	2210	4.45E-03	1.34E-02
WK-563	3.57	0.0648	2.05E-06	2184	4.47E-03	1.34E-02
WK-563	3.57	0.0648	2.07E-06	2113	4.37E-03	1.31E-02
PNNL-644BZ-101	6.59	0.610	1.10E-05	719	7.91E-03	2.37E-02
PNNL-644BZ-101	6.59	0.610	1.13E-05	708	8.00E-03	2.40E-02
PNNL-644BZ-101	6.59	0.610	1.31E-04	394	5.17E-02	1.55E-01
PNNL-644BZ-101	6.59	0.610	1.54E-04	312	4.81E-02	1.44E-01
PNNL-644BZ-101	6.59	0.610	3.21E-03	63	2.02E-01	6.06E-01
PNNL-644BZ-101	6.59	0.610	3.27E-03	60	1.97E-01	5.91E-01
PNNL-644BZ-107	5.61	0.024	5.53E-06	1256	6.95E-03	2.08E-02
PNNL-644BZ-107	5.61	0.024	7.59E-06	877	6.66E-03	2.00E-02
PNNL-644BZ-107	5.61	0.024	9.84E-05	515	5.06E-02	1.52E-01
PNNL-644BZ-107	5.61	0.024	2.22E-04	158	3.51E-02	1.05E-01
PNNL-644BZ-107	5.61	0.024	3.41E-03	54	1.85E-01	5.56E-01
PNNL-644BZ-107	5.61	0.024	3.44E-03	53	1.82E-01	5.47E-01
DM-A	5.07	0.448	8.00E-06	950	7.60E-03	2.28E-02
DM-A	5.07	0.448	8.13E-06	938	7.63E-03	2.29E-02
DM-B	5.70	0.140	7.73E-05	896	6.93E-02	2.08E-01
DM-B	5.70	0.140	7.97E-05	862	6.87E-02	2.06E-01
DM-C	5.71	0.026	7.62E-06	1037	7.90E-03	2.37E-02
DM-C	5.71	0.026	7.73E-06	1020	7.88E-03	2.36E-02
NH-563	5.25	0.121	1.35E-08	1155	1.56E-05	4.68E-05
NH-563	5.25	0.121	1.52E-08	1210	1.84E-05	5.53E-05
NH-563	5.25	0.121	2.09E-07	1552	3.25E-04	9.74E-04
NH-563	5.25	0.121	2.09E-07	1582	3.31E-04	9.93E-04
NH-563	5.25	0.121	3.38E-06	1610	5.44E-03	1.63E-02
NH-563	5.25	0.121	3.43E-06	1520	5.22E-03	1.57E-02
NH-563	5.25	0.121	1.27E-04	758	9.65E-02	2.90E-01
NH-563	5.25	0.121	1.40E-04	678	9.50E-02	2.85E-01

Sample Description	Liquid Na ⁺ [M]	Liquid K ⁺ [M]	Liquid Cs ⁺ [M]	K _d [ml/g]	Solid Cs ⁺ [mmole/g]	Cs ⁺ loading ^a [-]
IBC-1.0	5.19	1.00	8.30E-04	93	7.72E-02	2.31E-01
IBC-1.0	5.19	1.00	6.12E-05	198	1.21E-02	3.64E-02
IBC-1.0	5.19	1.00	9.86E-06	307	3.03E-03	9.08E-03
IBC-0.5	5.19	0.50	3.24E-04	163	5.28E-02	1.58E-01
IBC-0.5	5.19	0.50	2.07E-05	347	7.20E-03	2.16E-02
IBC-0.5 ^b	5.19	0.50	3.70E-07	3222	1.19E-03	3.58E-03
IBC-0.3	5.19	0.30	1.57E-04	179	2.81E-02	8.44E-02
IBC-0.3	5.19	0.30	1.23E-05	337	4.16E-03	1.25E-02
IBC-0.3 ^b	5.19	0.30	7.74E-07	253	1.96E-04	5.87E-04
IBC-0.1	5.19	0.10	6.91E-04	160	1.11E-01	3.32E-01
IBC-0.1	5.19	0.10	2.88E-05	534	1.54E-02	4.62E-02
IBC-0.1	5.19	0.10	7.41E-07	1288	9.54E-04	2.86E-03
IBC-0.05	5.19	0.05	3.46E-04	133	4.60E-02	1.38E-01
IBC-0.05	5.19	0.05	1.57E-05	405	6.36E-03	1.91E-02
IBC-0.05	5.19	0.05	2.47E-07	717	1.77E-04	5.31E-04

^a The Cesium loadings represent the fraction of resin sites occupied by total cesium where the total cation exchange capacity of the resin was assumed constant and set to the value 0.3333 mmole_{Cs}/g_{resin}.

^b Data point not used in the fitting process since source indicated that values appeared statistically out of line with other data and repeat experiments would be required.

Table 4-4. Estimated selectivity coefficients for the Cesium-SuperLig[®] 644 system based on a total of 57 batch contact tests and the ternary homovalent isotherm model.

Selectivity Coefficient	Definition	Parameter Estimate	Approx. Standard Error	Relative Error (%)	Lower Confidence Level	Upper Confidence Level
$\tilde{K}_{21}$	K ⁺ to Cs ⁺ selectivity	8.328694x10 ⁻⁴	2.4866x10 ⁻⁴	29.9%	4.0949x10 ⁻⁴	1.35941x10 ⁻³
$\tilde{K}_{31}$	Na ⁺ to Cs ⁺ selectivity	4.36723x10 ⁻⁵	7.64x10 ⁻⁶	17.5%	2.984x10 ⁻⁵	5.96x10 ⁻⁵
$\tilde{K}_{32}$	Na ⁺ to K ⁺ selectivity	5.24360x10 ⁻²	-	-	-	-
$\tilde{K}_{12}$	Cs ⁺ to K ⁺ selectivity	1,200.67	358.47	29.9%	735.61	2442.06
$\tilde{K}_{13}$	Cs ⁺ to Na ⁺ selectivity	22,897.81	4,005.73	17.5%	16,778.52	33,512.06
$\tilde{K}_{23}$	K ⁺ to Na ⁺ selectivity	19.07088	-	-	-	-

Table 4-5. Predicted (best estimate) total Cesium loadings^a on SuperLig[®] 644 based on the ternary homovalent cation exchange isotherm model.

Equilibrium Aqueous Cs ⁺ , [M]	WK Cs ⁺ loading [-]	NH Cs ⁺ loading [-]	DM-A Cs ⁺ loading [-]	DM-B Cs ⁺ loading [-]	DM-C Cs ⁺ loading [-]	IBC Cs ⁺ loading [-]
Aqueous Na ⁺ , [M]	5.00	5.25	5.07	5.70	5.71	5.19
Aqueous K ⁺ , [M]	0.0908	0.121	0.448	0.140	0.026	0.100
0.0000E+00	0.0000E+00	0.0000E+00	0.0000E+00	0.0000E+00	0.0000E+00	0.0000E+00
1.0000E-08	3.4010E-05	3.0297E-05	1.6819E-05	2.7357E-05	3.6896E-05	3.2285E-05
2.0000E-08	6.8018E-05	6.0592E-05	3.3638E-05	5.4712E-05	7.3789E-05	6.4568E-05
4.0000E-08	1.3603E-04	1.2118E-04	6.7274E-05	1.0942E-04	1.4757E-04	1.2913E-04
6.0000E-08	2.0403E-04	1.8175E-04	1.0091E-04	1.6412E-04	2.2133E-04	1.9368E-04
1.0000E-07	3.4000E-04	3.0289E-04	1.6817E-04	2.7350E-04	3.6884E-04	3.2276E-04
2.0000E-07	6.7977E-04	6.0559E-04	3.3628E-04	5.4685E-04	7.3740E-04	6.4530E-04
5.0000E-07	1.6977E-03	1.5126E-03	8.4027E-04	1.3660E-03	1.8415E-03	1.6117E-03
1.0000E-06	3.3896E-03	3.0206E-03	1.6791E-03	2.7283E-03	3.6762E-03	3.2182E-03
5.0000E-06	1.6721E-02	1.4923E-02	8.3397E-03	1.3494E-02	1.8114E-02	1.5887E-02
1.0000E-05	3.2893E-02	2.9407E-02	1.6541E-02	2.6629E-02	3.5584E-02	3.1276E-02
5.0000E-05	1.4534E-01	1.3156E-01	7.7574E-02	1.2033E-01	1.5575E-01	1.3899E-01
1.0000E-04	2.5380E-01	2.3253E-01	1.4398E-01	2.1481E-01	2.6952E-01	2.4406E-01
5.0000E-04	6.2971E-01	6.0237E-01	4.5681E-01	5.7768E-01	6.4849E-01	6.1749E-01
1.0000E-03	7.7279E-01	7.5185E-01	6.2714E-01	7.3231E-01	7.8677E-01	7.6351E-01
2.0000E-03	8.7183E-01	8.5835E-01	7.7085E-01	8.4548E-01	8.8066E-01	8.6590E-01

^a The Cesium loadings represent the fraction of resin sites occupied by total cesium where the total cation exchange capacity of the resin was assumed constant and set to the value 0.3333 mmole_{Cs}/g_{resin}.

Table 4-6. The resulting correlation coefficient matrix for the fit of the selectivity coefficients for the Cesium-SuperLig[®] 644 system based on 57 batch contact tests and the ternary homovalent isotherm model.

Selectivity Coefficient	$\tilde{K}_{21}$	$\tilde{K}_{31}$
$\tilde{K}_{21}$	1.0000	-0.6861
$\tilde{K}_{31}$	-0.6861	1.0000

Table 4-7. Parameter settings for Freundlich/Langmuir Hybrid equilibrium isotherm model for Cesium on SuperLig[®] 644 based on ternary homovalent system.

Parameter	Cesium (component 1)	Potassium (component 2)	Sodium (component 3)	Cesium (effective single component)
a_i (gmoles/L _{BV})	1.1165×10^{-1} (a)	9.2993×10^{-5} (a)	4.8763×10^{-6} (a)	1.1165×10^{-1} (a)
b_i (M ⁻¹)	1.0	8.3287×10^{-4}	4.3672×10^{-5}	1.0
M_{ai}	1.0	1.0	1.0	1.0
M_{bi}	1.0	1.0	1.0	1.0
β_i (-)	0.0	0.0	0.0	2.9366×10^{-4} (b)

^a The total cation exchange capacity of the resin was assumed to be 0.3333 mmole_{Cs}/g_{resin} and the bed density was assumed to be 0.335 g_{resin}/ml_{BV}.

^b Value depends on potassium and sodium feed concentrations. Value shown is based on 5.001 M Na⁺ and 0.090 M K⁺.

Figure 4-1. Variation in measured total cesium loadings on SuperLig[®] 644 resin with respect to total liquid cesium concentration. The database shown contains data taken from three different sites and several different batches for a total of 59 data points.

Figure 4-2. Variation in measured total cesium distribution coefficient on SuperLig[®] 644 resin with respect to total liquid cesium concentration. The database shown contains data taken from three different sites and several different batches for a total of 59 data points.

Figure 4-3. Variation in measured total cesium distribution coefficient on SuperLig[®] 644 resin with respect to the ratio of total liquid cesium concentration versus total sodium plus potassium concentrations. The database shown contains data taken from three different sites and several different batches for a total of 59 data points.

Figure 4-4. A direct comparison of predicted versus measured total cesium loadings on SuperLig[®] 644 resin. The database shown contains data taken from three different sites and several different batches for a total of 59 data points.

Figure 4-5. A direct comparison of predicted versus measured total cesium loadings on SuperLig[®] 644 resin for a simulated Envelope A waste (King et al., 2000).

Figure 4-6. A direct comparison of predicted versus measured total cesium loadings on SuperLig[®] 644 resin for a sample of Envelope A waste (Hassan et al., 1999b).

Figure 4-7. A direct comparison of predicted versus measured total cesium loadings on SuperLig® 644 resin for a simulated waste (IBC Advanced Technologies, 1996).

Figure 4-8. A direct comparison of predicted versus measured total cesium loadings on SuperLig® 644 resin for a sample of Envelope A waste (Hassan and McCabe, 1997c).

Figure 4-9. A direct comparison of predicted versus measured total cesium loadings on SuperLig[®] 644 resin for a sample of Envelope B waste (McCabe, 1997).

Figure 4-10. A direct comparison of predicted versus measured total cesium loadings on SuperLig[®] 644 resin for a sample of Envelope C waste (Hassan and McCabe, 1998).

Figure 4-11. A direct comparison of predicted versus measured total cesium loadings on SuperLig[®] 644 resin for a sample and simulant of Envelope A waste (Brown et al., 1995b).

Figure 4-12. A scatter plot showing the domain of the database for measured total cesium loadings on SuperLig[®] 644 resin (59 data points).

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 a 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.

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:

$$\varepsilon_T = \varepsilon_b + (1 - \varepsilon_b)\varepsilon_p, \quad (5-1)$$

and

$$\rho_b = \rho_s(1 - \varepsilon_T), \quad (5-2)$$

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:

$$\varepsilon_b = \frac{V_{\text{void}} - V_{\text{pore}}}{V_{\text{bed}}}; \quad \varepsilon_p = \frac{V_{\text{pore}}}{V_{\text{part}}}; \quad \varepsilon_T = \frac{V_{\text{void}}}{V_{\text{bed}}} = \frac{V_{\text{bed}} - V_{\text{sld}}}{V_{\text{bed}}}, \quad (5-3)$$

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 ("material") density of the resins has been measured based on buoyancy studies (Hassan et al., 1999a). A summary of their results is given in Table 5-1. For the column modeling presented in this report the average particle density listed in Table 5-1 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 no direct measure of the total amount of resin residing within the active beds was available (except for test case BN-SIM-A, Brown et al., 1995b). Therefore, a method of estimating column bed densities had to be developed.

Even though bed density is column and batch dependent, for the column model simulations presented in this report certain simplifications were made. During the IBC Advanced Technologies (1996) column studies two columns were operated for a total of ten cycles where the columns were reported to have been completely loaded. Based on elution data an average of 2.97 g of cesium had been loaded onto an average column. Using this fully loaded column an estimate of the bed density for those columns operating with a 5 M Na⁺ feed solution can be computed as:

$$\begin{aligned}\rho_b &\equiv \frac{m_{\text{resin}}}{V_{\text{bed}}} = \frac{m_{\text{Cs}}}{V_{\text{bed}} M_{\text{Cs}} \bar{C}_T} \\ &= \frac{2.97 \text{ g}_{\text{Cs}}}{(200 \text{ ml})(133 \text{ g}_{\text{Cs}} / \text{gmole}_{\text{Cs}})(0.0003333 \text{ gmole}_{\text{Cs}} / \text{g}_{\text{resin}})}, \quad (5-4) \\ &= 0.335 \text{ g}_{\text{resin}} / \text{ml}_{\text{bed}}\end{aligned}$$

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. It should be pointed out that the computed value of 0.335 above is lower than the stated bed density of 0.42 g/ml by IBC Advanced Technologies (1996) and the measured value of ~0.4 g/ml by Hassan et al. (1999a, value based on a 0.25 M Na⁺ solution). The value given in Eq. (5-4) provides better estimates of column breakthrough curve predictions than the higher values just mentioned.

5.3 Porosities

No measured bed, pore, or total porosities have been reported for the various column studies considered. Based on Eq. (5-2) the total porosity of a column is known once the particle and bed densities are specified. Using the values presented in the above subsection the total porosity becomes:

$$\epsilon_T \equiv 1 - \frac{\rho_b}{\rho_s} = 1 - \frac{0.335}{1.580} = 0.788. \quad (5-5)$$

The value for particle density used in Eq. (5-5) corresponds to the measured value in water where it is assumed that this value does not appreciably varies with respect to ionic strength. A range of possible void distribution exists between the pore and bed porosities constrained by Eq. (5-1) and any specified total porosity such as Eq. (5-5). In Table 5-2 the functional form of Eq. (5-1) for two different total porosity values is tabulated. The results provided in Table 5-2 are plotted in Figure 5-1. In Figure 5-1 the estimated region where the majority of columns operate is highlighted with a circle. This region is based on parameter estimation efforts performed during the assessment of the WK column tests (King et al., 2000). In particular, a series of values for the two porosities were used and the computed breakthrough curves were then compared to the measured values.

Also shown in Figure 5-1 is the average measured porosity for dense packing of mono-sized hard spheres (i.e., 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 resin particles, no specific lower limit can be uniquely specified.

During the review process for this report, new bed porosity data for the SuperLig 644 resin was published by its manufacturer (IBC, Inc.) for batch #981020MB48-563. Bruening (2000a) list bed porosity measurements with an average value of 36.4%. Three separate measurements of 33.7%, 36.1%, and 39.5% were made where the void measurement was made in an ~5M Na⁺ swollen state.

Table 5-1. Measured particle density of SuperLig[®] 644 based on buoyancy tests^a.

Specific volume (ml/g)	644BZ resin	981020MB48-563 resin	Average resin
Particle density, (g/ml)	1.611	1.549	1.580

^a Buoyancy tests on "as received" resins (Hassan et al., 1999a).

Table 5-2. Pore porosity as a function of bed porosity at two total porosity values for the SuperLig[®] 644 resin.

Bed porosity (-)	Pore porosity given $\varepsilon_T = 0.788$ (-)	Pore porosity given $\varepsilon_T = 0.806$ (-)
0.00	0.787975	0.806329
0.05	0.776815	0.796136
0.15	0.750558	0.772152
0.20	0.734968	0.757911
0.25	0.717300	0.741772
0.30	0.697107	0.723327
0.35	0.673807	0.702045
0.40	0.646624	0.671187
0.45	0.614499	0.647871
0.50	0.575949	0.612658
0.55	0.528833	0.569620
0.60	0.469937	0.515823
0.65	0.394213	0.446655
0.70	0.293249	0.354430
0.75	0.151899	0.225316
0.80	na	0.031646
0.85	na	na

Figure 5-1. Range of potential bed and pore porosities for the SuperLig[®] 644 resin.

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6.0 Particle Size Distributions

The majority of particle size distribution measurements made for SuperLig[®] 644 has been performed using traditional sieve analyses with dry "as received" resin. For two of the various batches of resin (i.e., 644BZ and 981020MB48-593) particle size distribution measurements have also been made in a 0.25 M Na⁺ simulated waste solution using a MicroTrac. The MicroTrac equipment used was limited to particle sizes less than ~704 μm . As reported in Hassan et al. (1999a), SuperLig[®] 644 resin swells by as much as 145% when dry "as received" resin is placed in 0.25 Na⁺ simulated waste solution and then shrinks back down by 29% when placed in a 5.0 Na⁺ solution. When dry "as received" resin is placed into de-mineralized water an increase in size of 39% occurs. During column operations the active bed length of a column varies depending upon the total ionic strength of the feed solution. After each complete cycle (i.e., loading, washing, elution, and pretreatment) the bed length generally returns to approximately its initial value as observed by King et al. (2000).

Since the total ionic strength of the feed solution passes through a column within the first few column volumes, our column modeling is based on column sizes predicted at feed conditions and no attempt to adjust column height during a transport simulation is made.

The SuperLig[®] 644 resin is granular and not spherical as assumed in the governing equations used to model the ion-exchange process. The column models also assume that the mass transfer and pore diffusion processes can be model using a single average size particle to represent the entire population of granular resin particles. Given the level of knowledge with regard to particle size and shape distributions, the above assumptions should be acceptable.

6.1 Sieve Analysis Data

As mentioned above dry sieve analysis data for several of the batches have been reported. Table 6-1 contains sieve analysis data for two batches of resins (i.e., 644BZ and 981020MB48-593) reported in Hassan et al. (1999a). The particle diameter values listed for wet resin are based on the reported swelling characteristics of the resins (Hassan et al., 1999a). The volume changes used to shift the particle size distributions are provided in Table 6-2 where the cube roots of the volume ratios are applied. The distribution data listed in Table 6-1 was used to generate distribution functions for each of the two batches. The computed distribution functions for each batch at three key fluid states are plotted in Figure 6-1.

As illustrated in each of the plots in Figure 6-1, a wide range of particles sizes exist within a given batch. The actual distribution of sizes between batches also varies significantly. For use in column modeling an estimated mean particle radius is required. Mean particle radii were computed from these distribution functions using:

$$\langle R_p \rangle = \frac{\int_0^{\infty} [R_p] f(R_p) dR_p}{\int_0^{\infty} f(R_p) dR_p}, \quad (6-1a)$$

and

$$\left\langle \frac{1}{R_p} \right\rangle = \frac{\int_0^{\infty} \left[\frac{1}{R_p} \right] f(R_p) dR_p}{\int_0^{\infty} f(R_p) dR_p}. \quad (6-1b)$$

Computed values based on Eqs. (6-1) are labeled in Figure 6-1. As these numbers indicate, large differences exist between the batches and also depend on which averaging technique is chosen (i.e., Eq. (6-1a) or Eq. (6-1b)). Arguments can be made in favor of either averaging technique; however, given the wide range of particle size distributions currently being observed and the limited detailed sieve data, Eq. (6-1a) was chosen for the column simulations presented in this report.

Results from sieve analyses for other batches are available (e.g., see Brown et al. (1996) and Kurath et al., (1999)). In general the available sieve analysis data is very coarse.

6.2 MicroTrac Technology

When using MicroTrac a sample flow system circulates the carrier fluid, usually deionized water, containing the particulate sample through the quartz sample cell. Light from the MicroTrac laser passes through the cell, interacts with the particles in the fluid to produce a diffraction pattern. The intensities of the diffraction pattern are measured by a photodiode detector, and the pattern is fitted with a Bessel function. The Bessel function is manipulated by proprietary computer algorithms to obtain the particle size distribution.

As mentioned above MicroTrac data were also taken for these two batches. Even though the equipment was limited to particle sizes (i.e., diameters) up to 704 μm , a partial comparison of this distribution data to the 0.25 M Na^+ solution adjusted sieved analysis data can be made. The computed particle size distribution functions are shown in the plots of Figure 6-2 based on the MicroTrac results for a 0.25 M Na^+ solution test sample. The MicroTrac results are tabulated in Table 6-3 for both batches.

These distribution functions require no adjustments and a direct comparison can be made between them and those shown in Figure 6-1. Over the limited particle size range available reasonable agreement is observed in single versus dual-mode distribution function behavior. However, differences in diameter sizes are observed.

6.3 Laser Technology

During the review process for this report, new particle size distribution data for the SuperLig 644 resin was published by its manufacturer (IBC, Inc.) for batch #981020MB48-563. Bruening (2000a) list particle size measurements for this resin in its swollen state in a 3 M NaOH/2 M NaNO₃ solution. Three separate replicate measurements were made for two different resin samples of the same batch. The measurements for replicate 1 for both samples are plotted in Figure 6-3. Bruening (2000a) indicates that the measurements were made using a laser instrument. Both distributions appear to be continuing to rise at their upper particle size range suggesting that the laser instrument saturates at some upper limit. Average particle radius's of 373 and 377 μm were computed for samples 1 and 2, respectively.

Table 6-1. Particle size distributions of SuperLig[®] 644 based on sieve analyses^a.

Measurement diameter range "as received" (μm)	Calculated diameter range "in 0.25 M" (μm)	Calculated diameter range "in 5.0 M" (μm)	Fraction of 644BZ resin	Fraction of 981020MB48-563 resin
<62	<84	<74	-	-
62 - 212	84 - 288	74 - 251	0.02	0.03
212 - 425	288 - 577	251 - 504	0.40	0.24
425 - 600	577 - 814	504 - 711	0.44	0.22
>600	>814	>711	0.14	0.51

^a Sieve analysis performed on "as received" resins (Hassan et al., 1999a).

Table 6-2. Swelling characteristics of SuperLig[®] 644 resins^a.

Specific volume (ml/g)	644BZ resin	981020MB48-563 resin	Average resin
Dry "as received"	1.080	na	1.080
Wet "0.25 M Na"	2.652	2.742	2.697
Wet "5.0 M Na"	1.888	1.708	1.798

^a Swelling characteristics of resins during pretreatment reported by Hassan et al. (1999a).

Table 6-3. Particle size distributions of SuperLig[®] 644 based on MircoTrac Technology^a.

Particle diameter range (μm)	Particle diameter midpoint (μm)	BZ664 resin pdf (Dia)	BZ664 resin cdf (Dia)	981020MB48-563 resin pdf (Dia)	981020MB48-563 resin cdf (Dia)
0.0 - 0.97	0.4860	0.0000	0.0000	0.0000	0.0000
0.97 - 1.37	1.1735	0.0000	0.0000	0.0000	0.0000
1.37 - 1.94	1.6600	0.0000	0.0000	0.0000	0.0000
1.94 - 2.75	2.3475	0.0000	0.0000	0.0000	0.0000
2.75 - 3.88	3.3195	0.0000	0.0000	0.0000	0.0000
3.88 - 5.50	4.6945	0.0000	0.0000	0.0000	0.0000
5.50 - 7.77	6.6390	0.0000	0.0000	0.0000	0.0000
7.77 - 11.00	9.3890	0.0000	0.0000	0.0000	0.0000
11.00 - 15.56	13.2800	0.0000	0.0000	0.0000	0.0000
15.56 - 22.00	18.7800	0.0000	0.0000	0.0017	0.0017
22.00 - 31.11	26.5550	0.0004	0.0004	0.0053	0.0070
31.11 - 44.00	37.5550	0.0031	0.0035	0.0188	0.0258
44.00 - 62.23	53.1150	0.0060	0.0095	0.0482	0.0740
62.23 - 88.00	75.1150	0.0084	0.0179	0.0769	0.1509
88.00 - 124.50	106.2500	0.0127	0.0306	0.0704	0.2213
124.50 - 176.00	150.2500	0.0207	0.0513	0.0471	0.2684
176.00 - 248.90	212.4500	0.0259	0.0772	0.0554	0.3238
248.90 - 352.00	300.4500	0.1582	0.2354	0.1279	0.4517
352.00 - 497.80	424.9000	0.4213	0.6567	0.2363	0.6880
497.80 - 704.00	600.9000	0.3433	1.0000	0.3120	1.0000

^a MircoTrac analysis performed on resins in 0.25 M Na⁺ solutions and results are normalized.

Figure 6-1. Estimated particle size distribution functions based on sieve analysis under various solution conditions for two specific batches of SuperLig® 644 resin.

Figure 6-2. Estimated particle size probability distribution functions (pdf's) based on MircoTrac technology under a 0.25 M Na^+ solution for two specific batches of SuperLig® 644 resin.

Figure 6-3. Volume fraction measurements of particles as a function of particle size for two specific samples of the SuperLig[®] 644 resin (batch 981020MB48-563) based on laser technology under a 5 M Na⁺ solution (data from Bruening,2000a).

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7.0 Pore Diffusion

As mention earlier 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. In this section we discuss the “effective” binary molecular (Brownian motion) diffusion and pore diffusion coefficients used in the column models.

7.1 Waste Density and Viscosity

Fluid properties for a simulated waste of Envelope A were measured and reported by Steimke et al. (1999). The measured values of density and dynamic viscosity for the simulated waste and for pure water are listed in Table 7-1 at 20 °C. Property values for the waste at 25 °C were computed based on the measured pure water values also provided in Table 7-1.

7.2 Molecular Diffusion Coefficients

Binary diffusion (sometimes referred to as free stream or Brownian motion) coefficients of electrolytes originating from a single salt under dilute conditions can be reasonably estimated by the Nernst-Haskell equation (Reid et al., 1977):

$$D_{\pm}^{\infty} = \left(\frac{RT}{F^2} \right) \left[\frac{\frac{1}{z_+} + \frac{1}{z_-}}{\frac{1}{\lambda_+^{\circ}} + \frac{1}{\lambda_-^{\circ}}} \right], \quad (7-1)$$

where

- $D_{\pm}^{\infty}$ - binary diffusion coefficient at infinite dilution, cm²/s
- $\lambda_+^{\circ}, \lambda_-^{\circ}$ - limiting ionic conductance for cation and anion, mhos/equiv
- z_+, z_- - valences of cation and anion, respectively
- F - Faraday constant, 96,500 C/g-equiv
- R - gas constant, 8.314 J/gmole-K
- T - absolute temperature, K

Ionic conductance for the various ions of interest are tabulated in Table 7-2 (Reid et al., 1977; Perry, 1973). Binary pairs for the dominant cation-anion pairs based on a simulated waste for Envelope A (Steimke et al., 1999) were considered and their computed diffusion coefficients are listed in Table 7-3.

To account for fluid property differences between the simulated waste and pure water a correction factor was applied. Based on a hydrodynamic theory the following expression typically referred to as the Stokes-Einstein equation is obtained (Bird et al., 1960, page 514):

$$\frac{D_{AB}\mu_B}{\kappa T} = \frac{1}{6\pi R_A}, \quad (7-2)$$

where

- D_{AB} - binary diffusion coefficient for A diffusing through solvent B
- μ_B - dynamic viscosity of solvent mixture
- R_A - radius of diffusing particle
- κ - Boltzmann's constant

Based on Eq. (7-2), as a correction factor the ratio of dynamic viscosities (i.e., pure water versus waste) was applied to the computed diffusion coefficients from Eq. (7-1). The viscosity corrected values are also provided in Table 7-3. In Cussler (1984) the "effective" binary ionic diffusion coefficient of cesium in essentially pure water is $1.236 \times 10^{-3} \text{ cm}^2/\text{min}$ at 25°C , which is within 16% of the estimated value computed from Eq. (7-1).

The ionic radii of sodium and potassium are 0.95 and 1.33 angstroms with average hydration numbers of 4 and 3, respectively. All metal cations are hydrated in aqueous media, where, for example, sodium migrates perhaps in the form $\text{Na}(\text{H}_2\text{O})_4^+$. Reasonable values for the radii of the hydrated alkali metal ions sodium and potassium are ~ 2.76 and ~ 2.32 angstroms (Peters et al., 1974), respectively. Therefore, sodium is bigger and slower moving than potassium in aqueous solutions consistent with the predictions listed in Table 7-3. Anions are characteristically less heavily hydrated.

Molecular diffusion coefficients are important in determining key dimensionless numbers (e.g., Schmidt Number, Sc) used in various constitutive law correlations pertinent to column transport modeling. They also provide an upper bound for pore diffusion coefficients.

7.3 Pore Diffusion Coefficients

Within the complicated pore structure of the resin particles we assume that net fluid motion is approximately zero resulting in equal-molar counter-diffusion. "Effective" binary diffusion coefficients based on Fick's law are assumed where surface migration is considered negligible. Surface migration generally becomes increasingly more important as the migrating ions increase in size relative to the pore aperture (Froment and Bishoff, 1979). Knudsen diffusion occurs when the molecular dimensions of the ions approach their mean free path lengths.

Specific information on the actual pore sizes were not available at the time of this report; however, IBC vendor information suggests that the pore sizes are large relative to the size of migrating ions of interest and that pore diffusion coefficients should not be significantly lower than their molecular 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 (Smith, 1981; Froment and Bishoff, 1979) defined as:

$$D_{pi} \equiv \frac{1}{\tau_p} D_{\infty i}, \quad (7-3)$$

Typical values for catalyst particle tortuosity are between 2 and 8. Based on the expected large pore diameters the tortuosity values for SuperLig® 644 may actually range as low as from near 1 to 2.

For small ions Mackie and Meares (1955) suggest that the intra-particle pore diffusion coefficient can be estimated from

$$D_{pi} \cong \left[\frac{\epsilon_p}{(2 - \epsilon_p)^2} \right] D_{\infty i}, \quad (7-4)$$

However, for larger molecules pore diffusion coefficient experiments are required. Ideally, pore diffusion coefficients can be derived from batch kinetics distribution studies where the mass transfer resistance associated with film diffusion is minimized through significant mechanical mixing (note that, mixing techniques must be limited such that physical grinding of the particles does not become excessive). A time-dependent cesium distribution study was performed in simulated DSSF waste by Brown et al., 1996. As noted in their report the solid/solution mixing (based on manual swirling and orbital shakers) had a measurable effect on the kinetics of the cesium uptake process. The kinetics data presented incorporate a significant film diffusion resistance to mass transfer.

If we look at steady-state mass transfer across a liquid film in series with diffusion down a given pore, the following approximate "overall" diffusion coefficient can be considered:

$$\tilde{D}_{pi} \cong \frac{D_{pi}}{1 + \left(\frac{D_{pi}}{k_f < \Delta r >} \right)}, \quad (7-5)$$

where

- $\tilde{D}_{pi}$ - "overall" diffusion coefficient, cm²/min
- D_{pi} - "actual" binary pore diffusion coefficient, cm²/min
- k_f - liquid film mass transfer (diffusion) coefficient, cm/min
- $< \Delta r >$ - average radial distance down pore, cm

Batch kinetics tests, where inadequate mixing is achieved between the solid and solution, result in overall diffusion coefficients that are in effect smaller than the actual pore diffusion coefficient. Therefore, the use of the batch kinetics data taken by Brown et al. (1996) can provide us with a lower bound estimate of cesium pore diffusion, while the molecular coefficient value becomes our upper bound.

To estimate an overall diffusion coefficient for the kinetics test presented in Brown et al. (1996), a VERSE-LC model was set up consistent with the experimental conditions specified in their report:

- Initially 0.067 g of resin was placed into contact with 10 ml of simulant solution at concentrations of 5 M Na⁺, 0.475 M K⁺, and 1.00x10⁻⁴ M Cs⁺;

- VERSE-LC geometry parameters were set consistent with the experimental setup, while other parameters were set consistent with the parameters discussed in the column modeling section of this report;
- The film mass transfer and axial dispersion coefficients were set to high values in order to appropriately model the experimental behavior using VERSE-LC;
- Transient liquid cesium concentrations were computed using VERSE-LC, while experimental values were computed from the transient Lambda values (Figure 3.1 of Brown et al., 1996) and associated information contained within their report; and
- An equilibrium isotherm was used consistent with the late time (i.e., 120 hour contact time) measured Lambda value.

Sample VERSE-LC input and output decks are provided in Appendix E. The computed transient liquid cesium concentrations based on the experimentally measured Lambda values are also provided in Table E-1 of Appendix E. Table E-2 contains various key parameters used in this analysis.

Several VERSE-LC simulations were run by varying the inputted pore diffusion coefficient value. Three key cases are compared to the experimental data in the semi-log plot presented in Figure 7-1. As expected, a faster than measured cesium uptake response is seen when the pore diffusion coefficient is set to cesium's molecular diffusion value. For the slower response data (associated with mixing from the orbital shakers) an "overall" pore diffusion coefficient of approximately 10% of the molecular diffusion value is observed. For the case where manual swirling was used as a means of mechanical mixing, 70% of the molecular diffusion value is computed. For the column modeling predictions and assessment presented in later sections of this report the pore diffusion coefficient for each ion of interest is set to 70% of the ion's molecular diffusion value. The values used are listed in Table 7-3. These values correspond to a particle tortuosity of approximately 1.43.

Table 7-1. Fluid density and dynamic viscosity for water and simulated 5 M sodium waste solution.

Fluid property	Pure water	Simulated 5 M Na ⁺ waste solution ^a
For 20 °C		
Density, g/ml	0.99823	1.225 ^a
Dynamic viscosity, cp	1.002	2.94 ^a
For 25 °C		
Density, g/ml	0.9970479	1.22355 ^b
Dynamic viscosity, cp	0.8904	2.61255 ^b

^a A 5 M sodium simulated waste consistent with Envelope A where properties were measured at 20 °C (Steimke et al., 1999).

^b Measured properties were adjusted to new temperature based on pure water values.

Table 7-2. Limiting ionic conductances in water at 25 °C (Reid et al., 1977; Perry, 1973).

Ion	Limiting ionic conductance MHOS/equivalent
Cations	
Cs ⁺	77.30
K ⁺	73.50
Na ⁺	50.10
Anions	
OH ⁻	198.60
NO ₃ ⁻	71.46

Table 7-3. Estimated binary molecular and pore diffusion coefficients at 25 °C.

Ion Pair	Diffusion coef. for water cm ² /min	Diffusion coef. for simulated 5M Na waste ^b cm ² /min	Pore diffusion coef. for simulated 5M Na waste ^c cm ² /min
For cesium			
Cs ⁺ - OH ⁻	1.778x10 ⁻³	6.048x10 ⁻⁴	
Cs ⁺ - NO ₃ ⁻	1.187x10 ⁻³	4.036x10 ⁻⁴	
Mole avg. value ^a	1.426x10 ⁻³	4.850x10 ⁻⁴	3.395x10 ⁻⁴
For potassium			
K ⁺ - OH ⁻	1.714x10 ⁻³	5.831x10 ⁻⁴	
K ⁺ - NO ₃ ⁻	1.158x10 ⁻³	3.938x10 ⁻⁴	
Mole avg. value ^a	1.383x10 ⁻³	4.704x10 ⁻⁴	3.293x10 ⁻⁴
For sodium			
Na ⁺ - OH ⁻	1.278x10 ⁻³	4.348x10 ⁻⁴	
Na ⁺ - NO ₃ ⁻	9.411x10 ⁻⁴	3.201x10 ⁻⁴	
Mole avg. value ^a	1.078x10 ⁻³	3.666x10 ⁻⁴	2.566x10 ⁻⁴

^a Relative mole fractions of 59.5% NO₃⁻ and 40.5% OH⁻ based on simulated waste composition (Steimke et al., 1999).

^b Fluid viscosity correction ratio applied based on a measured simulated waste viscosity of 2.94 cP at 20 °C (Steimke et al., 1999).

^c Pore diffusion coefficient set to 70% of the estimated molecular diffusion value based on analysis of batch kinetics test data of Brown et al. (1996).

Figure 7-1. Estimation of the “overall” pore diffusion coefficient based on batch kinetics tests performed by Brown et al. (1996) for cesium uptake on SuperLig[®] 644.

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8.0 Axial Dispersion and Film Diffusion

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:

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

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:

$$E_b = \frac{2R_p u \epsilon_b}{0.2 + 0.011 Re^{0.48}}, \quad (8-2)$$

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:

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

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. As listed in Table 9.1 of Section 9, several of the column experiments considered have column-to-particle diameter ratios less than 30. 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:

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

where column length is in units of cm. As listed in Table 9-1 of Section 9, several of the column experiments considered have column lengths less than 20. 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

Numerous 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. A listing of the currently known columns for full-scale, pilot-scale, intermediate-scale, and small-scale studies is provided in Table 9-1. Key features associated with each column are also given in Table 9-1.

VERSE-LC was used to model 11 of these column experiments where cesium breakthrough curves were experimentally measured for the SuperLig[®] 644 resin. Figures 9-1 through 9-11 show comparisons of these model calculations to the corresponding experimental data. The VERSE-LC input and output files for each of the 11 simulations are listed in Appendix D. Some of the model parameters were adjusted during the assessment phase for the WK series of tests and were then held fixed throughout the remainder of the analysis effort. For each column test discussed below, a comparison of the isotherm model used versus the appropriate subset of batch equilibrium data is given in Section 4.

9.1 Intermediate-Scale (WK) Tests

Figures 9-1 through 9-4 show model predictions compared to data from a series of experiments by King et al. (2000) measuring cesium removal from a simulant of Hanford Envelope A waste. The four experiments were all run on the same resin (i.e., fixed amount of resin) in two different columns. The experiments are numbered in the order in which they were run. Tests 1, 2, and 3 were run using the same packed column, while for test 4 the resin was repacked into a shorter and wider (approximately same volume) column. In essence test 4 should be an estimate of the breakthrough curve approximately halfway down the test 1 column.

Figure 4-5 compares the isotherm model used with the appropriate batch equilibrium data for the WK series of column tests. Over the entire cesium concentration range (i.e., inlet feed to zero) the isotherm model provides a reasonable estimate for adsorption onto the resin. However, at the higher liquid-phase concentrations the isotherm model over predicts the data.

The plots are ordered from lowest flow in Experiments 3 and 4 to highest flow in Experiment 2. The column volume is nominally 50 ml in 0.25 M Na⁺. When exposed to simulant at 5.0 M Na⁺, the resin shrank about 10%. Since the resin bed depth was measured during these experiments, the model calculations were made using the bed depths measured in simulant feed. These true column volumes were also used to adjust the reported experimental data so that data and calculated results in the figures are on the same basis. Table 9-2 lists the experimentally determined column volumes and volumetric flow rates for each of the experiments. Given the column-to-particle diameter ratios of these two columns, as shown in Table 9-1, excessive flow maldistribution most likely did not occur. However, the short active column lengths with inlet void headspaces (similar in size to an active bed portion) probably resulted in end-effects that increased the "effective" axial dispersion of the columns. Increased "effective" axial dispersion results in earlier breakthrough curves.

Since the column volumes in Experiments 1 and 2 were identical and these experiments were the first ones run, it was assumed that the nominal bed density of 0.335 g/ml applied to these experiments (see Section 5 for bed density specification). For experiments 3 and 4 the bed density was adjusted to account for the observed increase in column volume. It was also assumed that the change in column volume could be attributed entirely to the swelling of the resin particles where the constraint between bed and particle porosities was maintained. Therefore, the nominal particle radius was assumed to apply to Experiments 1 and 2 and a slightly larger particle radius was used to model Experiments 3 and 4.

This set of experimental data was judged to be the most consistent and complete set available for model evaluation and parameter adjustment if necessary. The data also extended to higher column loadings than were achieved in many of the other experiments. Therefore, the unspecified model parameter of bed void was selected such that the model provided a good representation to all of the experimental data for this set of experiments. Note that, although the same resin material was reused in all of these experiments, the calculations assume that fresh resin is in the column at the start of each experiment since the resin was thoroughly eluted between each test. A listing of the best estimate (nominal) values for all the necessary VERSE-LC column modeling parameters is tabulated in Table 9-3. These nominal values are used throughout all column modeling simulations discussed in this report (excluding certain specified parameter variations resulting from known column conditions; such as volume changes). It should be pointed out that some of the parameter settings chosen are not unique and other subsets of parameter values may provide results comparable to the results presented in this assessment section.

The parameters in Table 9-3 are ordered into groups based on their level of importance with respect to the determination of cesium exit breakthrough curves. The ordering of these parameters is based on the numerous simulation runs made during this assessment effort and our sensitivity study for the full-scale facility as discussed in Section 10.

9.2 "Hot" Small-Scale (NH) Test

Figure 9-5 shows the model prediction of breakthrough data taken by Hassan et al. (1999b) using actual Hanford Envelope A radioactive waste on a small 6.1 ml ion exchange column (where 25% on a mole basis of ^{137}Cs was present). Column swelling and shrinkage data were not reported for this experiment so nominal values of the model parameters were used in the calculation. For this experiment, the model predicts a faster column breakthrough than was observed experimentally.

Given the low column-to-particle diameter ratio and the inlet void headspaces, end-effects and flow maldistribution probably occurred. Even so, the model simulation predicted earlier breakthrough. Figure 4-6 compares the isotherm model used with the appropriate batch equilibrium data for the NH column test. Over the entire cesium concentration range (i.e., inlet feed to zero) the isotherm model provides a reasonable estimate for adsorption onto the resin.

9.3 "Hot" Small-Scale (DM-A, DM-B, DM-C) Tests

Figures 9-6 through 9-8 show model predictions of breakthrough data measured by Hassan and McCabe (1997a, 1997b, and 1997c) on a small 5.5 ml ion exchange column. The experiments were conducted using actual radioactive Hanford waste from Envelopes A, B and C. Envelopes A and C contained 25% on a mole basis of ^{137}Cs , while the Envelope B waste was spiked with ^{133}Cs such that only 3.45% ^{137}Cs was present. These experiments were all conducted on the same resin material that was eluted between tests. Column swelling and shrinkage data were not reported for these experiments, so nominal model parameters were used to make the calculations. The model gives a reasonably good prediction for the Envelope A waste experiment plotted in Figure 9-6. Model predictions consistently fall slightly under the data. However, the shape of the experimental data is well represented by the model calculation. The Envelope B waste was spiked with cold cesium to approximately 10 times the total cesium than was used in the other experiments. This higher total cesium leads to faster breakthrough that is captured fairly accurately by the model calculation as shown in Figure 9-7. As can be seen in Figure 9-8, the model is not able to accurately predict the Envelope C breakthrough curve. Envelope C waste contains uranium that is known to be a competitor for ion exchange sites based on analytical analysis of the eluate from this experiment. Envelope C waste also contains more organic material than the other wastes that may inhibit ion exchange or mass transfer into the particle pores.

Given the low column-to-particle diameter ratio and the inlet void headspaces, end-effects and flow maldistribution probably occurred. Figures 4-8 through 4-10 compare the isotherm model used with the appropriate batch equilibrium data for the DM series of column tests. Only batch equilibrium data at low liquid cesium concentrations were available for comparison.

9.4 Intermediate-Scale Vendor (IBC) Tests

Figures 9-9 and 9-10 show model predictions of breakthrough data obtained by IBC Advanced Technologies (1996). These experiments consisted of 10 loading and elution cycles performed on a lead-lag system of identical 200 ml resin columns. Multiple test cycles were performed to ascertain the "chemical" stability of the SuperLig[®] 644 resin. Cycles 2-10 are plotted in Figure 9-9 and Cycle 1, which used a lower inlet cesium concentration, is plotted in Figure 9-10. The batch of SuperLig[®] 644 used in these experiments was not identified but it is different from the material used in the more recent experiments. However, since basic data from these experiments was not available, nominal model parameters were used in the calculations. In general the model predicts a faster breakthrough than was observed experimentally. Note the large amount of scatter in the experimental data at 80 and 100 column volumes shown in Figure 9-9. Also note that, even though Cycle 1 was reported to have a lower inlet cesium concentration, the measured breakthrough during Cycle 1 is actually faster than that reported for every other cycle except for Cycle 10. The model, of course, predicts a delayed breakthrough for Cycle 1 since the lower inlet cesium can be adsorbed over more column volumes.

Each column had a total length of 21.5 cm with a resin bed depth of 11.1 cm with inactive packing at its entrance and exit. As given in Table 9-1, end-effects and flow maldistribution probably were small for this set of tests. Figure 4-7 compares the isotherm model used with the

appropriate batch equilibrium data for the IBC series of column tests. The isotherm model greatly over predicts adsorption at the moderate to high liquid cesium concentration levels.

9.5 Intermediate-Scale PNNL (BN-SIM-A) Test

Early on Brown et al. (1995) performed column experiments on several candidate ion exchange resins (including SuperLig[®] 644) for evaluation and comparison. Figure 9-11 shows the model prediction of the breakthrough curve measured by Brown et al. (1995). This earlier experiment was again likely performed using a different batch of SuperLig[®] 644 resin than was used in the later experiments. However, the column data reported for this experiment is more complete than for the other data sets. In particular, the mass of resin in the column is reported as 47.12 g dry resin in a 210 ml column. This data gives the experimental bed density that is the single most important model parameter (note that this earlier sample of SuperLig[®] 644 resin had a much lower swollen bed density [0.224 g/ml] than in all other subsequent experiments). Using the bed density and assuming that the particle porosity is the same as the nominal value used for our other calculations, the bed porosity and particle radius were estimated. With this input, the model prediction falls quite close to the experimental data. There was a change in the slope of the curve based on the experimental data at about 115 column volumes that is not explained in the reference report, nor can it be explained by the model.

Figure 4-11 compares the isotherm model used with the appropriate batch equilibrium data for the BN-SIM-A column test. The isotherm model greatly over predicts adsorption at the high liquid cesium concentration levels.

Table 9-1. Key features of Cesium-SuperLig[®] 644 fixed bed full-, pilot-, intermediate-, and small-scale columns.

Column ID	Active bed volume (ml)	Diameter (cm)	Length (cm)	Column-to-particle diameter ratio	Superficial velocity (cm/min)	CV/hr	Feed conc.: Cs ⁺ [M] K ⁺ [M] Na ⁺ [M]	Comments
Full scale plant (FSP)	1.047x10 ⁶	77.0	225.0	1,160	11.3	3.01	Ranges over waste tanks	End-effects & flow maldistribution unlikely
Pilot scale (TFL)	1,140	2.54	225.0	38	11.3 6.6	3.01 1.76	7.0x10 ⁻⁵ M 0.090 M 5.001 M	End-effects unlikely; No Cs-SL644 data taken yet
PNNL tests (BN-SIM-A)	210	2.54	41.44	38	5.92	9.0	5.0x10 ⁻⁴ M 0.12 M 5.00 M	Bed density specified; early on one of several resins tested for evaluation
Vendor tests (IBC)	200	4.7897	11.1 (active) 21.5 (packed)	72	1.665	9.0	1.0x10 ⁻³ M 0.10 M 5.1851 M	Est. bed density; multiple cycles for column "chemical" stability; packing at front/back of bed
Intermediate scale (WK)	46.3 42.3 42.3	2.69	8.15 7.45 7.45	41	0.87 6.0 10.6	6.41 48.37 85.46	6 to 7x10 ⁻⁵ M 0.090 M 5.001 M	End-effects possible; used to assess dispersion and mass transfer coef. correlations
Intermediate scale (WK)	44.0	4.00	3.50	60	0.83	13.98	6.429x10 ⁻⁵ M 0.090 M 5.001 M	End effects probable; same mass of resin used in other WK tests
"Hot" Small scale (NH)	6.1	1.10	6.42	17	0.321	3.0	6.987x10 ⁻⁵ M 0.117 M 4.990 M	25% ¹³⁷ Cs; end-effects and flow maldistribution possible
"Hot" Small scale (DMA)	5.5	0.95	7.76	14	0.353	2.73	8.100x10 ⁻⁵ M 0.448 M 5.070 M	25% ¹³⁷ Cs; end-effects and flow maldistribution possible
"Hot" Small scale (DMB)	5.5	0.95	7.76	14	0.440	3.40	7.640x10 ⁻⁴ M 0.140 M 5.700 M	3.45% ¹³⁷ Cs; end-effects and flow maldistribution possible
"Hot" Small scale (DMC)	5.5	0.95	7.76	14	0.437	3.38	6.332x10 ⁻⁵ M 0.026 M 5.710 M	25% ¹³⁷ Cs; end-effects and flow maldistribution possible

Table 9-2. Unique test conditions for experiments WK-1 to WK-4.

Experiment ID	Column Volume in Simulant (ml)	Volumetric Flow Rate (ml/min)	Bed Density (g/ml)
WK-1	42.3	34.08	0.335
WK-2	42.3	60.25	0.335
WK-3	46.3	4.94	0.306
WK-4	44.0	10.25	0.322

Table 9-3. Summary of recommended nominal parameter settings for Cesium-SuperLig[®] 644 system column modeling.

Key parameter	Definition	Priority for predicting break-through curve	Recommended B. E. settings	Comments
m_{resin}	mass of resin in column	1	column specific	Key quantity generally a constant during a series of runs.
$\bar{C}_T$	total ionic capacity of resin	1	0.3333 mmole _{Cs} /g _{resin}	Provided by IBC vendor testing
ρ_b	bed density	1	0.335 g _{resin} /ml B.V.	Estimated from IBC elution column runs.
$\tilde{K}_{12}$	Cs ⁺ to K ⁺ selectivity coefficient	1	1,200.67	Based on conc's not activities.
$\tilde{K}_{13}$	Cs ⁺ to Na ⁺ selectivity coefficient	1	22,897.81	Based on conc's not activities.
L, D, V _b	Length, diameter, & volume of column	1	column specific	Varies significantly with total ionic strength.
$\langle R_p \rangle$	avg. effective radius of resin	2	332 μm (mean values)	Impacts both film and pore diffusion. Averaging process remains in question.
U, Q	superficial velocity & volumetric flow rate	2	column specific	For mass transfer limited columns flow perturbation dependent.
C ₀	Cs ⁺ , K ⁺ , & Na ⁺ inlet conc's	2	column specific	For favorable isotherms higher inlet conc's sharpen breakthru curves

Table 9-3. Summary of recommended nominal parameter settings for Cesium-SuperLig[®] 644 system column modeling (continued).

Key parameter	Definition	Priority for predicting break-through curve	Recommended B. E. settings	Comments
ϵ_b, ϵ_p	bed & particle porosities	3	0.45 & 0.614 for nominal conditions	Packing & ionic strength dependent.
D_p	pore diffusion coefficient	3	70% of Brownian diffusion value	Pores assumed to be relatively large with low tortuosity.
k_f	liquid film mass transfer coefficient	3	Wilson and Geankoplis (1966) correlation	This correlation spans the velocity & particle sizes of resin.
D_∞	Brownian motion diffusion coefficient	3	Cs^+ $4.85 \times 10^{-4} \text{ cm}^2/\text{min}$ K^+ $4.70 \times 10^{-4} \text{ cm}^2/\text{min}$ Na^+ $3.67 \times 10^{-4} \text{ cm}^2/\text{min}$	Based on Nernst-Haskell eqn. & published ionic conductances at 25 °C.
E_b	axial longitudinal dispersion coefficient	4	Chung & Wen (1968) correlation	This correlation based on long column data for wide range of column conditions.
$E_b(L)/E_b(\infty)$	short column impact ratio	4	Liles & Geankoplis (1960) data	Power law fit to limited short column tests with end effects.
V_{CSTR}	CSTR volumes at entrance/exit of columns	4	column specific	Estimated based on specified volumes for each test series.

Figure 9-1. VERSE-LC calculation compared to data from WK Experiment 3,
 $D = 2.69 \text{ cm}$, $L = 8.15 \text{ cm}$, $U = 0.87 \text{ cm/min}$.

Figure 9-2. VERSE-LC calculation compared to data from WK Experiment 4,
 $D = 4.00 \text{ cm}$, $L = 3.50 \text{ cm}$, $U = 0.83 \text{ cm/min}$.

Figure 9-3. VERSE-LC calculation compared to data from WK Experiment 1,
 $D = 2.69 \text{ cm}$, $L = 7.45 \text{ cm}$, $U = 6.0 \text{ cm/min}$.

Figure 9-4. VERSE-LC calculation compared to data from WK Experiment 2,
 $D = 2.69 \text{ cm}$, $L = 7.45 \text{ cm}$, $U = 10.6 \text{ cm/min}$.

Figure 9-5. VERSE-LC calculation compared to data from NH Experiment A,
 $D = 1.10 \text{ cm}$, $L = 6.42 \text{ cm}$, $U = 0.321 \text{ cm/min}$.

Figure 9-6. VERSE-LC calculation compared to data from DM Experiment A,
 $D = 0.95 \text{ cm}$, $L = 7.76 \text{ cm}$, $U = 0.353 \text{ cm/min}$.

Figure 9-7. VERSE-LC calculation compared to data from DM Experiment B,
 $D = 0.95 \text{ cm}$, $L = 7.76 \text{ cm}$, $U = 0.440 \text{ cm/min}$.

Figure 9-8. VERSE-LC calculation compared to data from DM Experiment C,
 $D = 0.95 \text{ cm}$, $L = 7.76 \text{ cm}$, $U = 0.437 \text{ cm/min}$.

Figure 9-9. VERSE-LC calculation compared to data from IBC Cycles 2-10,
 $D = 4.79 \text{ cm}$, $L = 11.1 \text{ cm}$, $U = 1.665 \text{ cm/min}$.

Figure 9-10. VERSE-LC calculation compared to data from IBC Cycle 1,
 $D = 4.79 \text{ cm}$, $L = 11.1 \text{ cm}$, $U = 1.665 \text{ cm/min}$.

Figure 9-11. VERSE-LC calculation compared to data from BN-SIM-A,
 $D = 2.54 \text{ cm}$, $L = 41.44 \text{ cm}$, $U = 5.92 \text{ cm/min}$.

10.0 Full-Scale Column Predictions

Under best estimate conditions, the predicted performance of the proposed full-scale ion-exchange facility is discussed in this section. The sensitivity associated with key parameter variation is discussed also. The predictions are based on a VERSE-LC model of the lead and lag columns where the parameter settings are consistent with the values used during the assessment of the laboratory-scale column experiments. The feed concentrations chosen simulate an Envelope A Hanford waste and are consistent with those for the pilot-scale facility (Steimke et al., 1999). Since the key parameters for the pilot-scale and full-scale facilities are identical (excluding column diameter), these full-scale facility predictions can also be used as pre-test predictions for the upcoming pilot-scale tests.

10.1 Basic FlowSheet

The basic flowsheet for the full-scale ion-exchange columns is shown in Figure 10.1. The key parameters defining the full-scale facility are provided in Table 10-1. Two identically sized columns in series (i.e., a lead and a lag column) are used where an exit cesium concentration criterion (i.e., $< 1 \mu\text{Ci/ml}$ for the first case and $< 0.0874 \mu\text{Ci/ml}$ for the second) is imposed on the lag column. Each column has a void headspace that is approximately the same size as each column. Prior to loading both columns are pretreated and contain an aqueous native solution with an ionic strength of approximately 0.25 M sodium (i.e., essentially zero cesium and potassium are present). During the loading phase the feed solution's ionic strength increases significantly to approximately 5 M sodium and 0 to 1 M potassium. Inlet feed concentration of cesium can vary from 0 to 1×10^{-4} M. A design flowrate of ~ 3 CV/hr is used during the cesium loading phase. Upon reaching the lag column exit concentration criterion, the cesium loading phase is terminated and for subsequent loading cycles the lag column is placed in the lead column position with a fresh column being placed in the lag position. The loaded lead column is eluted and pretreated for future use. Fresh column implies a cesium free bed. It is assumed that the isotopic feed concentrations on a mole basis are 25% ^{137}Cs and 75% ^{133}Cs .

The cesium, potassium, and sodium concentration profiles along the column train varies with time. Due to the significant selectivity for cesium by SuperLig[®] 644 resin, the column exit breakthrough for potassium and sodium occurs very early (i.e., within 5-10 column volumes) with cesium's breakthrough significantly retarded. Key concentration points along the facility are numbered from 0 through 4 as shown in Figure 10-1. The inlet conditions correspond to point 0 while the exit product criterion is imposed at point 4. Points 1 and 3 represent the locations where the headspace ends and the active bed begins.

10.2 VERSE-LC Model of Full-Scale Facility

The VERSE-LC model representing the full-scale flowsheet is shown in Figure 10-2. To model the full-scale facility using VERSE-LC the headspaces are considered to be continuous stirred tank reactors (CSTRs). In these CSTRs perfect mixing is assumed where no chemical reactions

are taking place. During a VERSE-LC simulation exit breakthrough curves at points 2 and 4 are generated along with concentration profiles over both columns at key points in time.

During the loading phase for modeling purposes a time invariant flowrate and inlet feed conditions are assumed. Both the ternary homovalent system and an effective single component system have been studied. The VERSE-LC input parameters are listed in Table F-1 of Appendix F. The VERSE-LC input and output files for a typical run are also provided in Appendix F. The feed concentrations chosen are those for the pilot-scale facility (Steimke et al., 1999) and intermediate-scale WK column tests (King et al., 2000) that simulates an Envelope A Hanford waste. The simulations were run out for over 2000 column volumes such that a repeating pattern occurs during subsequent cycling. Six repeating cycles occurred as shown in the lead-column and lag-column exit breakthrough curves for cesium in Figure 10-3. The start of each cycle represents the replacement of the lead-column with the lag-column and insertion of a fully eluted (assumes perfect cesium elution) and regenerated column in the lag position. For the results presented in Figure 10-3, cycle initiation occurred when the exiting cesium concentration from the lag-column reached 1 $\mu\text{Ci/ml}$ (assuming on a mole basis 25% ^{137}Cs and the remainder ^{133}Cs). A cesium activity level of 1 $\mu\text{Ci/ml}$ corresponds to a total cesium concentration of 3.37528×10^{-7} M where the radioactive half-life of 30.17 years for ^{137}Cs is used (see Table 10-1).

By the fifth cycle a repeating pattern is achieved and no additional cycles are necessary to demonstrate the long-term behavior of the facility. This is easily seen in Figure 10-3 by: (1) the repeating peak leadcolumn exit concentrations and (2) the repeating number of column volumes required to reach the lagcolumn exit criterion. A close-up of cycle number 5 is shown in Figure 10-4. Cycle 5 and beyond require approximately 305 column volumes to reach a cesium-137 exit concentration in the lag-column of 1 $\mu\text{Ci/ml}$. As shown in Figure 10-4 once this exit criterion is reached the exit cesium concentration of the lead-column is 77% of its feed value.

At the end of the fifth cycle (and beyond) the lead-column overall contains on average (i.e., its axial average) greater than ~99% of its total cesium loading capacity as shown by the cesium concentration profiles presented in Figure 10-5 (note, the fraction of column cesium loading is estimated by integrating the predicted concentration profile over the column's axial length and dividing by column length). The mixing impact associated with the void headspace (i.e., modeled as a CSTR) between the two columns is negligible as seen in Figure 10-5. The overall cesium loading (i.e., axial average) for the lag-column is less than ~25% for cycle number 3 and beyond. Profile development during the course of subsequent cycles is also shown in Figure 10-5 for cycle numbers 1, 2, and 5 (note: cycles 3,4, 6, and beyond are essentially the same as the results for cycle 5). The overall column cesium loadings are tabulated in Table 10-2.

To assess the impact resulting from a tighter exit cesium concentration criterion the above set of calculations was remade where the lag-column exit criterion was set to 0.0874 $\mu\text{Ci/ml}$ (i.e., a 11.5 factor reduction in allowable cesium-137 exit concentrations corresponding to a total cesium concentration of 2.9500×10^{-8} M). As expected the number of column volumes required to reach the criterion is reduced, as well as the level of lead-column loading. As shown in Figures 10-6 and 10-7, only an ~6% reduction in treated column volumes results, with a cesium exit concentration from the lead-column of ~47% (at the end of the later cycles). The overall column cesium loadings are also tabulated in Table 10-2.

As shown in Figures 10-3 and 10-6, the number of column volumes required to reach a given exit criterion varies during the first few cycles. This characteristic variation (i.e., initially drops and then rises up and levels off) can be explained with reference to Figure 10-5 or 10-7 where the changes in concentration profile over both columns at various cycles are shown. At the end of the first cycle the highest level of concentrations within the lag-column are experienced due to its initially "cesium-free" state. Therefore, for subsequent cycles the lag-column experiences migration of cesium into its bed at the outset (due to the initial presence of cesium loading throughout in the upstream lead-column) reducing the number of column volumes required to reach the exit criterion. After a few cycles (note that the adsorption isotherm is non-linear and more than two cycles is required) the concentration profile throughout both columns becomes repeatable.

10.3 Facility Decontamination Factor

An overall average decontamination factor (D.F.) can be defined for multiple cycles as:

$$D.F. \equiv \frac{\int_{\text{cycles}} (Qc_{Cs^+}^{\text{feed}}) dt}{\int_{\text{cycles}} (Qc_{Cs^+}^{\text{lag-exit}}) dt}, \quad (10-1)$$

where the integration can be performed over several loading cycles or limited to specific loading cycles. The highest D.F. occurs for the first cycle where both columns are fresh, while during later cycles the lead-column is partially loaded at the onset of a cycle, resulting in reduced D.F. values. Equation (10-1) represents the ratio of total cesium entering the facility versus the total amount exiting. For example, for a 5 cycle simulation a cumulative D.F. of ~1,795 was achieved for a < 1 $\mu\text{Ci/ml}$ exit criterion and ~22,471 for a < 0.0874 $\mu\text{Ci/ml}$ exit criterion.

For each lag-column exit criterion studied, the D.F. for the complete range of possible operating cycles is tabulated in Table 10-3 (on a cumulative basis) and in Table 10-4 (on a per cycle basis). The cumulative D.F.'s listed in Table 10-3 are also plotted in Figure 10-8 where the functional dependence on the number of operating cycles considered is shown. Note that this functional dependence is nearly identical regardless of the exit criterion assumed and that the number of column volumes per cycle is less for the more stringent exit criterion. The product of D.F. times the exit criterion for each case are reasonably close and for estimating D.F.'s for other exit criterion values this product can be assumed to be fixed.

The D.F.s listed in Table 10-3 and presented in Figure 10-8 are D.F. values based on Eq. (10-1). For example, the D.F. value for an exit criterion of < 1 $\mu\text{Ci/ml}$ after three complete cycles is 1,990. This value was computed using Eq. (10-1) where integration was applied over the entire time period (i.e., includes cycles 1, 2, and 3). D.F. values for individual cycles (such as, operation during cycle 3 alone) are listed in Table 10-4 and presented in Figure 10-9.

10.4 Parameter Sensitivity Study

The sensitivity of the predicted column breakthrough curve for cesium to variations in several of the model parameters was investigated to provide an indication of the reliability of the best estimate (i.e., nominal) calculated results. For this study, we chose to use the full-scale column as the test case. These results then give an indication of the difference between nominal and worst case results that might be used to develop a conservative column design.

Table 10-5 summarizes the sensitivity parameters chosen for the study and gives a qualitative indication of model sensitivity to the parameter value. In each case, the nominal value of a single parameter was varied to a high or a low setting while the test case run was made with all other parameters held at their nominal values. In most cases, the range over which the parameters were varied was chosen to be indicative of the uncertainty in the parameter. Results from the sensitivity calculations are plotted in Figures 10-10 through 10-15.

10.4.1 Axial Dispersion Sensitivity

Figure 10-10 shows that the cesium breakthrough curve is insensitive to the value of the axial dispersion coefficient. The nominal value of the axial dispersion coefficient is based on the Chung-Wen correlation (1968) that has an actual uncertainty on the order of $\pm 50\%$. Column breakthrough curves at this level of uncertainty were indistinguishable from the nominal case. Therefore, runs were made at $1/10^{\text{th}}$ and 10 times the nominal axial dispersion coefficient so the results could be differentiated from the nominal case. These results indicate that use of the Chung-Wen correlation is certainly acceptable for column design calculations.

10.4.2 Film Diffusion/Mass Transfer Sensitivity

Figure 10-11 shows sensitivity of the predicted breakthrough curve to a $\pm 50\%$ variation in the mass transfer coefficient. The nominal mass transfer coefficient is based on the Wilson-Geankoplis correlation (1966). Comparison to other mass transfer correlations for packed columns at low Reynolds number (Foo and Rice, 1975) indicates the $\pm 50\%$ is a reasonable estimate of the uncertainty in this correlation. A lower mass transfer coefficient causes faster breakthrough and a slower approach to saturation. However, the effect is quite small over the sensitivity range tested and use of the nominal correlation appears to be acceptable for design calculations.

10.4.3 Pore Dispersion Sensitivity

Figure 10-12 shows model sensitivity to the pore diffusion coefficient. As a nominal value we have used 70% of the estimated molecular diffusion coefficient (see Section 7 for details on the basis of this estimate) to account for pore restriction and tortuosity. Since the pore diffusion coefficient can be no larger than the molecular diffusion coefficient, this value was chosen as the upper bound and the lower bound was set to 43% of the nominal value (40% of the molecular diffusion coefficient) to give equal high and low incremental changes. The results show a moderate sensitivity to the pore diffusion coefficient. In particular, lower pore diffusion coefficients lead to faster breakthrough and slower approach to saturation. The pore diffusion

coefficient can be estimated from kinetic batch contact experiments. Data on the rate of approach to adsorption equilibrium under conditions where liquid film mass transfer effects are small and pore diffusion dominates can be used to fit a value to the pore diffusion coefficient. Adequate data for this purpose were not available for this system and it is recommended that such data be taken so that a more accurate estimate of the pore diffusion coefficient can be obtained. However, a comparison to the available kinetics data is provided in Section 7.

10.4.4 Bed and Pore Porosity Sensitivity

Figure 10-13 shows model sensitivity to the bed porosity. As shown in Section 5, bed porosity is related to particle porosity so that varying the bed porosity necessitates changing the particle porosity as well. The nominal values of 0.450 for bed porosity and 0.614 for particle porosity are based on obtaining a good fit to some of the column experimental data. Variation of the bed porosity by ± 0.10 represents an estimate of the reasonable extremes in porosity. That is, we do not expect bed porosity to be greater than 55% or less than 35% and the predicted breakthrough curve is not extremely sensitive to the chosen value. Nevertheless, the bed porosity can be measured experimentally. Such experimental measurements are not currently available for this system and it is recommended that they be conducted. Even though results are only moderately sensitive to bed porosity, it is very useful to the modeling effort to have as many parameters as possible defined by accurate measurements. A direct measurement of bed porosity will also help to minimize the overall uncertainty in column design calculations. The recent measurement of bed porosity ($\sim 36.4\%$) by Bruening (2000a) resides within the bounds as shown in Figure 10-13.

10.4.5 Particle Radius Sensitivity

Figure 10-14 shows model sensitivity to particle radius. The nominal value is taken from measurements of the particle size of dry resin corrected for swelling in solvent. The data show a particle size distribution that appears to be truncated at higher values from instrument limitations. The model can only use a single estimate of the particle radius and hence only approximates the true physical situation. In addition, the model assumes a spherical particle whereas actual particle shape may be irregular. The model appears to be more sensitive to a smaller particle radius that sharpens the breakthrough curve. Therefore, it is more conservative to assume a larger particle radius for column design purposes. More accurate measurements of the particle size distribution would be desirable.

10.4.6 Bed Density Sensitivity

Figure 10-15 shows model sensitivity to the ion-exchange bed density. A variation in total ionic exchange capacity results in similar behavior as shown in Figure 10-15. Calculated results are very sensitive to the bed density since this parameter is a direct measurement of the amount of resin in the column and thereby the total column capacity for ion exchange. The nominal value of 0.335 g/ml was estimated from data obtained by IBC, the resin manufacturer, even though a bed density of 0.4 g/ml has been reported (see Section 5 for further discussion). The upper limit of 0.389 g/ml was estimated from SRTC data and the lower limit simply taken as an equal difference from the nominal value. The bed density is likely between 0.3 and 0.4 g/ml but has not been measured accurately in the column experiments reported thus far. As the calculations

demonstrate, a 16% decrease in bed density significantly lowers bed capacity and gives a faster breakthrough curve. Therefore, an accurate measurement of this parameter is essential to obtaining reliable model predictions.

10.4.7 Flow rate Sensitivity

Figure 10-16 shows model sensitivity to the volumetric flow rate in CV/hr. The results are for the first cycle only where similar relative behavior exists for later cycle comparisons. All input parameter values were fixed at their nominal values, while the input volumetric flow rate was varied from 1.5 to 6.0 CV/hr. However, the film diffusion coefficient varied consistent with the correlation expressed by Eq. (8-1) due to the variation in Reynolds number. For each of the five simulations shown, the exit breakthrough curve for the lead column is plotted up to the point when the cesium concentration exiting the lag column exceeds the criterion of 1 $\mu\text{Ci/ml}$. The number of column volumes required to reach 50% cesium breakthrough at the exit of the lead column and to reach the specified cesium exit criterion for the lag column are tabulated in Table 10-5. As shown in Table 10-5 and in plotted in Figure 10-17, the number of column volumes required to reach 50% breakthrough in the lead column is somewhat insensitive to flow rate. On the other hand, the slower the flow rate the sharper the concentration profile remains leading to progressively higher cesium loadings on the lead column prior to reaching a fixed exit criterion for the lag column.

10.4.8 Sensitivity Summary

As listed in Table 10-6 axial dispersion down the column and liquid film mass transfer across the particle boundary have a low impact on the exit breakthrough curve. Pore diffusion and bed porosity (along with pore porosity) have moderate impact. Average particle radius and bed density have high impacts. Variations in average particle radius impact both the available particle surface area per unit of column volume for mass transfer and the diffusional length down each pore. Therefore, particle radius impacts both the liquid film mass transfer and pore diffusion simultaneously. Once a column volume is specified the bed density sets the total amount of resin contained within the column.

As a general rule if the predicted breakthrough curve does not cross the data near the 50% relative concentration point, then either the isotherm model or the bed density will require adjustments. As demonstrated by the sensitivity studies shown in Figures 10-10 through 10-16, only the variations in bed density shifted the predicted curves significantly at the 50% relative concentration level. All the other parameter variations in essence rotated the curve about the ~50% point.

10.5 Mass Transfer Limitations

Resistances to mass transfer across the liquid film and diffusion down the pores contribute to local non-equilibrium with respect to the adsorption isotherm. When a significant departure exists between the actual cesium concentration on the resin and the predicted value corresponding to the equilibrium adsorption isotherm, the ion-exchange process is said to be mass transfer limited. To estimate the degree of resistance resulting from the mass transfer

processes, a comparison of the nominal case was made to simulations where the liquid film and pore diffusion coefficients were set to very large values (i.e., large values result in negligible mass transfer resistances). Figure 10-18 shows the impact that mass transfer resistances have on the exit breakthrough curve for the lead column.

For the case where both the liquid film and pore diffusion coefficients were set to large values, the resulting breakthrough curve becomes very sharp. The slight spread (i.e., deviation from a square wave) in the breakthrough curve is a direct result of axial dispersion which appears to be a minor component. The 50% breakthrough point occurs at ~317 column volumes as compared to the nominal value of ~314. As mentioned earlier, the 50% breakthrough point is predominately set by the adsorption isotherm.

The results for simulations where only liquid film resistance or pore diffusion resistance is accounted for are also provided in Figure 10-18. From these simulations we see that liquid film resistance is having a negligible impact on the breakthrough curve. However, mass transfer resistance due to pore diffusion has a significant impact on the shape of the breakthrough curve.

10.6 Impact of Feed Concentrations

Operation of the facility is being designed to handle a range in inlet feed conditions. For an approximately fixed inlet concentration of 5 M sodium, a range of inlet concentrations of potassium and cesium will be experienced. The previous series of results presented above in this section assumed a fixed inlet feed of 5 M sodium, 0.090 M potassium, and 6.089×10^{-5} M cesium. Below the impact on breakthrough curves and column performance is addressed for a range of potassium and cesium inlet feed conditions believed to span the expected range of intended operations.

10.6.1 Impact of Potassium Feed Concentration

As discussed in Section 4, potassium competes with cesium (with lesser selectivity) for available adsorption sites. Using the Freundlich/Langmuir Hybrid adsorption isotherm model, Eq. (4-21), and the fitted parameters to that model provided in Table 4-7, a sensitivity study was performed to estimate the impact on column performance resulting from variations in potassium inlet feed concentration.

The nominal value in potassium feed presented in earlier results was set to 0.090 M. Potassium feed concentrations of 0.250 and 0.450 M are also considered (where the 0.450 M value represents an anticipated upper bound). Both lead and lag column cesium breakthrough curves for these three potassium feed concentration levels are presented in Figure 10-19. The number of column volumes required to reach 50% cesium breakthrough in the lead column and to reach the lag column exit cesium criterion are listed in Table 10-7. As seen in Figure 10-19 and tabulated in Table 10-7, the inlet feed concentration of potassium has a significant impact on overall performance of the two columns. The results shown in Figure 10-19 and tabulated in Table 10-7 refer to a case where both columns were initially cesium free (e.g., the first cycle).

As discussed in Section 4.6, with respect to Eq. (4-21), the beta parameter for cesium becomes dependent upon the potassium and sodium feed concentrations when using the effective single-component approach. Variations in inlet potassium or sodium feed concentrations (or their associated selectivity coefficients) that result in the same computed beta parameter for cesium result in identical cesium breakthrough curves. Therefore, using results from the above potassium sensitivity study the impact of variations in either the selectivity coefficients or the sodium feed concentration can be estimated.

10.6.2 Impact of Cesium Feed Concentration

For a linear cesium adsorption isotherm model, a linear transport equation is obtained where the inlet feed concentration can be factored out normalizing the transport equation. Under such conditions the normalized breakthrough curves (i.e., C/C_0 versus column volume plots) will show no dependence on cesium feed concentration. However, as can be seen by Eq. (4-21), the chosen cesium adsorption isotherm model is nonlinear and a dependence on inlet cesium conditions are expected. A sensitivity study was performed to estimate the impact on column performance resulting from variations in cesium inlet feed concentrations.

The nominal value in cesium feed presented in earlier results was set to 6.089×10^{-5} M. Cesium feed concentrations of 1.8×10^{-4} M and 3.0×10^{-4} M are also considered (where the 3.0×10^{-4} M value represents an anticipated upper bound). Both lead and lag column cesium breakthrough curves for these three cesium feed concentration levels are presented in Figure 10-20. The number of column volumes required to reach 50% cesium breakthrough in the lead column and to reach the lag column exit cesium criterion are listed in Table 10-8. As seen in Figure 10-20 and tabulated in Table 10-8, the inlet feed concentration of cesium has a significant impact on overall performance of the two columns. The results shown in Figure 10-20 and tabulated in Table 10-8 refer to a case where both columns were initially cesium free (e.g., the first cycle).

Table 10-1. Key column parameters for the full-scale facility.

Parameter	Lead column	Lag column
Column diameter, (cm)	77.0	77.0
Active bed length ^a , (cm)	~225.0	~225.0
Active column volume ^a , (L)	~1047.74	~1047.74
Headspace length, (cm)	225.0	225.0
Superficial flow velocity, (cm/min)	11.3	11.3
Volumetric flow rate, (ml/min)	52,619.9	52,619.9
Volumetric flow rate, (CV/hr)	3.0	3.0
Column feed concentrations: Cesium [M] Potassium [M] Sodium [M]	6.089x10 ⁻⁵ 0.090 5.001	6.089x10 ⁻⁵ 0.090 5.001
Column exit cesium conc. criterion (case 1) ^b , (μCi/ml and [M])	None	< 1.0 [< 3.37528x10 ⁻⁷]
Column exit cesium conc. criterion (case 2) ^b , (μCi/ml and [M])	None	< 0.0874 [< 2.9500x10 ⁻⁸]

^a Swelling due to feed ionic strength variations can alter the original bed geometry and the numbers provided assume the bed's approximate size during 5 M Na⁺ loading conditions.

^b An isotopic mixture on a mole basis of 25% ¹³⁷Cs⁺ and 75% ¹³³Cs⁺ is assumed, where use is made of the conversion factor 1 μCi/ml equals 8.4382x10⁻⁸ M of ¹³⁷Cs⁺. A radioactive half-life of 30.17 years for ¹³⁷Cs⁺ is used.

Table 10-2. Estimated overall column cesium loadings at the end of the first and fifth cycles.

Column	Cycle number	Lag column exit criterion, 1 $\mu\text{Ci/ml}$	Lag column exit criterion, 0.0874 $\mu\text{Ci/ml}$
Lead	1	99%	97%
Lag	1	35%	17%
Lead	5	97%	91%
Lag	5	22%	9%

Table 10-3. Estimated cesium decontamination factors (D.F.) on a cumulative basis as a function of the number of cycles performed.

Number of cycles performed	Lag column exit criterion, 1 $\mu\text{Ci/ml}$		Lag column exit criterion, 0.0874 $\mu\text{Ci/ml}$	
	Column volumes	D.F.	Column volumes	D.F.
1	423	2,878	360	36,480
2	708	2,223	625	27,956
3	1005	1,990	905	24,891
4	1306	1,870	1191	23,320
5	1611	1,795	1478	22,471
6	1915	1,756	1102	21,935

Table 10-4. Estimated cesium decontamination factors (D.F.) on a per cycle basis as a function of the number of cycles performed.

Number of cycles performed	Lag column exit criterion, 1 $\mu\text{Ci/ml}$		Lag column exit criterion, 0.0874 $\mu\text{Ci/ml}$	
	Column volumes	D.F.	Column volumes	D.F.
1	423	2,878	360	36,480
2	708	1,665	625	21,231
3	1005	1,590	905	20,010
4	1306	1,557	1191	19,441
5	1611	1,532	1478	19,518
6	1915	1,530	1102	19,509

Table 10-5. Sensitivity of volumetric flow rate on the exit cesium breakthrough curve for the lead column.

Volumetric Flow Rate (CV/hr)	Column Volumes Required to Reach 50% Breakthrough in Lead Column (CV)	Column Volumes Required to Reach Exit Criterion in Lag Column ^a (CV)
1.5	316	493
2.25	315	455
3.0	314	423
4.5	312	373
6.0	307	334

^a Each simulation was run up to the lag column exit cesium concentration of 1 $\mu\text{Ci/ml}$.

Table 10-6. Sensitivity variables studied and their level of impact on exit cesium breakthrough curves.

Parameter	Nominal Value	Variation	Sensitivity
Axial Dispersion	3.6 cm ² /min	10% and 1000% nominal	Very Low
Mass Transfer	0.2046 cm/min	±50%	Low
Pore Diffusion	3.395×10 ⁻⁴ cm ² /min (70% D _∞)	±43%	Moderate
Bed Porosity	0.45	±0.10	Moderate
Flow Rate	3.0 CV/hr	1.5 to 6.0 CV/hr	Moderate
Particle Radius	332 μm	±100 μm	High
Bed Density	0.335 g/ml	±16%	Very High

Table 10-7. Sensitivity of potassium feed concentration on the number of column volumes required to reach 50% breakthrough in the lead column and to reach the lag column exit cesium criteria.^a

Liquid K ⁺ Feed Concentration [M]	Column Volumes Required to Reach 50% Breakthrough in Lead Column (CV)	Column Volumes Required to Reach lag column exit cesium criterion of 1 μCi/ml (CV)	Column Volumes Required to Reach lag column exit cesium criterion of 0.0874 μCi/ml (CV)
0.090	314	423	360
0.250	228	296	251
0.450	170	215	182

^a The column volume numbers listed refer to a case where both columns were initially cesium free (e.g., the first cycle of operation only).

Table 10-8. Sensitivity of cesium feed concentration on the number of column volumes required to reach 50% breakthrough in the lead column and to reach the lag column exit cesium criteria.^a

Liquid Cs ⁺ Feed Concentration [M]	Column Volumes Required to Reach 50% Breakthrough in Lead Column (CV)	Column Volumes Required to Reach lag column exit cesium criterion of 1 $\mu\text{Ci/ml}$ (CV)	Column Volumes Required to Reach lag column exit cesium criterion of 0.0874 $\mu\text{Ci/ml}$ (CV)
6.089×10^{-5}	314	423	360
1.800×10^{-4}	237	357	307
3.000×10^{-4}	190	316	281

^a The column volume numbers listed refer to a case where both columns were initially cesium free (e.g., the first cycle of operation only).

Figure 10-1. Basic flowsheet for full-scale ion exchange facility for removal of cesium using the SuperLig[®] 644 resin.

Figure 10-2. VERSE-LC model representing the full-scale flowsheet for removal of cesium using the SuperLig[®] 644 resin.

Figure 10-3. VERSE-LC model best estimate predictions for multiple cycling of the full-scale facility for the removal of cesium using the SuperLig® 644 resin.

Figure 10-4. VERSE-LC model best estimate predictions for cycle number 5 of the full-scale facility for the removal of cesium using the SuperLig® 644 resin.

Figure 10-5. VERSE-LC model best estimate prediction of the cesium column profiles for all cycles of the full-scale facility for the removal of cesium using the SuperLig[®] 644 resin.

Figure 10-6. VERSE-LC model predictions for multiple cycling of the full-scale facility for the removal of cesium using the SuperLig[®] 644 resin at a lower exit criterion.

Figure 10-7. VERSE-LC model prediction of the cesium column profiles for all cycles of the full-scale facility for the removal of cesium using the SuperLig® 644 resin at a lower exit criterion.

Figure 10-8. Variation of the overall cesium decontamination factors on a cumulative basis with respect to the number of operating cycles assumed for each lag column exit criterion.

Figure 10-9. Variation of the overall cesium decontamination factors on a per cycle basis for each lag column exit criterion.

Figure 10-10. Sensitivity of full-scale column breakthrough curve to axial dispersion.

Figure 10-11. Sensitivity of full-scale column breakthrough curve to mass transfer film coefficient.

Figure 10-12. Sensitivity of full-scale column breakthrough curve to pore diffusivity.

Figure 10-13. Sensitivity of full-scale column breakthrough curve to bed and particle porosity.

Figure 10-14. Sensitivity of full-scale column breakthrough curve to particle radius.

Figure 10-15. Sensitivity of full-scale column breakthrough curve to bed density.

Figure 10-16. Sensitivity of volumetric flow rate on the exit cesium breakthrough curve for the lead column.

Figure 10-17. The number of column volumes required to reach 50% cesium breakthrough on the lead column and 1 $\mu\text{Ci/ml}$ cesium exit criterion on the lag column.

Figure 10-18. Impact of mass transfer resistance on the exit cesium breakthrough curve for the lead column.

Figure 10-19. Impact of potassium feed concentration on the exit cesium breakthrough curves for the lead and lag columns given an initially cesium free set of columns.

Figure 10-20. Impact of cesium feed concentration on the exit cesium breakthrough curves for the lead and lag columns given an initially cesium free set of columns.

11.0 Design Check

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6/19/00
Date

11.0 References

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Appendix A (Isotherm Model Improvement Studies)

As mentioned in Section 4, several attempts were made to improve on the ternary homovalent isotherm model, with the objective to significantly reduce correlation uncertainties associated with the algebraic model. Unfortunately, no major reduction in correlation uncertainty was achieved. Some of the attempts made were by:

- Significantly adding more K_d data to the database;
- Adding a fourth competing cation (i.e., the hydrogen ion H^+);
- Looking at the available column tests where analytical measurements were made on the eluate to help in determining which resident cations are potential competitors (e.g., uranyl [UO_2^{+2}]);
- Allowing the various material batches to have different total cesium ion-exchange capacities;
- Allowing some functional dependence in the average selectivity coefficients to account for solution non-idealities (through liquid-phase activity coefficients);
- Incorporating pH effect K_d data directly into the database used for fitting purposes; and
- Omitting various subsets of K_d data from the database based on statistical outlier arguments.

Below we discuss some of these attempts and present additional data to the K_d database for any future isotherm model development activities. Below the results associated with the updated isotherm model efforts are also discussed.

A.1 Comparison to Earlier Isotherm Data

In the 1995 to 1996 timeframe, experimental evaluation studies were performed to assess numerous ion exchange materials (including SuperLig[®] 644) as potential candidates for cesium removal from Hanford waste alkaline supernates (Brown et al., 1995a; Brown et al., 1995b; Brown et al., 1996; and Bray et al., 1995). We became aware of this additional batch equilibrium isotherm data after the majority of analyses presented in this report were completed. For completeness a comparison of the earlier data with respect to the database discussed in Section 4 is provided in this appendix. The additional K_d data sets are summarized in Table A-1 and the data points are listed in Table A-2.

Total cesium loadings and distribution coefficients for all data (117 data points; limited to 20-27 °C temperature range) are shown in Figure A-1 and A-2, respectively. As shown in Figure A-1, cesium loadings in excess of the vendors quoted amount are observed where a total cesium ion exchange capacity of ~1 mmole/g appears more appropriate. The higher cesium loading data corresponds to the earlier resin material with a lower bed density as one might expect.

To assist in separating out the variation in sodium and potassium concentrations, the cesium K_d values are plotted with respect to the ratio of total cesium -to- sodium plus potassium levels. As

shown in Figure A-2, bands of data (though overlapping due to batch and analytical uncertainties) emerge.

A.2 The Impact of Hydronium Ion on Adsorption

A K_d study where the impact associated with varying pH was performed and reported by Bray et al., 1995 (see Figure 3.6 of that report). An initial solution at 25°C containing 5 M Na^+ and 5×10^{-4} M Cs^+ was contacted with SuperLig[®] 644 resin at various pH conditions. As reported by Bray et al. (1995) the cesium K_d value for SuperLig[®] 644 resin drops off rapidly in a <13 pH environment illustrating the elutability of this resin when cesium loaded.

To make use of this pH data the final liquid-phase cesium concentration for each data point must be known. The initial high alkaline solution test data are discussed in Brown et al. (1995b) where during each K_d batch contact test 0.1 g of resin was placed in 15 ml of solution. The final cesium liquid-phase concentration can be computed using

$$C_{\text{final}}^{\text{Cs}} = \frac{C_{\text{initial}}^{\text{Cs}}}{1 + K_d \frac{m_{\text{resin}} F}{V_{\text{sol'n}}}}, \quad (\text{A-1})$$

where the as received resin mass is adjusted by the F factor. The results of this computation are provided in Table A-3 where the measured K_d value and cesium loadings are also listed. The results of Table A-3 are plotted in Figures A-3 and A-4 for K_d value and cesium loadings, respectively. The cesium distribution coefficient exhibits two basic regions as shown in Figure A-3. For pH levels greater than ~7 the K_d value continues to increase (even beyond pH of 14) and for pH levels below ~7 the K_d value is essentially a constant. The impact on cesium loading can be seen in Figure A-4 where for pH values above ~11 only modest changes occur with varying pH followed by a rapid drop off for pH values between 11 and 7. Based on this limited data set acidity levels in excess of pH = 5 do not result in further cesium elution of the resin.

A.3 Potential Competing Cations

To further investigate the observed data scatter between the equilibrium data and the isotherm model, the feed and eluate analytical results for three of the column tests were considered (i.e., DM-A, DM-B, and DM-C). The mole ratios between cations in the eluate versus their original ratios in the column feeds should provide some level of information as to potential competing cations for adsorption onto the SuperLig[®] 644 resin.

After the initial loading of the lead columns, the columns were washed and then eluted using several column volumes of 0.5 M HNO_3 solution (for experimental details see Hassan et al., 1997a; Hassan et al., 1997d; and Hassan et al., 1997b). The eluate from each lead column was measured for several cations where the concentration of these cations result from residual feed liquid remaining within the pores after the wash cycle and feed left on the column de-adsorption of species during ion-exchange with the hydronium cation. The potential and varying amount of residual complicates the analysis and introduces additional errors in the interpretations.

For the three-column tests mention above the available mole ratios (with respect to sodium and with respect to cesium) were computed. Then the ratio of eluate -to- feed for these mole ratios was computed and is provided in Table A-4. The results from duplicate eluate samples are also provided in Table A-4. Values in excess of unity might indicate some level of affinity to adsorb onto the resin. Unfortunately, no conclusive list of competing cations was determined from these ratios. Also, it is possible that the presence of metals in the eluate was due to precipitation, not ion-exchange on the resin. If the metals had precipitated, they would have been captured on the glass wool on top of the resin, then re-dissolved during elution. Recent studies of the eluate indicate that chromium may also be competing for adsorption sites.

In Table A-4 uranium (probably in the form of uranyl, UO_2^{+2}) demonstrates a ratio even larger than cesium; however, uranium concentrations are not generally reported in the various column and batch equilibrium test reports. Prior to publication of the report on Envelope C, it was not known that this resin extracted UO_2^{+2} from solution.

A.4 The 4-Component Homovalent Isotherm Model

As mentioned earlier to perform elution modeling the pH effect on resin loadings must be built into the isotherm model. One simple extension to the ternary homovalent isotherm model would be to include hydronium into the cation-exchange competition. Hydronium concentrations (obtained from free hydroxyl ion $[\text{OH}^-]$ concentration) are reported in most of the batch equilibrium tests. Tables A-3 and A-5 list the data sets where hydronium concentrations are available.

The simplest upgrade to the ternary homovalent isotherm model is to add the following surface mass-action expression to the other competing exchange processes

The 4-component (Cs^+ , K^+ , Na^+ , and H^+) homovalent isotherm model for cesium takes the form

$$q_{\text{Cs}^+} = \frac{c_{\text{pCs}^+}}{c_{\text{pCs}^+} + \tilde{K}_{21}c_{\text{pK}^+} + \tilde{K}_{31}c_{\text{pNa}^+} + \tilde{K}_{41}c_{\text{pH}^+}}. \quad (\text{A-3})$$

A non-linear regression analysis based on the maximum likelihood principle (see Anderson et al., 1978) was performed on Eq. (A-3) along with the Cs loading database highlighted in Tables A-3 and A-5. The results of the fitting process are given in Tables A-6 and A-7 for the estimated selectivity coefficients and their cross-correlation coefficients, respectively.

The predicted selectivity coefficients produced for the 4-component model differ significantly from those for the ternary model (see Table 4-4 of Section 4). For the 4-component model the resin has roughly the same level of affinity for potassium as it does for sodium. This is somewhat consistent with the sodium and potassium ratios presented in Table A-4 for feed-to-eluate comparison. As expected and designed into the resin, a significant affinity for hydronium versus cesium exists. As for the ternary model a reasonable amount of cross-correlation exists

between potassium and sodium for the 4-component model as shown in Table A-7. However, the cross-correlation of either potassium or sodium with hydronium is small.

Unfortunately, the 4-component model only provides a small decrease in overall residuals between the data and the model. Other competing cations (e.g., uranyl) are probably having significant impacts, while smaller impacts may also be occurring due to measurement uncertainties.

Table A-1. Adsorption isotherm “K_d” data for Cesium-SuperLig® 644 system (batch contact test data not used in computing isotherm model parameter estimates; data made available after model created).

Test ID	SL644 batch ID	Simulated waste envelope & tank #	Mole % ¹³⁷ Cs	Range of Cs ⁺ [M]	K ⁺ [M]	Na ⁺ [M]	Maximum % Cs loading on resin	Comments
BN-SIM	10-SM-171 made Nov 1994	Simulant A 70% AW-101 20% AP-106 10% AP-102	Trace amount	9.22x10 ⁻⁹ to 9.50x10 ⁻² M	0.475	0.2 to 5.0	233.4%	Comparison of 8 ion exchange materials; 72 hr contact time used
BN-ACT	10-SM-171 made Nov 1994	Sample A 70% AW-101 20% AP-106 10% AP-102	25%	1.53x10 ⁻⁷ to 4.43x10 ⁻² M	0.478	5.01	222.2%	Comparison of 8 ion exchange materials; 72 hr contact time used
BN-SIM-A	na	Simulant A NCAW	Trace amount	4.3x10 ⁻⁵ to 5.4x10 ⁻⁵ M	0.12	5.00	19.5%	Comparison of 3 ion exchange materials; 16 hr contact time used
BN-SIM-RAD	na	Simulant A NCAW	Trace amount	3.23x10 ⁻⁶ to 9.62x10 ⁻³ M	0.12	5.00	137.6%	Chemical and radiation stability study
BN-SIM-pH	na	Simulant A NCAW	Trace amount	4.30x10 ⁻⁵ to 4.86x10 ⁻⁴ M	0.12	5.00	19.5%	Effect of pH on cesium loading study

Table A-2. Additional equilibrium data for Cesium on SuperLig® 644 based on batch contact tests (not used in the isotherm model parameter fitting).

Sample Description	Liquid Na ⁺ [M]	Liquid K ⁺ [M]	Liquid Cs ⁺ [M]	K _d [ml/g]	Solid Cs ⁺ [mmole/g]	Cs ⁺ loading ^a [-]
BN-SIM-0.2	0.200000	0.475000	2.00000E-03	230.50	4.6100E-01	1.3831E+00
BN-SIM-0.2	0.200000	0.475000	2.04123E-03	221.50	4.5213E-01	1.3565E+00
BN-SIM-0.2	0.200000	0.475000	2.65322E-05	3492.00	9.2651E-02	2.7798E-01
BN-SIM-0.2	0.200000	0.475000	2.58933E-05	3575.00	9.2569E-02	2.7773E-01
BN-SIM-0.2	0.200000	0.475000	1.11111E-06	9853.00	1.0948E-02	3.2847E-02
BN-SIM-0.2	0.200000	0.475000	1.11111E-06	9852.00	1.0947E-02	3.2843E-02
BN-SIM-0.2	0.200000	0.475000	9.87654E-08	12280.00	1.2128E-03	3.6389E-03
BN-SIM-0.2	0.200000	0.475000	9.76563E-08	12400.00	1.2109E-03	3.6332E-03
BN-SIM-0.2	0.200000	0.475000	9.22084E-09	12710.00	1.1720E-04	3.5163E-04
BN-SIM-0.2	0.200000	0.475000	9.33271E-09	12520.00	1.1685E-04	3.5057E-04
BN-SIM-1.0	1.000000	0.475000	1.59974E-02	38.06	6.0886E-01	1.8268E+00
BN-SIM-1.0	1.000000	0.475000	1.59898E-02	38.27	6.1193E-01	1.8360E+00
BN-SIM-1.0	1.000000	0.475000	7.55858E-04	250.80	1.8957E-01	5.6876E-01
BN-SIM-1.0	1.000000	0.475000	7.83699E-04	241.60	1.8934E-01	5.6808E-01
BN-SIM-1.0	1.000000	0.475000	1.68520E-05	1775.00	2.9912E-02	8.9746E-02
BN-SIM-1.0	1.000000	0.475000	1.71733E-05	1770.00	3.0397E-02	9.1199E-02
BN-SIM-1.0	1.000000	0.475000	1.11707E-06	2983.00	3.3322E-03	9.9976E-03
BN-SIM-1.0	1.000000	0.475000	1.15141E-06	2869.00	3.3034E-03	9.9112E-03
BN-SIM-1.0	1.000000	0.475000	1.01286E-07	3306.00	3.3485E-04	1.0047E-03
BN-SIM-1.0	1.000000	0.475000	1.03810E-07	3189.00	3.3105E-04	9.9325E-04
BN-SIM-3.0	3.000000	0.475000	5.42692E-02	13.15	7.1364E-01	2.1411E+00
BN-SIM-3.0	3.000000	0.475000	5.42888E-02	13.02	7.0684E-01	2.1207E+00
BN-SIM-3.0	3.000000	0.475000	4.61538E-03	65.45	3.0208E-01	9.0632E-01
BN-SIM-3.0	3.000000	0.475000	4.61538E-03	64.97	2.9986E-01	8.9967E-01
BN-SIM-3.0	3.000000	0.475000	2.01884E-04	477.20	9.6339E-02	2.8905E-01
BN-SIM-3.0	3.000000	0.475000	1.96335E-04	463.80	9.1060E-02	2.7321E-01
BN-SIM-3.0	3.000000	0.475000	6.52174E-06	1387.00	9.0457E-03	2.7140E-02
BN-SIM-3.0	3.000000	0.475000	6.52174E-06	1345.00	8.7717E-03	2.6318E-02
BN-SIM-3.0	3.000000	0.475000	5.45455E-07	1861.00	1.0151E-03	3.0456E-03
BN-SIM-3.0	3.000000	0.475000	5.45455E-07	1859.00	1.0140E-03	3.0423E-03
BN-SIM-5.0	5.000000	0.475000	9.48947E-02	8.20	7.7804E-01	2.3344E+00

Sample Description	Liquid Na ⁺ [M]	Liquid K ⁺ [M]	Liquid Cs ⁺ [M]	K _d [ml/g]	Solid Cs ⁺ [mmole/g]	Cs ⁺ loading ^a [-]
BN-SIM-5.0	5.000000	0.475000	9.49668E-02	8.07	7.6610E-01	2.2985E+00
BN-SIM-5.0	5.000000	0.475000	7.85299E-03	41.59	3.2661E-01	9.7992E-01
BN-SIM-5.0	5.000000	0.475000	7.82595E-03	42.68	3.3401E-01	1.0021E+00
BN-SIM-5.0	5.000000	0.475000	3.69822E-04	268.10	9.9149E-02	2.9748E-01
BN-SIM-5.0	5.000000	0.475000	3.67647E-04	271.00	9.9632E-02	2.9893E-01
BN-SIM-5.0	5.000000	0.475000	1.45180E-05	940.60	1.3656E-02	4.0971E-02
BN-SIM-5.0	5.000000	0.475000	1.48412E-05	936.10	1.3893E-02	4.1683E-02
BN-SIM-5.0	5.000000	0.475000	1.03284E-06	1439.00	1.4863E-03	4.4592E-03
BN-SIM-5.0	5.000000	0.475000	1.01523E-06	1448.00	1.4701E-03	4.4106E-03
BN-ACT-5.0	5.010000	0.478000	4.28205E-02	17.30	7.4079E-01	2.2226E+00
BN-ACT-5.0	5.010000	0.478000	4.43363E-02	11.90	5.2760E-01	1.5830E+00
BN-ACT-5.0	5.010000	0.478000	3.36242E-03	65.60	2.2057E-01	6.6179E-01
BN-ACT-5.0	5.010000	0.478000	3.36242E-03	65.60	2.2057E-01	6.6179E-01
BN-ACT-5.0	5.010000	0.478000	1.33245E-04	358.00	4.7702E-02	1.4312E-01
BN-ACT-5.0	5.010000	0.478000	1.32540E-04	360.00	4.7714E-02	1.4316E-01
BN-ACT-5.0	5.010000	0.478000	3.15094E-05	532.00	1.6763E-02	5.0294E-02
BN-ACT-5.0	5.010000	0.478000	3.15094E-05	533.00	1.6795E-02	5.0389E-02
BN-ACT-5.0	5.010000	0.478000	1.01829E-05	805.00	8.1973E-03	2.4594E-02
BN-ACT-5.0	5.010000	0.478000	1.01008E-05	811.00	8.1918E-03	2.4578E-02
BN-ACT-5.0	5.010000	0.478000	1.53211E-07	1150.00	1.7619E-04	5.2863E-04
BN-ACT-5.0	5.010000	0.478000	1.53211E-07	1150.00	1.7619E-04	5.2863E-04
BN-SIM-5.0-A	5.000000	0.120000	5.40000E-05	1176.00	6.3504E-02	1.9053E-01
BN-SIM-5.0-A	5.000000	0.120000	4.30000E-05	1509.00	6.4887E-02	1.9468E-01
BN-SIM-5.0-RAD	5.000000	0.120000	9.61538E-03	47.70	4.5865E-01	1.3761E+00
BN-SIM-5.0-RAD	5.000000	0.120000	8.47458E-04	145.50	1.2331E-01	3.6995E-01
BN-SIM-5.0-RAD	5.000000	0.120000	5.88235E-05	500.00	2.9412E-02	8.8244E-02
BN-SIM-5.0-RAD	5.000000	0.120000	3.22581E-06	1454.50	4.6919E-03	1.4077E-02

^a The Cesium loadings represent the fraction of resin sites occupied by total cesium where the total cation exchange capacity of the resin was assumed constant and set to the value 0.3333 mmole_{Cs}/g_{resin}.

Table A-3. Measured pH effect on K_d values for Cesium on SuperLig[®] 644 based on batch contact tests (Bray et al., 1995).

Sample Description	Liquid H ⁺ [M]	Liquid Na ⁺ [M]	Liquid K ⁺ [M]	Liquid Cs ⁺ [M]	Solid Cs ⁺ [mmole/g]	K_d [ml/g]
BN-SIM-A ^a	5.95238E-15	5.00	0.12	5.40000E-05	6.35040E-02	1176.00
BN-SIM-A ^a	5.95238E-15	5.00	0.12	4.30000E-05	6.48870E-02	1509.00
BY-SIM-A-pH	5.49541E-13	5.00	0.12	1.38381E-04	5.42429E-02	391.982
BY-SIM-A-pH	1.00000E-09	5.00	0.12	3.85518E-04	1.71723E-02	44.543
BY-SIM-A-pH	1.48594E-09	5.00	0.12	3.85518E-04	1.71723E-02	44.543
BY-SIM-A-pH	7.76247E-09	5.00	0.12	4.59100E-04	6.13497E-03	13.363
BY-SIM-A-pH	2.94442E-08	5.00	0.12	4.71969E-04	4.20463E-03	8.909
BY-SIM-A-pH	8.95365E-08	5.00	0.12	4.71969E-04	4.20463E-03	8.909
BY-SIM-A-pH	1.25026E-07	5.00	0.12	4.71969E-04	4.20463E-03	8.909
BY-SIM-A-pH	2.71644E-07	5.00	0.12	4.71969E-04	4.20463E-03	8.909
BY-SIM-A-pH	5.29663E-07	5.00	0.12	4.71969E-04	4.20463E-03	8.909
BY-SIM-A-pH	1.74181E-07	5.00	0.12	4.85580E-04	2.16294E-03	4.454
BY-SIM-A-pH	7.39605E-07	5.00	0.12	4.85580E-04	2.16294E-03	4.454
BY-SIM-A-pH	2.89734E-05	5.00	0.12	4.85580E-04	2.16294E-03	4.454
BY-SIM-A-pH	4.51856E-05	5.00	0.12	4.85580E-04	2.16294E-03	4.454
BY-SIM-A-pH	1.37404E-04	5.00	0.12	4.85580E-04	2.16294E-03	4.454
BY-SIM-A-pH	1.01625E-03	5.00	0.12	4.85580E-04	2.16294E-03	4.454
BY-SIM-A-pH	5.55904E-02	5.00	0.12	4.85580E-04	2.16294E-03	4.454

^a The original alkaline batch tests as report by Brown et al. (1995b).

Table A-4. Ratio of eluate-to-feed mole ratios for the various measured cations in the feed and eluted solutions obtained during several column tests^a.

Cation ratios	DM-A eluate- 1/feed	DM-A eluate- 2/feed	DM-B eluate- 1/feed	DM-B eluate- 2/feed	DM-C eluate- 1/feed	DM-C eluate- 2/feed
<i>Na ratios</i>						
Na/Na	1.000	1.000	1.000	1.000	1.000	1.000
Al/Na	0.920	0.917	0.567	0.553	99.656	50.535
Ca/Na	9.021	8.769	83.182	11.634	4.190	4.076
Cd/Na	7.269	3.084				
Cr/Na	0.993	0.755	0.616	0.606	21.927	19.681
Fe/Na	3.074	1.394			23.387	22.704
Mo/Na	2.857	2.060				
Ni/Na	15.943	4.906				
K/Na	1.112	1.078	0.305	0.272		
Pb/Na	4.408	3.531			10.432	4.976
Si/Na	5.661	3.220	3.067	0.606		
Sn/Na	1.060	0.644				
Zn/Na	5.539	1.880			36.223	26.370
Zr/Na	6.981	6.610				
K/Na	1.076	1.231	1.141	1.134	4.503	4.738
U/Na			260.646	259.612		
Cs/Na	9.278	10.702	128.188	129.202	713.766	744.545
<i>Cs ratios</i>						
Na/Cs	0.108	0.093	0.008	0.008	0.001	0.001
Al/Cs	0.099	0.086	0.004	0.004	0.140	0.068
Ca/Cs	0.972	0.819	0.649	0.090	0.006	0.005
Cd/Cs	0.784	0.288				
Cr/Cs	0.107	0.071	0.005	0.005	0.031	0.026
Fe/Cs	0.331	0.130			0.033	0.030
Mo/Cs	0.308	0.193				
Ni/Cs	1.718	0.458				
K/Cs	0.120	0.101	0.002	0.002		
Pb/Cs	0.475	0.330	0.024	0.005	0.015	0.007
Si/Cs	0.610	0.301	0.024	0.005		
Sn/Cs	0.114	0.060				
Zn/Cs	0.597	0.176			0.051	0.035
Zr/Cs	0.752	0.618				
K/Cs	0.116	0.115	0.009	0.009	0.006	0.006
U/Cs			2.033	2.009		
Cs/Cs	1.000	1.000	1.000	1.000	1.000	1.000

^aThe cation concentrations were measured and reported by Hassan et al. (1997a) for DM-A testing; Hassan et al. (1997d) for DM-B testing; and Hassan et al. (1997b) for DM-C testing.

Table A-5. Liquid-phase hydronium concentrations^a for equilibrium data for Cesium on SuperLig[®] 644 resin.

Sample Description	Liquid H ⁺ [M]	Liquid Na ⁺ [M]	Liquid K ⁺ [M]
WK-563	6.25000E-15	5.000659	0.090804
WK-644BZ	6.25000E-15	5.000659	0.090804
WK-563	6.25000E-15	3.569197	0.064811
PNNL-644BZ-101	3.22581E-15	6.590000	0.610000
PNNL-644BZ-107	1.85185E-14	5.610000	0.024000
DM-A	4.29185E-15	5.070000	0.448000
DM-C	2.53807E-14	5.710000	0.026000
NH-563	4.61681E-15	5.250000	0.121000
IBC-1.0	6.66667E-15	5.185100	1.000000
IBC-0.5	6.66667E-15	5.185100	0.500000
IBC-0.3	6.66667E-15	5.185100	0.300000
IBC-0.1	6.66667E-15	5.185100	0.100000
IBC-0.05	6.66667E-15	5.185100	0.050000
BN-SIM-0.2	4.60829E-15	0.200000	0.475000
BN-SIM-1.0	4.60829E-15	1.000000	0.475000
BN-SIM-3.0	4.60829E-15	3.000000	0.475000
BN-SIM-5.0	4.60829E-15	5.000000	0.475000
BN-SIM-5.0-A	5.95238E-15	5.000000	0.120000
BN-SIM-5.0-RAD	5.95238E-15	5.000000	0.120000

^a Hydronium concentrations are computed from reported measured free hydroxyl ion concentrations.

Table A-6. Estimated selectivity coefficients for the Cesium-SuperLig[®] 644 system based on the 4-component homovalent isotherm model and all available batch contact tests with reported hydroxyl ion concentrations.

Selectivity Coefficient	Definition	Parameter Estimate	Approx. Standard Error	Relative Error (%)
$\tilde{K}_{21}$	K ⁺ to Cs ⁺ selectivity	5.32948×10^{-5}	1.739×10^{-5}	32.6%
$\tilde{K}_{31}$	Na ⁺ to Cs ⁺ selectivity	6.57703×10^{-5}	5.38×10^{-6}	8.2%
$\tilde{K}_{41}$	H ⁺ to Cs ⁺ selectivity	3.054053×10^{-7}	9.55129×10^{-6}	31.3%
$\tilde{K}_{12}$	Cs ⁺ to K ⁺ selectivity	18,763.84	6,117.01	32.6%
$\tilde{K}_{13}$	Cs ⁺ to Na ⁺ selectivity	15,204.43	1,246.76	8.2%
$\tilde{K}_{14}$	Cs ⁺ to H ⁺ selectivity	3.274337×10^{-8}	1.024867×10^{-8}	31.3%

Table A-7. The resulting correlation coefficient matrix for the fit of the selectivity coefficients for the Cesium-SuperLig[®] 644 system based on the 4-component homovalent isotherm model.

Selectivity Coefficient	$\tilde{K}_{21}$	$\tilde{K}_{31}$	$\tilde{K}_{41}$
$\tilde{K}_{21}$	1.0000	-0.3331	-0.0024
$\tilde{K}_{31}$	-0.3331	1.0000	-0.0112
$\tilde{K}_{41}$	-0.0024	-0.0112	1.0000

Figure A-1. Variation in measured total cesium loadings on SuperLig® 644 resin with respect to total liquid cesium concentration. The database shown contains data taken from three different sites and several different batches for a total of 117 data points.

Figure A-2. Variation in measured total cesium distribution coefficient on SuperLig® 644 resin with respect to the ratio of total liquid cesium concentration versus total sodium plus potassium concentrations. The database shown contains data taken from three different sites and several different batches for a total of 117 data points.

Figure A-3. Cesium distribution as a function of equilibrium hydronium concentration at 25 °C for the SuperLig® 644 resin (Bray et al., 1995).

Figure A-4. Cesium loading as a function of equilibrium hydronium concentration at 25 °C for the SuperLig® 644 resin (Bray et al., 1995).

Appendix B (The Basis behind the Lambda Value)

In previous work a loading capacity was computed and documented for each of the small-scale and intermediate-scale column tests. The technique employed was referred to as the "Lambda value" which is a column distribution coefficient that can, under certain limiting conditions, represent the computed number of column volumes to reach 50% exit breakthrough. The Lambda values were calculated from the simple formula:

$$\lambda = \rho_b K_d \quad (\text{B-1})$$

The Lambda value estimates the adsorption affinity of a particular ion on a column volume basis, while the K_d value is the adsorption affinity on a mass of resin basis. For some resin types the Lambda value is also an adequate predictor of 50% exit breakthrough, but care must be taken in its general use.

In some cases the Lambda value provided a consistent value (based on K_d data obtained during batch contact tests) when later compared to the column tests. In other cases significant differences resulted. In this appendix we shall derive the Lambda value illustrating the necessary assumptions which it encompasses. From these assumptions one can infer when and in what direction the Lambda value approach will err.

The Lambda value is based on linear wave theory (Helfferich and Carr, 1993) applied to the single-component solute transport equation where the following assumptions are made:

1. Local chemical equilibrium exists between the pore fluid and its neighboring adsorption sites;
2. Film and pore diffusion rates are not limiting; and
3. Linear isotherms apply over the entire range of contaminant concentrations (i.e., inlet to exit) implying constant K_d values.

When either assumptions 1 or 2 are violated the computed column volumes (i.e., Lambda value) are over predicted. The effect of non-linear isotherms (e.g., Langmuir isotherm) results in compositionally dependent K_d values and under these conditions the Lambda value can either under or over predict the measured column volumes. These assessments can be seen in the following derivation of the Lambda value formula Eq. (B-1).

For porous particles if we assume that the two mass transfer mechanisms (i.e., film and pore diffusion) are very rapid, then the mobile phase (bed) and pore phase transport equations can be combined. Defining the total porosity contained within the ion exchange column as

$$\varepsilon_T \equiv \varepsilon_b + (1 - \varepsilon_b) \varepsilon_p, \quad (\text{B-2})$$

the combined transport equation for both the bed and the pores contained within the porous particles becomes

$$\epsilon_T \frac{\partial c_b}{\partial t} + \epsilon_T u \nabla c_b = \epsilon_T E_b \nabla^2 c_b - \rho_s (1 - \epsilon_T) K_d \frac{\partial c_b}{\partial t}. \quad (B-3)$$

Note that the bed density for the column is defined as

$$\rho_b = \rho_s (1 - \epsilon_T). \quad (B-4)$$

Using Eq. (B-4), Eq. (B-3) can be rearranged into the standard form of the transport equation given by

$$\frac{\partial c_b}{\partial t} + \left[\frac{\epsilon_T u}{\epsilon_T + \rho_b K_d} \right] \nabla c_b = \left[\frac{\epsilon_T E_b}{\epsilon_T + \rho_b K_d} \right] \nabla^2 c_b. \quad (B-5)$$

The bracketed portion of the advective term is typically referred to as the retarded linear interstitial velocity

$$u' = \frac{\epsilon_T u}{\epsilon_T + \rho_b K_d}. \quad (B-6)$$

Wave theory states that the mean value of the concentration profile travels at this retarded species velocity and as such we have

$$u' = \frac{L}{\Delta t_{50\%}} = \frac{\epsilon_T u}{\lambda}. \quad (B-7)$$

Equating Eqs. (B-6) and (B-7) results in the Lambda value formula

$$\lambda = \epsilon_T + \rho_b K_d \rightarrow \rho_b K_d. \quad (B-8)$$

For solute species with a high affinity for the ion exchange resin the total porosity will be negligible when compared to the adsorption term as indicated by the above arrow.

It is easy to see that any steps containing finite rates of mass transfer (such as, non-equilibrium surface adsorption, film diffusion, or pore diffusion) will result in earlier breakthrough curves than predicted by Eq. (B-8). The impact of having a non-linear adsorption isotherm is more difficult to see and can result in under and over predictions of the 50% exit breakthrough.

As discussed in Helfferich and Carr (1993), waves (concentration profiles) and particles (solute molecules) only travel at the same speed for linear isotherms where the tangential and chord of the isotherm are always equal to a constant K_d value. Under these conditions the chosen solute concentration corresponding to the measured value of K_d is unimportant. However, for non-linear isotherms (e.g., the Langmuir isotherm) the K_d value varies with solute concentration and the choice in where to measure an "effective" K_d value becomes important. For a favorable (convex) isotherm as shown in Figure B-1 a K_d value measured at too small a solute concentration results in an over estimated Lambda value, while a K_d value measured at too large a solute concentration results in an under estimated Lambda value.

The adsorption isotherm for the Cesium-SuperLig[®] 644 system is a favorable isotherm that closely follows the Langmuir form. Table B-1 provides a listing of the measured and predicted Lambda values for several of the column tests assessed in the main body of this report. In all cases the chosen solute concentration used to measure a K_d value was less than the inlet concentration to the corresponding column tests. Through Eq. (B-6) an average retarded velocity results from an average "effective" K_d value where the average is computed based on the chord of the isotherm varying from the column inlet to the column exit concentration levels. In addition, for the SuperLig[®] 644 resin some level of mass transfer limiting conditions exists. Thus, typically the Lambda value should be expected to over predict the number of column volumes required to reach 50% breakthrough. As listed in Table B-1, measured Lambda values from 14% to 37% of their computed values were observed.

Table B-1. Comparison of measured versus computed Lambda values for the various batch equilibrium tests and column experiments presented in the main body of this report.

Column Test ID	Column C_s^* inlet conc. C_{b0} [M]	Measured 50% breakthrough point (CV)	Assumed bed density ρ_b (g/ml)	Equilibrium C_s^* conc. C_b where K_d value taken [M]	K_d (ml/g)	Computed Lambda value (CV)	Ratio of Measured to Computed Lambda value (%)	Reference report
WK3	7.01×10^{-5}	240	0.4	3.11×10^{-6}	2070	828	29%	King et al., 2000
NH	6.99×10^{-5}	>180 (only ran to 12% of bk-thru)	0.4	2.09×10^{-7}	1564	626	>29%	Hassan et al., 1999b
DM-A	7.64×10^{-4}	140	0.4	7.85×10^{-5}	944	378	37%	Hassan and McCabe, 1997a
DM-B	8.10×10^{-5}	120	0.4	8.07×10^{-6}	879	352	14%	Hassan and McCabe, 1997d
DM-C	6.33×10^{-5}	150	0.4	7.67×10^{-6}	1024	410	37%	Hassan and McCabe, 1997b

Figure B-1. A favorable isotherm with tangents (dq_i/dc_{pi}) at $c_{pi} = 0$ and at a point $c_{pi} > 0$, and with a chord of that point.

Appendix C (Batch Kinetics Test Input and Output Files)

For reference the VERSE-LC input and output files for the batch kinetics test simulations are provided in this appendix. Several simulations were run. Table C-1 and C-2 contain the computed transient liquid-phase cesium response corresponding to the batch kinetics tests performed and reported by Brown et al. (1996).

Table C-1. Computed transient liquid-phase cesium concentrations based on measured distribution coefficients during the batch kinetics tests of Brown et al., 1996.

Contact time (hrs)	Lambda value (-)	K _d value (ml/g)	Liquid Cesium conc. [M]
0.00011	0.00	0.00	1.000E-04
0.01667	8.50	37.98	8.012E-05
0.03333	3.20	14.30	9.146E-05
0.13000	10.00	44.68	7.740E-05
0.52000	30.00	134.05	5.331E-05
2.00000	75.00	335.12	3.135E-05
20.00000	180.00	804.29	1.599E-05
72.00000	188.00	840.04	1.541E-05
120.00000	190.00	848.97	1.528E-05

Table C-2. Key parameters measured or specified during the batch kinetics tests of Brown et al., 1996.

Parameter	Parameter setting
MW of Cesium	133.0 g/gmole
Initial liquid Cesium conc.	1.0x10 ⁻⁴ M
Initial liquid sample volume	10 ml
Bed density assumed	0.2238 g/ml
F factor	0.9751

VERSE Input for Batch Kinetic Test (Brown et al., 1996)

```

[BN] Simulation of Cs removal on Superlig 644 in batch kinetic test
batch kinetic test data taken from (Brown et al., 1996)
1, 1, 1, 6          ncomp, nelem, ncol-bed, ncol-part
MUUNA              isotherm, axial-disp, film-coef, surf-diff, BC-col  FCUNA
NNNYN              input-only, perfusable, feed-equil, datafile.yio
G                  comp-conc units
1.98185059, 2.54, 0.000000001, 0.0 Length(cm), Diam(cm), Q-flow(ml/min), CSTR-vol(ml)
332.0, 0.989119286, 0.614, 0.0 part-rad(um), bed-void, part-void, sorb-cap()
0.0                initial concentration (M)
S                  COMMAND - conc step change
1, 0.0, 1.0067542e-4, 1, 0.0 spec id, time(min), conc(M), freq, dt(min) 1.14587e-3
V                  COMMAND - viscosity/density change
0.0261255, 1.223549 fluid viscosity(posie), density(g/cm^3)
h                  COMMAND - effluent history dump
1, 1.0, 1.0, 0.25, 0.1 unit op#, ptscale(1-4) filtering
h                  COMMAND - effluent history dump
2, 1.0, 1.0, 0.25, 0.1 unit op#, ptscale(1-4) filtering
D
-1, 0.01, 1, 0.0
D
-1, 0.05, 1, 0.0
D
-1, 0.20, 1, 0.0
D
-1, 0.50, 1, 0.0
D
-1, 1, 1, 0.0
D
-1, 2, 1, 0.0
D
-1, 5, 1, 0.0
D
-1, 10, 1, 0.0
D
-1, 20, 1, 0.0
D
-1, 30, 1, 0.0
D
-1, 50, 1, 0.0
D
-1, 70, 1, 0.0
D
-1, 100, 1, 0.0
D
-1, 200, 1, 0.0
D
-1, 300, 1, 0.0
D
-1, 500, 1, 0.0
D
-1, 800, 1, 0.0
-
end of commands
8000.0, 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 , 1.0d0 , 1.0d0 size exclusion factor
5.0                axial-dispersion (very high value)
3.395d-4           part-pore diffusivities (cm^2/min)
4.85d-4            Brownian diffusivities (cm^2/min) 4.85d-4
100.0              specified film coefficients (very high value)
5.52318537         Multi-Langmuir a (ml/ml B.V.)
0.0                Multi-Langmuir b (ml/mg) 0.0

```

VERSE Output for Batch Kinetic Test (Brown et al., 1996)

```

=====
VERSE v7.80 by R. D. Whitley and N.-H. L. Wang, c1999 PRF
=====
Input file: case
[BN] Simulation of Cs removal on Superlig 644 in batch kinetic test
batch kinetic test data taken from (Brown et al., 1996)
Begin Run: 10:41:42 on 11-24-1999 running under Windows 95/8
Finite elements - axial: 1 particle: 1
Collocation points - axial: 1 particle: 6 => Number of eqns: 26
Inlet species at equilib.? N Perfusable sorbent? N Feed profile only? N
Use Profile File? Y Generate Profile File? N
Axial dispersion correlation: User-specified
Film mass transfer correlation: User-specified
=====
SYSTEM PARAMETERS (at initial conditions):

t(stop)      = 8000.00000 min          dtheta max   = 1.00000 BV
abs. tol.    = .10000E-06             rel. tol.    = .10000E-03
Total Length = 1.98185 cm             D            = 2.54000 cm
Tot. Capacity = .00000 eq/L solid     Col. Vol.    = 10.04219 mL
F            = .00000 mL/min          Uo (linear)   = .00000 cm/min
R            = 332.00000 microns       L/R          = 59.69429
Bed Void frac. = .98912              Pcl. Porosity = .61400
Spec. Area   = .98320 1/cm           Time/BV      = ***** min
Vol CSTRs    = .00000 mL

Component no. = 1
Ke [-]        = .10000E+01
Eb [cm2/min]  = .50000E+01
Dp [cm2/min]  = .33950E-03
Doo [cm2/min] = .48500E-03
kf [cm/min]   = .10000E+03
Ds [cm2/min]  = .00000E+00

Dimensionless Groups:
Re           = .10229E-10
Sc(i)        = .26415E+04
Peb(i)       = .79085E-10
Bi(i)        = .15927E+05
Nf(i)        = .98734E+12
Np(i)        = .18785E+10
Pep(i)       = .31778E-07

Isotherm      = Multi-component Langmuir
Iso. Const. 1 = .55232E+01
Iso. Const. 2 = .00000E+00
Init. Conc.   = .00000E+00
Conc. at eqb. = .00000E+00
Conc. units   = mg/mL
=====
COMMAND LIST:
1: Step conc. of component 1 at .0000 min to .1007E-03 mg/mL
   Execute 1 times, every .0000 mins.
2: User set viscosity to .2613E-01 poise and density to 1.224 g/cm3
3: Monitor conc. history at stream 1. Filename = case.h01
   Output density adjustments:
   1.0 *default abs conc delta, 1.0 *default rel conc delta,
   .25 *default force w/ conc delta, .10 *default force w/o conc delta
4: Monitor conc. history at stream 2. Filename = case.h02
   Output density adjustments:
   1.0 *default abs conc delta, 1.0 *default rel conc delta,
   .25 *default force w/ conc delta, .10 *default force w/o conc delta
5: Dump full profile file at .1000E-01 min
   Execute 1 times, every .0000 mins.
6: Dump full profile file at .5000E-01 min
   Execute 1 times, every .0000 mins.
7: Dump full profile file at .2000 min
   Execute 1 times, every .0000 mins.
8: Dump full profile file at .5000 min
   Execute 1 times, every .0000 mins.

```

9: Dump full profile file at 1.000 min
Execute 1 times, every .0000 mins.
10: Dump full profile file at 2.000 min
Execute 1 times, every .0000 mins.
11: Dump full profile file at 5.000 min
Execute 1 times, every .0000 mins.
12: Dump full profile file at 10.00 min
Execute 1 times, every .0000 mins.
13: Dump full profile file at 20.00 min
Execute 1 times, every .0000 mins.
14: Dump full profile file at 30.00 min
Execute 1 times, every .0000 mins.
15: Dump full profile file at 50.00 min
Execute 1 times, every .0000 mins.
16: Dump full profile file at 70.00 min
Execute 1 times, every .0000 mins.
17: Dump full profile file at 100.0 min
Execute 1 times, every .0000 mins.
18: Dump full profile file at 200.0 min
Execute 1 times, every .0000 mins.
19: Dump full profile file at 300.0 min
Execute 1 times, every .0000 mins.
20: Dump full profile file at 500.0 min
Execute 1 times, every .0000 mins.
21: Dump full profile file at 800.0 min
Execute 1 times, every .0000 mins.

=====

VERSE-LC finished in 226 steps. Average step size 35.40 minutes
End run: 10:41:42 on 11-24-1999
Integrated Areas in History Files:
case.h01 .805403
case.h02 .124543

Appendix D (Column Test Input and Output Files)

For reference the VERSE-LC input and output files for the laboratory-scale test columns are provided in this appendix. Eleven simulations were run. The input and output files for each case are listed below.

VERSE Input for Intermediate-Scale Column (WK3)

```
Simulation of Cs removal on 46.3 ml Superlig 644 column
3 component (Cs, K, Na) isotherm
1, 50, 3, 6
FUWNA
NNNNN
MMM
8.15, 2.69, 4.944, 50.0
342.0, 0.411, 0.671, 0.0
0.0, 0.0, 0.25
V
0.0261255, 1.223549
S
1, 0.0, 7.008d-5, 1, 0.0
h
2, 1.0, 1.0, 0.25, 0.1
D
-1, 2400.0, 1, 0.0
-
4800.0, 1.0
1.0d-7, 1.0d-4
-
1.0d0, 1.0d0, 1.0d0
1.677
3.395d-4, 4.70d-4, 3.67d-4
4.85d-4, 4.70d-4, 3.67d-4
1.0206d-1, 8.5004d-5, 4.4573d-6
1.0, 8.3287d-4, 4.3672d-5
1.0, 1.0, 1.0
1.0, 1.0, 1.0
2.940d-4, 0.0, 0.0

ncomp, nelelem, ncol-bed, ncol-part
isotherm, axial-disp, film-coef, surf-diff, BC-col
input-only, perfusable, feed-equil, datafile.yio
comp-conc units
Length(cm), Diam(cm), Q-flow(ml/min), CSTR-vol(ml)
part-rad(um), bed-void, part-void, sorb-cap()
initial concentrations (M)
COMMAND - viscosity/density change
fluid viscosity(posie), density(g/cm^3)
COMMAND - conc step change
spec id, time(min), conc(M), freq, dt(min)
COMMAND - effluent history dump
unit op#, ptscale(1-4) filtering
end of commands
end time(min), max dt in B.V.s
abs-tol, rel-tol
non-negative conc constraint
size exclusion factor
Brownian diffusivities (cm^2/min)
Brownian diffusivities (cm^2/min)
Freundlich/Langmuir Hybrid a (moles/L B.V.)
Freundlich/Langmuir Hybrid b (1/M)
Freundlich/Langmuir Hybrid Ma (-)
Freundlich/Langmuir Hybrid Mb (-)
Freundlich/Langmuir Hybrid beta (-)
```

VERSE Output for Intermediate-Scale Column (WK3)

```
=====
VERSE v7.80 by R. D. Whitley and N.-H. L. Wang, c1999 PRF
=====
Input file: wk_3x
Simulation of Cs removal on 46.3 ml Superlig 644 column
3 component (Cs, K, Na) isotherm
Begin Run: 08:44:55 on 11-15-1999 running under Windows 95/8
Finite elements - axial: 50 particle: 1
Collocation points - axial: 3 particle: 6 => Number of eqns: 1610
Inlet species at equilib.? N Perfusable sorbent? N Feed profile only? N
Use Profile File? N Generate Profile File? N
Axial dispersion correlation: User-specified
Film mass transfer correlation: Wilson & Geankoplis (1966)
=====
SYSTEM PARAMETERS (at initial conditions):

t(stop) = 4800.00000 min dtheta max = 1.00000 BV
abs. tol. = .10000E-06 rel. tol. = .10000E-03
Total Length = 8.15000 cm D = 2.69000 cm
Tot. Capacity = .00000 eq/L solid Col. Vol. = 46.31824 mL
F = 4.94400 mL/min Uo (linear) = 2.11662 cm/min
R = 342.00000 microns L/R = 238.30409
Bed Void frac. = .41100 Pcl. Porosity = .67100
Spec. Area = 51.66667 1/cm Time/BV = 3.85048 min
```

Vol CSTRs = 50.00000 mL

Component no. = 1
 Ke [-] = .10000E+01
 Eb [cm²/min] = .16770E+01
 Dp [cm²/min] = .33950E-03
 Doo [cm²/min] = .48500E-03
 kf [cm/min] = .93441E-01
 Ds [cm²/min] = .00000E+00

Dimensionless Groups:

Re = .46446E-01
 Sc(i) = .26415E+04
 Peb(i) = .10286E+02
 Bi(i) = .14028E+02
 Nf(i) = .45229E+02
 Np(i) = .74994E+00
 Pep(i) = .31776E+03

Isotherm = Freundlich/Langmuir Hybrid

Iso. Const. 1 = .10206E+00
 Iso. Const. 2 = .10000E+01
 Iso. Const. 3 = .10000E+01
 Iso. Const. 4 = .10000E+01
 Iso. Const. 5 = .29400E-03
 Init. Conc. = .00000E+00
 Conc. at eqb. = .00000E+00
 Conc. units = M

COMMAND LIST:

- 1: User set viscosity to .2613E-01 poise and density to 1.224 g/cm³
- 2: Step conc. of component 1 at .0000 min to .7008E-04 M
 Execute 1 times, every .0000 mins.
- 3: Monitor conc. history at stream 2. Filename = wk_3x.h01
 Output density adjustments:
 1.0 *default abs conc delta, 1.0 *default rel conc delta,
 .25 *default force w/ conc delta, .10 *default force w/o conc delta
- 4: Dump full profile file at 2400. min
 Execute 1 times, every .0000 mins.

=====

VERSE-LC finished in 1323 steps. Average step size 3.628 minutes

End run: 08:47:52 on 11-15-1999

Integrated Areas in History Files:

wk_3x.h01 .155395

VERSE Input for Intermediate-Scale Column (WK4)

Simulation of Cs removal on 44.0 ml Superlig 644 column

3 component (Cs, K, Na) isotherm

1, 50, 3, 6

FUWNA

NNNNN

MMM

3.50, 4.00, 10.25, 50.0

336.0, 0.433, 0.641, 0.0

0.0, 0.0, 0.25

V

0.0261255, 1.223549

S

1, 0.0, 6.429d-5, 1, 0.0

h

2, 1.0, 1.0, 0.25, 0.1

D

-1, 1200.0, 1, 0.0

-

2400.0, 1.0

1.0d-7, 1.0d-4

-

1.0d0, 1.0d0, 1.0d0

1.946

3.395d-4, 4.70d-4, 3.67d-4

4.85d-4, 4.70d-4, 3.67d-4

1.0734d-1, 8.9401d-5, 4.6879d-6

ncomp, nelem, ncol-bed, ncol-part

isotherm, axial-disp, film-coef, surf-diff, BC-col

input-only, perfusable, feed-equil, datafile.yio

comp-conc units

Length(cm), Diam(cm), Q-flow(ml/min), CSTR-vol(ml)

part-rad(um), bed-void, part-void, sorb-cap()

initial concentrations (M)

COMMAND - viscosity/density change

fluid viscosity(posie), density(g/cm³)

COMMAND - conc step change

spec id, time(min), conc(M), freq, dt(min)

COMMAND - effluent history dump

unit op#, ptscale(1-4) filtering

end of commands

end time(min), max dt in B.V.s

abs-tol, rel-tol

non-negative conc constraint

size exclusion factor

dispersion coef (cm²/min) 50% deviation

part-pore diffusivities (cm²/min)

Brownian diffusivities (cm²/min)

Freundlich/Langmuir Hybrid a (moles/L B.V.)

```

1.0      , 8.3287d-4, 4.3672d-5  Freundlich/Langmuir Hybrid b  (1/M)
1.0      , 1.0      , 1.0      Freundlich/Langmuir Hybrid Ma  (-)
1.0      , 1.0      , 1.0      Freundlich/Langmuir Hybrid Mb  (-)
2.940d-4 , 0.0      , 0.0      Freundlich/Langmuir Hybrid beta (-)

```

VERSE Ouput for Intermediate-Scale Column (WK4)

=====

VERSE v7.80 by R. D. Whitley and N.-H. L. Wang, c1999 PRF

=====

Input file: wk_4x

Simulation of Cs removal on 44.0 ml Superlig 644 column

3 component (Cs, K, Na) isotherm

Begin Run: 08:55:40 on 11-15-1999 running under Windows 95/8

Finite elements - axial: 50 particle: 1

Collocation points - axial: 3 particle: 6 => Number of eqns: 1610

Inlet species at equilib.? N Perfusable sorbent? N Feed profile only? N

Use Profile File? N Generate Profile File? N

Axial dispersion correlation: User-specified

Film mass transfer correlation: Wilson & Geankoplis (1966)

=====

SYSTEM PARAMETERS (at initial conditions):

t(stop)	=	2400.00000 min	dtheta max	=	1.00000 BV
abs. tol.	=	.10000E-06	rel. tol.	=	.10000E-03
Total Length	=	3.50000 cm	D	=	4.00000 cm
Tot. Capacity	=	.00000 eq/L solid	Col. Vol.	=	43.98230 mL
F	=	10.25000 mL/min	Uo (linear)	=	1.88376 cm/min
R	=	336.00000 microns	L/R	=	104.16667
Bed Void frac.	=	.43300	Pcl. Porosity	=	.64100
Spec. Area	=	50.62500 l/cm	Time/BV	=	1.85798 min
Vol CSTRs	=	50.00000 mL			

Component no.	=	1
Ke [-]	=	.10000E+01
Eb [cm ² /min]	=	.19460E+01
Dp [cm ² /min]	=	.33950E-03
Doo [cm ² /min]	=	.48500E-03
kf [cm/min]	=	.87840E-01
Ds [cm ² /min]	=	.00000E+00

Dimensionless Groups:

Re	=	.42785E-01
Sc(i)	=	.26415E+04
Peb(i)	=	.33881E+01
Bi(i)	=	.13562E+02
Nf(i)	=	.19081E+02
Np(i)	=	.35815E+00
Pep(i)	=	.29085E+03

Isotherm = Freundlich/Langmuir Hybrid

Iso. Const. 1 = .10734E+00

Iso. Const. 2 = .10000E+01

Iso. Const. 3 = .10000E+01

Iso. Const. 4 = .10000E+01

Iso. Const. 5 = .29400E-03

Init. Conc. = .00000E+00

Conc. at eqb. = .00000E+00

Conc. units M

=====

COMMAND LIST:

- 1: User set viscosity to .2613E-01 poise and density to 1.224 g/cm³
 - 2: Step conc. of component 1 at .0000 min to .6429E-04 M
Execute 1 times, every .0000 mins.
 - 3: Monitor conc. history at stream 2. Filename = wk_4x.h01
Output density adjustments:
1.0 *default abs conc delta, 1.0 *default rel conc delta,
.25 *default force w/ conc delta, .10 *default force w/o conc delta
 - 4: Dump full profile file at 1200. min
Execute 1 times, every .0000 mins.
- =====

VERSE-LC finished in 1406 steps. Average step size 1.707 minutes
 End run: 08:59:34 on 11-15-1999
 Integrated Areas in History Files:
 wk_4x.h01 .790534E-01

VERSE Input for Intermediate-Scale Column (WK1)

```
Simulation of Cs removal on 42.3 ml Superlig 644 column
3 component (Cs, K, Na) isotherm
1, 50, 3, 6      ncomp, nele, ncol-bed, ncol-part
FUWNA           isotherm,axial-disp,film-coef,surf-diff,BC-col
NNNNN          input-only,perfusable,feed-equil,datafile.yio
MMM            comp-conc units
7.45, 2.69 , 34.08, 50.0   Length(cm),Diam(cm),Q-flow(ml/min),CSTR-vol(ml)
332.0, 0.450, 0.614, 0.0   part-rad(um), bed-void, part-void, sorb-cap()
0.0, 0.0 , 0.25           initial concentrations (M)
V                COMMAND - viscosity/density change
0.0261255, 1.223549       fluid viscosity(posie), density(g/cm^3)
S                COMMAND - conc step change
1, 0.0, 5.985d-5, 1, 0.0  spec id, time(min), conc(M), freq, dt(min)
h                COMMAND - effluent history dump
2, 1.0, 1.0, 0.25, 0.1    unit op#, ptscale(1-4) filtering
D
-1, 300.0, 1, 0.0
-
600.0, 1.0        end of commands
1.0d-7, 1.0d-4    end time(min), max dt in B.V.s
-                abs-tol, rel-tol
1.0d0 , 1.0d0 , 1.0d0 non-negative conc constraint
12.424           size exclusion factor
3.395d-4 , 4.70d-4 , 3.67d-4 dispersion coef (cm2/min)
4.85d-4 , 4.70d-4 , 3.67d-4 Brownian diffusivities (cm^2/min)
1.1166d-1, 9.2994d-5, 4.8763d-6 Brownian diffusivities (cm^2/min)
1.0 , 8.3287d-4, 4.3672d-5 Freundlich/Langmuir Hybrid a (moles/L B.V.)
1.0 , 1.0 , 1.0 Freundlich/Langmuir Hybrid b (1/M)
1.0 , 1.0 , 1.0 Freundlich/Langmuir Hybrid Ma (-)
1.0 , 1.0 , 1.0 Freundlich/Langmuir Hybrid Mb (-)
2.940d-4 , 0.0 , 0.0 Freundlich/Langmuir Hybrid beta (-)
```

VERSE Output for Intermediate-Scale Column (WK1)

```
=====
VERSE v7.80 by R. D. Whitley and N.-H. L. Wang, c1999 PRF
=====
Input file: wk_1x
Simulation of Cs removal on 42.3 ml Superlig 644 column
3 component (Cs, K, Na) isotherm
Begin Run: 12:28:26 on 11-12-1999 running under Windows 95/8
Finite elements - axial: 50 particle: 1
Collocation points - axial: 3 particle: 6 => Number of eqns: 1610
Inlet species at equilib.? N Perfusable sorbent? N Feed profile only? N
Use Profile File? N Generate Profile File? N
Axial dispersion correlation: User-specified
Film mass transfer correlation: Wilson & Geankoplis (1966)
=====
SYSTEM PARAMETERS (at initial conditions):

t(stop) = 600.00000 min dtheta max = 1.00000 BV
abs. tol. = .10000E-06 rel. tol. = .10000E-03
Total Length = 7.45000 cm D = 2.69000 cm
Tot. Capacity = .00000 eq/L solid Col. Vol. = 42.33999 mL
F = 34.08000 mL/min Uo (linear) = 13.32578 cm/min
R = 332.00000 microns L/R = 224.39759
Bed Void frac. = .45000 Pcl. Porosity = .61400
Spec. Area = 49.69880 1/cm Time/BV = .55907 min
Vol CSTRs = 50.00000 mL

Component no. = 1
Ke [-] = .10000E+01
```

```

Eb [cm2/min] = .12424E+02
Dp [cm2/min] = .33950E-03
Doo [cm2/min] = .48500E-03
kf [cm/min] = .16567E+00
Ds [cm2/min] = .00000E+00

```

Dimensionless Groups:

```

Re = .31080E+00
Sc(i) = .26415E+04
Peb(i) = .79907E+01
Bi(i) = .26385E+02
Nf(i) = .10229E+02
Np(i) = .10573E+00
Pep(i) = .21224E+04

```

Isotherm = Freundlich/Langmuir Hybrid

```

Iso. Const. 1 = .11166E+00
Iso. Const. 2 = .10000E+01
Iso. Const. 3 = .10000E+01
Iso. Const. 4 = .10000E+01
Iso. Const. 5 = .29400E-03
Init. Conc. = .00000E+00
Conc. at eqb. = .00000E+00
Conc. units M

```

COMMAND LIST:

- ```

1: User set viscosity to .2613E-01 poise and density to 1.224 g/cm3
2: Step conc. of component 1 at .0000 min to .5985E-04 M
 Execute 1 times, every .0000 mins.
3: Monitor conc. history at stream 2. Filename = wk_1x.h01
 Output density adjustments:
 1.0 *default abs conc delta, 1.0 *default rel conc delta,
 .25 *default force w/ conc delta, .10 *default force w/o conc delta
4: Dump full profile file at 300.0 min
 Execute 1 times, every .0000 mins.

```

VERSE-LC finished in 1224 steps. Average step size .4902 minutes

End run: 12:33:02 on 11-12-1999

Integrated Areas in History Files:

wk\_1x.h01 .185582E-01

## VERSE Input for Intermediate-Scale Column (WK2)

Simulation of Cs removal on 42.3 ml Superlig 644 column

3 component (Cs, K, Na) isotherm

1, 50, 3, 6

FUWNA

NNNNN

MMM

7.45, 2.69, 60.25, 50.0

332.0, 0.450, 0.614, 0.0

0.0, 0.0, 0.25

V

0.0261255, 1.223549

S

1, 0.0, 6.089d-5, 1, 0.0

h

2, 1.0, 1.0, 0.25, 0.1

D

-1, 240.0, 1, 0.0

-

480.0, 1.0

1.0d-7, 1.0d-4

-

1.0d0, 1.0d0, 1.0d0

21.76

3.395d-4, 4.70d-4, 3.67d-4

4.85d-4, 4.70d-4, 3.67d-4

1.1166d-1, 9.2994d-5, 4.8763d-6

1.0, 8.3287d-4, 4.3672d-5

1.0, 1.0, 1.0

1.0, 1.0, 1.0

2.940d-4, 0.0, 0.0

ncomp, nelem, ncol-bed, ncol-part

isotherm, axial-disp, film-coef, surf-diff, BC-col

input-only, perfusable, feed-equil, datafile.yio

comp-conc units

Length(cm), Diam(cm), Q-flow(ml/min), CSTR-vol(ml)

part-rad(um), bed-void, part-void, sorb-cap()

initial concentrations (M)

COMMAND - viscosity/density change

fluid viscosity(posie), density(g/cm^3)

COMMAND - conc step change

spec id, time(min), conc(M), freq, dt(min)

COMMAND - effluent history dump

unit op#, ptscale(1-4) filtering

end of commands

end time(min), max dt in B.V.s

abs-tol, rel-tol

non-negative conc constraint

size exclusion factor

dispersion coef (cm2/min)

Brownian diffusivities (cm^2/min)

Brownian diffusivities (cm^2/min)

Freundlich/Langmuir Hybrid a (moles/L B.V.)

Freundlich/Langmuir Hybrid b (1/M)

Freundlich/Langmuir Hybrid Ma (-)

Freundlich/Langmuir Hybrid Mb (-)

Freundlich/Langmuir Hybrid beta (-)

## VERSE Ouput for Intermediate-Scale Column (WK2)

=====

VERSE v7.80 by R. D. Whitley and N.-H. L. Wang, c1999 PRF

=====

Input file: wk\_2x  
 Simulation of Cs removal on 42.3 ml Superlig 644 column  
 3 component (Cs, K, Na) isotherm  
 Begin Run: 12:45:55 on 11-12-1999 running under Windows 95/8  
 Finite elements - axial: 50 particle: 1  
 Collocation points - axial: 3 particle: 6 => Number of eqns: 1610  
 Inlet species at equilib.? N Perfusable sorbent? N Feed profile only? N  
 Use Profile File? N Generate Profile File? N  
 Axial dispersion correlation: User-specified  
 Film mass transfer correlation: Wilson & Geankoplis (1966)

=====

### SYSTEM PARAMETERS (at initial conditions):

|                |   |                   |               |   |                 |
|----------------|---|-------------------|---------------|---|-----------------|
| t(stop)        | = | 480.00000 min     | dtheta max    | = | 1.00000 BV      |
| abs. tol.      | = | .10000E-06        | rel. tol.     | = | .10000E-03      |
| Total Length   | = | 7.45000 cm        | D             | = | 2.69000 cm      |
| Tot. Capacity  | = | .00000 eq/L solid | Col. Vol.     | = | 42.33999 mL     |
| F              | = | 60.25000 mL/min   | Uo (linear)   | = | 23.55863 cm/min |
| R              | = | 332.00000 microns | L/R           | = | 224.39759       |
| Bed Void frac. | = | .45000            | Pcl. Porosity | = | .61400          |
| Spec. Area     | = | 49.69880 1/cm     | Time/BV       | = | .31623 min      |
| Vol CSTRs      | = | 50.00000 mL       |               |   |                 |

Component no. = 1  
 Ke [-] = .10000E+01  
 Eb [cm2/min] = .21760E+02  
 Dp [cm2/min] = .33950E-03  
 Doo [cm2/min] = .48500E-03  
 kf [cm/min] = .20032E+00  
 Ds [cm2/min] = .00000E+00

### Dimensionless Groups:

Re = .54946E+00  
 Sc(i) = .26415E+04  
 Peb(i) = .80658E+01  
 Bi(i) = .31904E+02  
 Nf(i) = .69961E+01  
 Np(i) = .59805E-01  
 Pep(i) = .37521E+04

Isotherm = Freundlich/Langmuir Hybrid

Iso. Const. 1 = .11166E+00  
 Iso. Const. 2 = .10000E+01  
 Iso. Const. 3 = .10000E+01  
 Iso. Const. 4 = .10000E+01  
 Iso. Const. 5 = .29400E-03  
 Init. Conc. = .00000E+00  
 Conc. at eqb. = .00000E+00  
 Conc. units = M

=====

### COMMAND LIST:

- 1: User set viscosity to .2613E-01 poise and density to 1.224 g/cm3
  - 2: Step conc. of component 1 at .0000 min to .6089E-04 M  
 Execute 1 times, every .0000 mins.
  - 3: Monitor conc. history at stream 2. Filename = wk\_2x.h01  
 Output density adjustments:  
 1.0 \*default abs conc delta, 1.0 \*default rel conc delta,  
 .25 \*default force w/ conc delta, .10 \*default force w/o conc delta
  - 4: Dump full profile file at 240.0 min  
 Execute 1 times, every .0000 mins.
- =====

VERSE-LC finished in 1657 steps. Average step size .2897 minutes

End run: 12:51:08 on 11-12-1999

Integrated Areas in History Files:

wk\_2x.h01 .190410E-01

=====

## VERSE Input for "Hot" Small-Scale Column (NH)

```

Simulation of Cs removal on 6.1 ml Superlig 644 column
3 component (Cs, K, Na) isotherm
1, 50, 3, 6 ncomp, nelemt, ncol-bed, ncol-part
FUWNA isotherm, axial-disp, film-coef, surf-diff, BC-col
NNNNN input-only, perfusable, feed-equil, datafile.yio
MMM comp-conc units
 6.42, 1.10, 0.305, 6.0 Length(cm), Diam(cm), Q-flow(ml/min), CSTR-vol(ml)
332.0, 0.450, 0.614, 0.0 part-rad(um), bed-void, part-void, sorb-cap()
 0.0, 0.0, 0.25 initial concentrations (M)
V COMMAND - viscosity/density change
0.0261255, 1.223549 fluid viscosity(posie), density(g/cm^3)
S COMMAND - conc step change
1, 0.0, 6.987d-5, 1, 0.0 spec id, time(min), conc(M), freq, dt(min)
h COMMAND - effluent history dump
2, 1.0, 1.0, 0.25, 0.1 unit op#, ptscale(1-4) filtering
D
-1, 1800.0, 1, 0.0
-
3600.0, 1.0 end of commands
1.0d-7, 1.0d-4 end time(min), max dt in B.V.s
- abs-tol, rel-tol
1.0d0, 1.0d0, 1.0d0 non-negative conc constraint
0.7938 size exclusion factor
3.395d-4, 4.70d-4, 3.67d-4 dispersion coef (cm^2/min)
4.85d-4, 4.70d-4, 3.67d-4 part-pore diffusivities (cm^2/min)
1.1166d-1, 9.2994d-5, 4.8763d-6 Brownian diffusivities (cm^2/min)
1.0, 8.3287d-4, 4.3672d-5 Freundlich/Langmuir Hybrid a (moles/L B.V.)
1.0, 1.0, 1.0 Freundlich/Langmuir Hybrid b (1/M)
1.0, 1.0, 1.0 Freundlich/Langmuir Hybrid Ma (-)
1.0, 1.0, 1.0 Freundlich/Langmuir Hybrid Mb (-)
3.154d-4, 0.0, 0.0 Freundlich/Langmuir Hybrid beta (-)

```

## VERSE Output for "Hot" Small-Scale Column (NH)

=====

VERSE v7.80 by R. D. Whitley and N.-H. L. Wang, c1999 PRF

=====

Input file: nh\_1

Simulation of Cs removal on 6.1 ml Superlig 644 column

3 component (Cs, K, Na) isotherm

Begin Run: 14:22:32 on 11-12-1999 running under Windows 95/8

Finite elements - axial: 50 particle: 1

Collocation points - axial: 3 particle: 6 => Number of eqns: 1610

Inlet species at equilib? N Perfusable sorbent? N Feed profile only? N

Use Profile File? N Generate Profile File? N

Axial dispersion correlation: User-specified

Film mass transfer correlation: Wilson & Geankoplis (1966)

=====

SYSTEM PARAMETERS (at initial conditions):

|                |   |                   |               |   |               |
|----------------|---|-------------------|---------------|---|---------------|
| t(stop)        | = | 3600.00000 min    | dtheta max    | = | 1.00000 BV    |
| abs. tol.      | = | .10000E-06        | rel. tol.     | = | .10000E-03    |
| Total Length   | = | 6.42000 cm        | D             | = | 1.10000 cm    |
| Tot. Capacity  | = | .00000 eq/L solid | Col. Vol.     | = | 6.10113 mL    |
| F              | = | .30500 mL/min     | Uo (linear)   | = | .71320 cm/min |
| R              | = | 332.00000 microns | L/R           | = | 193.37349     |
| Bed Void frac. | = | .45000            | Pcl. Porosity | = | .61400        |
| Spec. Area     | = | 49.69880 1/cm     | Time/BV       | = | 9.00167 min   |
| Vol CSTRs      | = | 6.00000 mL        |               |   |               |

|                            |   |            |
|----------------------------|---|------------|
| Component no.              | = | 1          |
| Ke [-]                     | = | .10000E+01 |
| Eb [cm <sup>2</sup> /min]  | = | .79380E+00 |
| Dp [cm <sup>2</sup> /min]  | = | .33950E-03 |
| Doo [cm <sup>2</sup> /min] | = | .48500E-03 |
| kf [cm/min]                | = | .62432E-01 |

Ds [cm<sup>2</sup>/min] = .00000E+00

Dimensionless Groups:

Re = .16634E-01  
 Sc(i) = .26415E+04  
 Peb(i) = .57681E+01  
 Bi(i) = .99434E+01  
 Nf(i) = .62067E+02  
 Np(i) = .17024E+01  
 Pep(i) = .11359E+03

Isotherm = Freundlich/Langmuir Hybrid

Iso. Const. 1 = .11166E+00  
 Iso. Const. 2 = .10000E+01  
 Iso. Const. 3 = .10000E+01  
 Iso. Const. 4 = .10000E+01  
 Iso. Const. 5 = .31540E-03  
 Init. Conc. = .00000E+00  
 Conc. at eqb. = .00000E+00  
 Conc. units M

=====

COMMAND LIST:

- 1: User set viscosity to .2613E-01 poise and density to 1.224 g/cm<sup>3</sup>
- 2: Step conc. of component 1 at .0000 min to .6987E-04 M  
 Execute 1 times, every .0000 mins.
- 3: Monitor conc. history at stream 2. Filename = nh\_1.h01  
 Output density adjustments:  
 1.0 \*default abs conc delta, 1.0 \*default rel conc delta,  
 .25 \*default force w/ conc delta, .10 \*default force w/o conc delta
- 4: Dump full profile file at 1800. min  
 Execute 1 times, every .0000 mins.

=====

VERSE-IC finished in 406 steps. Average step size 8.867 minutes

End run: 14:23:02 on 11-12-1999

Integrated Areas in History Files:

nh\_1.h01 .194115E-01

## VERSE Input for "Hot" Small-Scale Column (DM-A)

Simulation of Cs removal on 5.5 ml Superlig 644 column

3 component (Cs, K, Na) isotherm

1, 50, 3, 6

FUWNA

NNNNN

MMM

7.76, 0.95, 0.250, 5.0

332.0, 0.450, 0.614, 0.0

0.0, 0.0, 1.0

V

0.0261255, 1.223549

S

1, 0.0, 8.100d-5, 1, 0.0

h

2, 1.0, 1.0, 0.25, 0.1

D

-1, 1800.0, 1, 0.0

-

3600.0, 1.0

1.0d-7, 1.0d-4

-

1.0d0, 1.0d0, 1.0d0

0.7173

3.395d-4, 4.70d-4, 3.67d-4

4.85d-4, 4.70d-4, 3.67d-4

1.1166d-1, 9.2994d-5, 4.8763d-6

1.0, 8.3287d-4, 4.3672d-5

1.0, 1.0, 1.0

1.0, 1.0, 1.0

5.945d-4, 0.0, 0.0

ncomp, nele, ncol-bed, ncol-part

isotherm, axial-disp, film-coef, surf-diff, BC-col

input-only, perfusable, feed-equil, datafile.yio

comp-conc units

Length(cm), Diam(cm), Q-flow(ml/min), CSTR-vol(ml)

part-rad(um), bed-void, part-void, sorb-cap()

initial concentrations (M)

COMMAND - viscosity/density change

fluid viscosity(posie), density(g/cm<sup>3</sup>)

COMMAND - conc step change

spec id, time(min), conc(M), freq, dt(min)

COMMAND - effluent history dump

unit op#, ptscale(1-4) filtering

end of commands

end time(min), max dt in B.V.s

abs-tol, rel-tol

non-negative conc constraint

size exclusion factor

dispersion coef (cm<sup>2</sup>/min)

part-pore diffusivities (cm<sup>2</sup>/min)

Brownian diffusivities (cm<sup>2</sup>/min)

Freundlich/Langmuir Hybrid a (moles/L B.V.)

Freundlich/Langmuir Hybrid b (1/M)

Freundlich/Langmuir Hybrid Ma (-)

Freundlich/Langmuir Hybrid Mb (-)

Freundlich/Langmuir Hybrid beta (-)

# VERSE Ouput for "Hot" Small-Scale Column (DM-A)

```

=====
VERSE v7.80 by R. D. Whitley and N.-H. L. Wang, c1999 PRF
=====
Input file: dm_a
Simulation of Cs removal on 5.5 ml Superlig 644 column
3 component (Cs, K, Na) isotherm
Begin Run: 14:17:27 on 11-12-1999 running under Windows 95/8
Finite elements - axial: 50 particle: 1
Collocation points - axial: 3 particle: 6 => Number of eqns: 1610
Inlet species at equilib.? N Perfusable sorbent? N Feed profile only? N
Use Profile File? N Generate Profile File? N
Axial dispersion correlation: User-specified
Film mass transfer correlation: Wilson & Geankoplis (1966)
=====
SYSTEM PARAMETERS (at initial conditions):

t(stop) = 3600.00000 min dtheta max = 1.00000 BV
abs. tol. = .10000E-06 rel. tol. = .10000E-03
Total Length = 7.76000 cm D = .95000 cm
Tot. Capacity = .00000 eq/L solid Col. Vol. = 5.50046 mL
F = .25000 mL/min Uo (linear) = .78377 cm/min
R = 332.00000 microns L/R = 233.73494
Bed Void frac. = .45000 Pcl. Porosity = .61400
Spec. Area = 49.69880 1/cm Time/BV = 9.90082 min
Vol CSTRs = 5.00000 mL

Component no. = 1
Ke [-] = .10000E+01
Eb [cm2/min] = .71730E+00
Dp [cm2/min] = .33950E-03
Doo [cm2/min] = .48500E-03
kf [cm/min] = .64426E-01
Ds [cm2/min] = .00000E+00

Dimensionless Groups:
Re = .18280E-01
Sc(i) = .26415E+04
Peb(i) = .84791E+01
Bi(i) = .10261E+02
Nf(i) = .70448E+02
Np(i) = .18724E+01
Pep(i) = .12483E+03

Isotherm = Freundlich/Langmuir Hybrid
Iso. Const. 1 = .11166E+00
Iso. Const. 2 = .10000E+01
Iso. Const. 3 = .10000E+01
Iso. Const. 4 = .10000E+01
Iso. Const. 5 = .59450E-03
Init. Conc. = .00000E+00
Conc. at eqb. = .00000E+00
Conc. units = M
=====
COMMAND LIST:
1: User set viscosity to .2613E-01 poise and density to 1.224 g/cm3
2: Step conc. of component 1 at .0000 min to .8100E-04 M
 Execute 1 times, every .0000 mins.
3: Monitor conc. history at stream 2. Filename = dm_a.h01
 Output density adjustments:
 1.0 *default abs conc delta, 1.0 *default rel conc delta,
 .25 *default force w/ conc delta, .10 *default force w/o conc delta
4: Dump full profile file at 1800. min
 Execute 1 times, every .0000 mins.
=====
VERSE-LC finished in 372 steps. Average step size 9.677 minutes
End run: 14:17:56 on 11-12-1999
Integrated Areas in History Files:
dm_a.h01 .528052E-01
=====

```

## VERSE Input for "Hot" Small-Scale Column (DM-B)

```

Simulation of Cs removal on 5.5 ml Superlig 644 column
3 component (Cs, K, Na) isotherm
1, 50, 3, 6 ncomp, nelemt, ncol-bed, ncol-part
FUWNA isotherm, axial-disp, film-coef, surf-diff, BC-col
NNNNN input-only, perfusable, feed-equil, datafile.yio
MMM comp-conc units
7.76, 0.95, 0.312, 5.0 Length(cm), Diam(cm), Q-flow(ml/min), CSTR-vol(ml)
332.0, 0.450, 0.614, 0.0 part-rad(um), bed-void, part-void, sorb-cap()
0.0, 0.0, 0.25 initial concentrations (M)
V COMMAND - viscosity/density change
0.0261255, 1.223549 fluid viscosity(posie), density(g/cm^3)
S COMMAND - conc step change
1, 0.0, 7.640d-4, 1, 0.0 spec id, time(min), conc(M), freq, dt(min)
h COMMAND - effluent history dump
2, 1.0, 1.0, 0.25, 0.1 unit op#, ptscale(1-4) filtering
D
-1, 1800.0, 1, 0.0
-
3600.0, 1.0 end of commands
1.0d-7, 1.0d-4 end time(min), max dt in B.V.s
- abs-tol, rel-tol
1.0d0, 1.0d0, 1.0d0 non-negative conc constraint
0.8944 size exclusion factor
3.395d-4, 4.70d-4, 3.67d-4 dispersion coef (cm2/min) (0.28527) 100%
4.85d-4, 4.70d-4, 3.67d-4 part-pore diffusivities (cm^2/min)
1.1166d-1, 9.2994d-5, 4.8763d-6 Brownian diffusivities (cm^2/min)
1.0, 8.3287d-4, 4.3672d-5 Freundlich/Langmuir Hybrid a (moles/L B.V.)
1.0, 1.0, 1.0 Freundlich/Langmuir Hybrid b (1/M)
1.0, 1.0, 1.0 Freundlich/Langmuir Hybrid Ma (-)
1.0, 1.0, 1.0 Freundlich/Langmuir Hybrid Mb (-)
3.655d-4, 0.0, 0.0 Freundlich/Langmuir Hybrid beta (-)

```

## VERSE Output for "Hot" Small-Scale Column (DM-B)

```

=====
VERSE v7.80 by R. D. Whitley and N.-H. L. Wang, c1999 PRF
=====
Input file: dm_b
Simulation of Cs removal on 5.5 ml Superlig 644 column
3 component (Cs, K, Na) isotherm
Begin Run: 14:13:27 on 11-12-1999 running under Windows 95/8
Finite elements - axial: 50 particle: 1
Collocation points - axial: 3 particle: 6 => Number of eqns: 1610
Inlet species at equilib.? N Perfusable sorbent? N Feed profile only? N
Use Profile File? N Generate Profile File? N
Axial dispersion correlation: User-specified
Film mass transfer correlation: Wilson & Geankoplis (1966)
=====
SYSTEM PARAMETERS (at initial conditions):

t(stop) = 3600.00000 min dtheta max = 1.00000 BV
abs. tol. = .10000E-06 rel. tol. = .10000E-03
Total Length = 7.76000 cm D = .95000 cm
Tot. Capacity = .00000 eq/L solid Col. Vol. = 5.50046 mL
F = .31200 mL/min Uo (linear) = .97815 cm/min
R = 332.00000 microns L/R = 233.73494
Bed Void frac. = .45000 Pcl. Porosity = .61400
Spec. Area = 49.69880 1/cm Time/BV = 7.93335 min
Vol CSTRs = 5.00000 mL

Component no. = 1
Ke [-] = .10000E+01
Eb [cm2/min] = .89440E+00
Dp [cm2/min] = .33950E-03
Doo [cm2/min] = .48500E-03
kf [cm/min] = .69364E-01
Ds [cm2/min] = .00000E+00

Dimensionless Groups:

```

```

Re = .22813E-01
Sc(i) = .26415E+04
Peb(i) = .84866E+01
Bi(i) = .11048E+02
Nf(i) = .60775E+02
Np(i) = .15003E+01
Pep(i) = .15579E+03

```

```

Isotherm = Freundlich/Langmuir Hybrid
Iso. Const. 1 = .11166E+00
Iso. Const. 2 = .10000E+01
Iso. Const. 3 = .10000E+01
Iso. Const. 4 = .10000E+01
Iso. Const. 5 = .36550E-03
Init. Conc. = .00000E+00
Conc. at eqb. = .00000E+00
Conc. units = M

```

---

COMMAND LIST:

```

1: User set viscosity to .2613E-01 poise and density to 1.224 g/cm3
2: Step conc. of component 1 at .0000 min to .7640E-03 M
 Execute 1 times, every .0000 mins.
3: Monitor conc. history at stream 2. Filename = dm_b.h01
 Output density adjustments:
 1.0 *default abs conc delta, 1.0 *default rel conc delta,
 .25 *default force w/ conc delta, .10 *default force w/o conc delta
4: Dump full profile file at 1800. min
 Execute 1 times, every .0000 mins.

```

---

VERSE-LC finished in 476 steps. Average step size 7.563 minutes

End run: 14:14:16 on 11-12-1999

Integrated Areas in History Files:

dm\_b.h01 1.39609

---

## VERSE Input for "Hot" Small-Scale Column (DM-C)

Simulation of Cs removal on 5.5 ml Superlig 644 column

3 component (Cs, K, Na) isotherm

1, 50, 3, 6

FUWNA

NNNNN

MMM

7.76, 0.95 , 0.310, 5.0

332.0, 0.450, 0.614, 0.0

0.0, 0.0 , 0.25

V

0.0261255, 1.223549

S

1, 0.0, 6.332d-5, 1, 0.0

h

2, 1.0, 1.0, 0.25, 0.1

D

-1, 1800.0, 1, 0.0

-

3600.0, 1.0

1.0d-7, 1.0d-4

-

1.0d0 , 1.0d0 , 1.0d0

0.8887

3.395d-4 , 4.70d-4 , 3.67d-4

4.85d-4 , 4.70d-4 , 3.67d-4

1.1166d-1, 9.2994d-5, 4.8763d-6

1.0 , 8.3287d-4, 4.3672d-5

1.0 , 1.0 , 1.0

1.0 , 1.0 , 1.0

2.710d-4 , 0.0 , 0.0

```

ncomp, nelem, ncol-bed, ncol-part
isotherm, axial-disp, film-coef, surf-diff, BC-col
input-only, perfusable, feed-equil, datafile.yio
comp-conc units
Length(cm), Diam(cm), Q-flow(ml/min), CSTR-vol(ml)
part-rad(um), bed-void, part-void, sorb-cap()
initial concentrations (M)
COMMAND - viscosity/density change
fluid viscosity(posie), density(g/cm^3)
COMMAND - conc step change
spec id, time(min), conc(M), freq, dt(min)
COMMAND - effluent history dump
unit op#, ptscale(1-4) filtering

end of commands
end time(min), max dt in B.V.s
abs-tol, rel-tol
non-negative conc constraint
size exclusion factor
dispersion coef (cm2/min) (0.28527) 100%
part-pore diffusivities (cm^2/min)
Brownian diffusivities (cm^2/min)
Freundlich/Langmuir Hybrid a (moles/L B.V.)
Freundlich/Langmuir Hybrid b (1/M)
Freundlich/Langmuir Hybrid Ma (-)
Freundlich/Langmuir Hybrid Mb (-)
Freundlich/Langmuir Hybrid beta (-)

```

---



# **VERSE Ouput for "Hot" Small-Scale Column (DM-C)**

=====

VERSE v7.80 by R. D. Whitley and N.-H. L. Wang, c1999 PRF

=====

Input file: dm\_c

Simulation of Cs removal on 5.5 ml Superlig 644 column

3 component (Cs, K, Na) isotherm

Begin Run: 14:19:35 on 11-12-1999 running under Windows 95/8

Finite elements - axial: 50 particle: 1

Collocation points - axial: 3 particle: 6 => Number of eqns: 1610

Inlet species at equilib.? N Perfusable sorbent? N Feed profile only? N

Use Profile File? N Generate Profile File? N

Axial dispersion correlation: User-specified

Film mass transfer correlation: Wilson & Geankoplis (1966)

=====

SYSTEM PARAMETERS (at initial conditions):

|                |   |                   |               |   |               |
|----------------|---|-------------------|---------------|---|---------------|
| t(stop)        | = | 3600.00000 min    | dtheta max    | = | 1.00000 BV    |
| abs. tol.      | = | .10000E-06        | rel. tol.     | = | .10000E-03    |
| Total Length   | = | 7.76000 cm        | D             | = | .95000 cm     |
| Tot. Capacity  | = | .00000 eq/L solid | Col. Vol.     | = | 5.50046 mL    |
| F              | = | .31000 mL/min     | Uo (linear)   | = | .97188 cm/min |
| R              | = | 332.00000 microns | L/R           | = | 233.73494     |
| Bed Void frac. | = | .45000            | Pcl. Porosity | = | .61400        |
| Spec. Area     | = | 49.69880 1/cm     | Time/BV       | = | 7.98454 min   |
| Vol CSTRs      | = | 5.00000 mL        |               |   |               |

|               |   |            |
|---------------|---|------------|
| Component no. | = | 1          |
| ke [-]        | = | .10000E+01 |
| Eb [cm2/min]  | = | .88870E+00 |
| Dp [cm2/min]  | = | .33950E-03 |
| Doo [cm2/min] | = | .48500E-03 |
| kf [cm/min]   | = | .69216E-01 |
| DS [cm2/min]  | = | .00000E+00 |

Dimensionless Groups:

|        |   |            |
|--------|---|------------|
| Re     | = | .22667E-01 |
| Sc(i)  | = | .26415E+04 |
| Peb(i) | = | .84863E+01 |
| Bi(i)  | = | .11024E+02 |
| Nf(i)  | = | .61036E+02 |
| Np(i)  | = | .15100E+01 |
| Pep(i) | = | .15479E+03 |

Isotherm = Freundlich/Langmuir Hybrid

Iso. Const. 1 = .11166E+00

Iso. Const. 2 = .10000E+01

Iso. Const. 3 = .10000E+01

Iso. Const. 4 = .10000E+01

Iso. Const. 5 = .27100E-03

Init. Conc. = .00000E+00

Conc. at eqb. = .00000E+00

Conc. units = M

=====

COMMAND LIST:

- 1: User set viscosity to .2613E-01 poise and density to 1.224 g/cm3
  - 2: Step conc. of component 1 at .0000 min to .6332E-04 M  
Execute 1 times, every .0000 mins.
  - 3: Monitor conc. history at stream 2. Filename = dm\_c.h01  
Output density adjustments:  
1.0 \*default abs conc delta, 1.0 \*default rel conc delta,  
.25 \*default force w/ conc delta, .10 \*default force w/o conc delta
  - 4: Dump full profile file at 1800. min  
Execute 1 times, every .0000 mins.
- =====

VERSE-LC finished in 458 steps. Average step size 7.860 minutes

End run: 14:20:06 on 11-12-1999

Integrated Areas in History Files:

dm\_c.h01 .131593E-01

=====

## VERSE Input for Intermediate-Scale Column (IBC2)

```

Simulation of Cs removal on 200 ml Superlig 644 column (from IBC Report)
3 component (Cs, K, Na) isotherm: (10 cycle stability study)
1, 50, 3, 6
FUWNA
NNNNN
MMM
11.1, 4.79 , 30.0, 25.0
332.0, 0.450, 0.614, 0.0
0.0, 0.0 , 1.00
V
0.0261255, 1.223549
S
1, 0.0, 1.0d-3, 1, 0.0
h
2, 1.0, 1.0, 0.25, 0.1
D
-1, 900.0, 1, 0.0
-
1800.0, 1.0
1.0d-7, 1.0d-4
-
1.0d0 , 1.0d0 , 1.0d0
1.382
3.395d-4 , 4.70d-4 , 3.67d-4
4.85d-4 , 4.70d-4 , 3.67d-4
1.1166d-1, 9.2994d-5, 4.8763d-6
1.0 , 8.3287d-4, 4.3672d-5
1.0 , 1.0 , 1.0
1.0 , 1.0 , 1.0
3.0973d-4, 0.0 , 0.0

ncomp, nele, ncol-bed, ncol-part
isotherm, axial-disp, film-coef, surf-diff, BC-col
input-only, perfusable, feed-equil, datafile.yio
comp-conc units
Length(cm), Diam(cm), Q-flow(ml/min), CSTR-vol(ml)
part-rad(um), bed-void, part-void, sorb-cap()
initial concentrations (M)
COMMAND - viscosity/density change
fluid viscosity(posie), density(g/cm^3)
COMMAND - conc step change
spec id, time(min), conc(M), freq, dt(min) 5.26316d-4
COMMAND - effluent history dump
unit op#, ptscale(1-4) filtering

end of commands
end time(min), max dt in B.V.s
abs-tol, rel-tol
non-negative conc constraint
size exclusion factor
dispersion coef (cm2/min)
part-pore diffusivities (cm^2/min)
Brownian diffusivities (cm^2/min)
Freundlich/Langmuir Hybrid a (moles/L B.V.)
Freundlich/Langmuir Hybrid b (1/M)
Freundlich/Langmuir Hybrid Ma (-)
Freundlich/Langmuir Hybrid Mb (-)
Freundlich/Langmuir Hybrid beta (-)

```

## VERSE Output for Intermediate-Scale Column (IBC2)

=====

VERSE v7.80 by R. D. Whitley and N.-H. L. Wang, c1999 PRF

=====

Input file: ibc\_2

Simulation of Cs removal on 200 ml Superlig 644 column (from IBC Report)

3 component (Cs, K, Na) isotherm: (10 cycle stability study)

Begin Run: 11:07:33 on 11-15-1999 running under Windows 95/8

Finite elements - axial: 50 particle: 1

Collocation points - axial: 3 particle: 6 => Number of eqns: 1610

Inlet species at equilib.? N Perfusable sorbent? N Feed profile only? N

Use Profile File? N Generate Profile File? N

Axial dispersion correlation: User-specified

Film mass transfer correlation: Wilson & Geankoplis (1966)

=====

SYSTEM PARAMETERS (at initial conditions):

|                |   |                   |               |   |                |
|----------------|---|-------------------|---------------|---|----------------|
| t(stop)        | = | 1800.00000 min    | dtheta max    | = | 1.00000 BV     |
| abs. tol.      | = | .10000E-06        | rel. tol.     | = | .10000E-03     |
| Total Length   | = | 11.10000 cm       | D             | = | 4.79000 cm     |
| Tot. Capacity  | = | .00000 eq/L solid | Col. Vol.     | = | 200.02482 mL   |
| F              | = | 30.00000 mL/min   | Uo (linear)   | = | 3.69954 cm/min |
| R              | = | 332.00000 microns | L/R           | = | 334.33735      |
| Bed Void frac. | = | .45000            | Pcl. Porosity | = | .61400         |
| Spec. Area     | = | 49.69880 1/cm     | Time/BV       | = | 3.00037 min    |
| Vol CSTRs      | = | 25.00000 mL       |               |   |                |

|               |   |            |
|---------------|---|------------|
| Component no. | = | 1          |
| Ke [-]        | = | .10000E+01 |
| Eb [cm2/min]  | = | .13820E+01 |
| Dp [cm2/min]  | = | .33950E-03 |
| Do0 [cm2/min] | = | .48500E-03 |
| kf [cm/min]   | = | .10807E+00 |
| Ds [cm2/min]  | = | .00000E+00 |

Dimensionless Groups:

```

Re = .86285E-01
Sc(i) = .26415E+04
Peb(i) = .29714E+02
Bi(i) = .17213E+02
Nf(i) = .35812E+02
Np(i) = .56742E+00
Pep(i) = .58922E+03

```

```

Isotherm = Freundlich/Langmuir Hybrid
Iso. Const. 1 = .11166E+00
Iso. Const. 2 = .10000E+01
Iso. Const. 3 = .10000E+01
Iso. Const. 4 = .10000E+01
Iso. Const. 5 = .30973E-03
Init. Conc. = .00000E+00
Conc. at eqb. = .00000E+00
Conc. units = M

```

---

COMMAND LIST:

```

1: User set viscosity to .2613E-01 poise and density to 1.224 g/cm3
2: Step conc. of component 1 at .0000 min to .1000E-02 M
 Execute 1 times, every .0000 mins.
3: Monitor conc. history at stream 2. Filename = ibc_2.h01
 Output density adjustments:
 1.0 *default abs conc delta, 1.0 *default rel conc delta,
 .25 *default force w/ conc delta, .10 *default force w/o conc delta
4: Dump full profile file at 900.0 min
 Execute 1 times, every .0000 mins.

```

---

```

VERSE-LC finished in 659 steps. Average step size 2.731 minutes
End run: 11:09:14 on 11-15-1999
Integrated Areas in History Files:
ibc_2.h01 1.22548

```

---

## VERSE Input for Intermediate-Scale Column (IBC1)

---

```

Simulation of Cs removal on 200 ml Superlig 644 column (from IBC Report)
3 component (Cs, K, Na) isotherm: (10 cycle stability study)
1, 50, 3, 6 ncomp, nele, ncol-bed, ncol-part
FUWNA isotherm, axial-disp, film-coef, surf-diff, BC-col
NNNNN input-only, perfusable, feed-equil, datafile.yio
MMM comp-conc units
11.1, 4.79, , 30.0, 25.0 Length(cm), Q-flow(ml/min), CSTR-vol(ml)
332.0, 0.450, 0.614, 0.0 part-rad(um), bed-void, part-void, sorb-cap()
0.0, 0.0, , 1.00 initial concentrations (M)
V COMMAND - viscosity/density change
0.0261255, 1.223549 fluid viscosity(posie), density(g/cm^3)
S COMMAND - conc step change
1, 0.0, 5.26316d-4, 1, 0.0 spec id, time(min), conc(M), freq, dt(min) 5.26316d-4
h COMMAND - effluent history dump
2, 1.0, 1.0, 0.25, 0.1 unit op#, ptscale(1-4) filtering
D
-1, 900.0, 1, 0.0
-
1800.0, 1.0 end of commands
1.0d-7, 1.0d-4 end time(min), max dt in B.V.s
- abs-tol, rel-tol
1.0d0, , 1.0d0, , 1.0d0 non-negative conc constraint
1.382 size exclusion factor
3.395d-4, 4.70d-4, , 3.67d-4 dispersion coef (cm^2/min)
4.85d-4, 4.70d-4, , 3.67d-4 part-pore diffusivities (cm^2/min)
1.1166d-1, 9.2994d-5, 4.8763d-6 Brownian diffusivities (cm^2/min)
1.0, , 8.3287d-4, 4.3672d-5 Freundlich/Langmuir Hybrid a (moles/L B.V.)
1.0, , 1.0, , 1.0 Freundlich/Langmuir Hybrid b (1/M)
1.0, , 1.0, , 1.0 Freundlich/Langmuir Hybrid Ma (-)
3.0973d-4, 0.0, , 0.0 Freundlich/Langmuir Hybrid Mb (-)
 Freundlich/Langmuir Hybrid beta (-)

```

---

# VERSE Ouput for Intermediate-Scale Column (IBC1)

=====

VERSE v7.80 by R. D. Whitley and N.-H. L. Wang, c1999 PRF

=====

Input file: ibc\_1

Simulation of Cs removal on 200 ml Superlig 644 column (from IBC Report)

3 component (Cs, K, Na) isotherm: (10 cycle stability study)

Begin Run: 15:38:19 on 11-24-1999 running under Windows 95/8

Finite elements - axial: 50 particle: 1

Collocation points - axial: 3 particle: 6 => Number of eqns: 1610

Inlet species at equilib.? N Perfusable sorbent? N Feed profile only? N

Use Profile File? N Generate Profile File? N

Axial dispersion correlation: User-specified

Film mass transfer correlation: Wilson & Geankoplis (1966)

=====

SYSTEM PARAMETERS (at initial conditions):

|                |   |                   |               |   |                |
|----------------|---|-------------------|---------------|---|----------------|
| t(stop)        | = | 1800.00000 min    | dtheta max    | = | 1.00000 BV     |
| abs. tol.      | = | .10000E-06        | rel. tol.     | = | .10000E-03     |
| Total Length   | = | 11.10000 cm       | D             | = | 4.79000 cm     |
| Tot. Capacity  | = | .00000 eq/L solid | Col. Vol.     | = | 200.02482 mL   |
| F              | = | 30.00000 mL/min   | Uo (linear)   | = | 3.69954 cm/min |
| R              | = | 332.00000 microns | L/R           | = | 334.33735      |
| Bed Void frac. | = | .45000            | Pcl. Porosity | = | .61400         |
| Spec. Area     | = | 49.69880 1/cm     | Time/BV       | = | 3.00037 min    |
| Vol CSTRs      | = | 25.00000 mL       |               |   |                |

|               |   |            |
|---------------|---|------------|
| Component no. | = | 1          |
| Ke [-]        | = | .10000E+01 |
| Eb [cm2/min]  | = | .13820E+01 |
| Dp [cm2/min]  | = | .33950E-03 |
| Do0 [cm2/min] | = | .48500E-03 |
| kf [cm/min]   | = | .10807E+00 |
| Ds [cm2/min]  | = | .00000E+00 |

Dimensionless Groups:

|        |   |            |
|--------|---|------------|
| Re     | = | .86285E-01 |
| Sc(i)  | = | .26415E+04 |
| Peb(i) | = | .29714E+02 |
| Bi(i)  | = | .17213E+02 |
| Nf(i)  | = | .35812E+02 |
| Np(i)  | = | .56742E+00 |
| Pep(i) | = | .58922E+03 |

Isotherm = Freundlich/Langmuir Hybrid

Iso. Const. 1 = .11166E+00

Iso. Const. 2 = .10000E+01

Iso. Const. 3 = .10000E+01

Iso. Const. 4 = .10000E+01

Iso. Const. 5 = .30973E-03

Init. Conc. = .00000E+00

Conc. at eqb. = .00000E+00

Conc. units M

=====

COMMAND LIST:

- 1: User set viscosity to .2613E-01 poise and density to 1.224 g/cm3
  - 2: Step conc. of component 1 at .0000 min to .5263E-03 M  
Execute 1 times, every .0000 mins.
  - 3: Monitor conc. history at stream 2. Filename = ibc\_1.h01  
Output density adjustments:  
1.0 \*default abs conc delta, 1.0 \*default rel conc delta,  
.25 \*default force w/ conc delta, .10 \*default force w/o conc delta
  - 4: Dump full profile file at 900.0 min  
Execute 1 times, every .0000 mins.
- =====

VERSE-LC finished in 650 steps. Average step size 2.769 minutes

End run: 15:39:55 on 11-24-1999

Integrated Areas in History Files:

ibc\_1.h01 .475485

=====

## VERSE Input for Intermediate-Scale Column (BN-SIM-A)

```

Simulation of Cs removal on 210 ml Superlig 644 column
3 component (Cs, K, Na) isotherm
1, 50, 3, 6
FCWNA
NNNNN
MMM
41.44, 2.54, 30.0, 5.0
357.0, 0.640, 0.614, 0.0
0.0, 0.0, 2.0
V
0.0261255, 1.223549
S
1, 0.0, 5.000d-4, 1, 0.0
h
2, 1.0, 1.0, 0.25, 0.1
D
-1, 750.0, 1, 0.0
-
1500.0, 1.0
1.0d-7, 1.0d-4
-
1.0d0, 1.0d0, 1.0d0
3.395d-4, 4.70d-4, 3.67d-4
4.85d-4, 4.70d-4, 3.67d-4
7.3326d-2, 9.2994d-5, 4.8763d-6
1.0, 8.3287d-4, 4.3672d-5
1.0, 1.0, 1.0
1.0, 1.0, 1.0
3.183d-4, 0.0, 0.0

ncomp, nelemt, ncol-bed, ncol-part
isotherm, axial-disp, film-coef, surf-diff, BC-col
input-only, perfusable, feed-equil, datafile.yio
comp-conc units
Length(cm), Diam(cm), Q-flow(ml/min), CSTR-vol(ml)
part-rad(um), bed-void, part-void, sorb-cap()
initial concentrations (M)
COMMAND - viscosity/density change
fluid viscosity(posie), density(g/cm^3)
COMMAND - conc step change
spec id, time(min), conc(M), freq, dt(min)
COMMAND - effluent history dump
unit op#, ptscale(1-4) filtering

end of commands
end time(min), max dt in B.V.s
abs-tol, rel-tol
non-negative conc constraint
size exclusion factor
Brownian diffusivities (cm^2/min)
Brownian diffusivities (cm^2/min)
Freundlich/Langmuir Hybrid a (moles/L B.V.)
Freundlich/Langmuir Hybrid b (1/M)
Freundlich/Langmuir Hybrid Ma (-)
Freundlich/Langmuir Hybrid Mb (-)
Freundlich/Langmuir Hybrid beta (-)

```

## VERSE Output for Intermediate-Scale Column (BN-SIM-A)

```

=====
VERSE v7.80 by R. D. Whitley and N.-H. L. Wang, c1999 PRF
=====
Input file: pnnl
Simulation of Cs removal on 210 ml Superlig 644 column
3 component (Cs, K, Na) isotherm
Begin Run: 15:17:59 on 11-24-1999 running under Windows 95/8
Finite elements - axial: 50 particle: 1
Collocation points - axial: 3 particle: 6 => Number of eqns: 1610
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) = 1500.00000 min dtheta max = 1.00000 BV
abs. tol. = .10000E-06 rel. tol. = .10000E-03
Total Length = 41.44000 cm D = 2.54000 cm
Tot. Capacity = .00000 eq/L solid Col. Vol. = 209.97958 mL
F = 30.00000 mL/min Uo (linear) = 9.25090 cm/min
R = 357.00000 microns L/R = 1160.78431
Bed Void frac. = .64000 Pcl. Porosity = .61400
Spec. Area = 30.25210 1/cm Time/BV = 4.47956 min
Vol CSTRs = 5.00000 mL

Component no. = 1
Ke [-] = .10000E+01
Eb [cm2/min] = .20475E+01
Dp [cm2/min] = .33950E-03
Doo [cm2/min] = .48500E-03
kf [cm/min] = .11051E+00
Ds [cm2/min] = .00000E+00

Dimensionless Groups:
Re = .32996E+00

```

Sc(i) = .26415E+04  
 Peb(i) = .18723E+03  
 Bi(i) = .18926E+02  
 Nf(i) = .23400E+02  
 Np(i) = .73267E+00  
 Pep(i) = .15843E+04

Isotherm = Freundlich/Langmuir Hybrid  
 Iso. Const. 1 = .73326E-01  
 Iso. Const. 2 = .10000E+01  
 Iso. Const. 3 = .10000E+01  
 Iso. Const. 4 = .10000E+01  
 Iso. Const. 5 = .31830E-03  
 Init. Conc. = .00000E+00  
 Conc. at eqb. = .00000E+00  
 Conc. units M

=====

COMMAND LIST:

- 1: User set viscosity to .2613E-01 poise and density to 1.224 g/cm3
- 2: Step conc. of component 1 at .0000 min to .5000E-03 M  
 Execute 1 times, every .0000 mins.
- 3: Monitor conc. history at stream 2. Filename = pnnl.h01  
 Output density adjustments:  
 1.0 \*default abs conc delta, 1.0 \*default rel conc delta,  
 .25 \*default force w/ conc delta, .10 \*default force w/o conc delta
- 4: Dump full profile file at 750.0 min  
 Execute 1 times, every .0000 mins.

=====

VERSE-LC finished in 397 steps. Average step size 3.778 minutes  
 End run: 15:18:46 on 11-24-1999  
 Integrated Areas in History Files:  
 pnnl.h01 .433308

---

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## Appendix E (Full-Scale Facility Input and Output Files)

For reference the VERSE-LC input and output files for the full-scale facility are provided in this appendix. Several simulations were run. The case presented here corresponds to the ternary homovalent case where the three ions (i.e., cesium, potassium, and sodium) are modeled. The effective single cesium cation case is a simple reduction from the 3-ion case and is also provided.

Table E-1. Key parameter settings for VERSE-LC simulation of ternary homovalent cation exchange for the full-scale facility.

| Parameter                                                           | Parameter setting                        |
|---------------------------------------------------------------------|------------------------------------------|
| Number of finite elements within bed                                | 50 for lead<br>50 for lag                |
| Number of internal collocation points per finite element within bed | 3 for lead<br>3 for lag                  |
| Number of internal collocation points within pores                  | 6 for lead<br>6 for lag                  |
| Number of components<br>1 - cesium<br>2 - potassium<br>3 - sodium   | 3                                        |
| Axial dispersion, $E_b$<br>( $\text{cm}^2/\text{min}$ )             | Chung and Wen (1968) correlation         |
| Film coefficient, $k_f$<br>( $\text{cm}/\text{min}$ )               | Wilson and Geankoplis (1966) correlation |
| Active column lengths, L                                            | 225.0 cm for lead<br>225.0 cm for lag    |
| Column diameters, D                                                 | 77.0 cm for lead<br>77.0 cm for lag      |
| Headspace volumes                                                   | 1047.74 L for lead<br>1047.74 L for lag  |
| Bed porosities, $\epsilon_b$<br>(-)                                 | 0.450 for lead<br>0.450 for lag          |
| Particle porosities, $\epsilon_p$<br>(-)                            | 0.614 for lead<br>0.614 for lag          |
| Native (initial) concentrations<br>cesium<br>potassium<br>sodium    | 0.0 M<br>0.0 M<br>0.25 M                 |
| Feed (loading) concentrations<br>cesium<br>potassium                | $6.089 \times 10^{-5}$ M<br>0.090 M      |



| Parameter                                                                                                         | Parameter setting                                                                                                                                                                      |
|-------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| sodium                                                                                                            | 5.001 M                                                                                                                                                                                |
| Fluid dynamic viscosity, $\mu_w$                                                                                  | 0.261255 poise                                                                                                                                                                         |
| Fluid density, $\rho_w$                                                                                           | 1.223549 g/ml                                                                                                                                                                          |
| Column switching exit cesium concentration criterion                                                              | none for lead<br>8.4382x10 <sup>-8</sup> M (1 $\mu$ Ci/ml) for lag                                                                                                                     |
| Molecular diffusion coefficients<br>cesium<br>potassium<br>sodium                                                 | 4.850x10 <sup>-4</sup> cm <sup>2</sup> /min<br>4.704x10 <sup>-4</sup> cm <sup>2</sup> /min<br>3.667x10 <sup>-4</sup> cm <sup>2</sup> /min                                              |
| Particle pore diffusion coefficients<br>cesium<br>potassium<br>sodium                                             | 3.395x10 <sup>-4</sup> cm <sup>2</sup> /min<br>3.293x10 <sup>-4</sup> cm <sup>2</sup> /min<br>2.566x10 <sup>-4</sup> cm <sup>2</sup> /min                                              |
| Freundlich-Langmuir Hybrid a coefficient<br>cesium<br>potassium<br>sodium                                         | (based on $\rho_b = 0.335$ g/ml)<br>1.1165x10 <sup>-1</sup> gmoles/L <sub>BV</sub><br>9.2993x10 <sup>-5</sup> gmoles/L <sub>BV</sub><br>4.8763x10 <sup>-6</sup> gmoles/L <sub>BV</sub> |
| Freundlich-Langmuir Hybrid b coefficient<br>cesium<br>potassium<br>sodium                                         | 1.0000x10 <sup>-0</sup> M <sup>-1</sup><br>8.3287x10 <sup>-4</sup> M <sup>-1</sup><br>4.3672x10 <sup>-5</sup> M <sup>-1</sup>                                                          |
| Freundlich-Langmuir Hybrid M <sub>a</sub> coefficient<br>cesium<br>potassium<br>sodium                            | 1.0 (-)<br>1.0 (-)<br>1.0 (-)                                                                                                                                                          |
| Freundlich-Langmuir Hybrid M <sub>b</sub> coefficient<br>cesium<br>potassium<br>sodium                            | 1.0 (-)<br>1.0 (-)<br>1.0 (-)                                                                                                                                                          |
| Freundlich-Langmuir Hybrid $\beta$ coefficient<br>cesium<br>potassium<br>sodium                                   | 0.0 (-)<br>0.0 (-)<br>0.0 (-)                                                                                                                                                          |
| Freundlich-Langmuir Hybrid $\beta$ coefficient for cesium when an effective single component approach is employed | 2.9366x10 <sup>-4</sup> (-)                                                                                                                                                            |

## VERSE Input for Full-Scale Facility (Ternary Homovalent Model)

```
[fullscale] Simulation of Cs removal on 1047.74 L Full-Scale Superlig 644 column
3 component (1-Cs, 2-K, 3-Na) isotherms; lead and lag columns with CSTRs
3, 100, 3, 6 ncomp, nelem, ncol-bed, ncol-part
FCWNA isotherm, axial-disp, film-coef, surf-diff, BC-col FCUNA
NNNNN input-only, perfusable, feed-equil, datafile.yio
MMM comp-conc units
450.0, 77.0, 52619.9, 1.04774d+6 Length(cm), Diam(cm), Q-flow(ml/min), CSTR-vol(ml)
332.0, 0.450, 0.614, 0.0 part-rad(um), bed-void, part-void, sorb-cap()
0.0, 0.0, 0.25 initial concentrations (M)
S COMMAND - conc step change
1, 0.0, 6.089d-5, 1, 0.0 spec id, time(min), conc(M), freq, dt(min)
S COMMAND - conc step change
2, 0.0, 0.090d+0, 1, 0.0 spec id, time(min), conc(M), freq, dt(min)
S COMMAND - conc step change
3, 0.0, 5.001d+0, 1, 0.0 spec id, time(min), conc(M), freq, dt(min)
V COMMAND - viscosity/density change
0.0261255, 1.223549 fluid viscosity(posie), density(g/cm^3)
m COMMAND - subcolumns
50,100,0,1,8.4382d-8,0.0,20000.0 elem-shift,e-watch,pp-watch,c-watch,c-thresh,t-e,t-ee
h COMMAND - effluent history dump
0, 1.0, 1.0, 0.25, 0.1 unit op#, ptscale(1-4) filtering
h COMMAND - effluent history dump
1, 1.0, 1.0, 0.25, 0.1 unit op#, ptscale(1-4) filtering
h COMMAND - effluent history dump
2, 1.0, 1.0, 0.25, 0.1 unit op#, ptscale(1-4) filtering
h COMMAND - effluent history dump
3, 1.0, 1.0, 0.25, 0.1 unit op#, ptscale(1-4) filtering
h COMMAND - effluent history dump
4, 1.0, 1.0, 0.25, 0.1 unit op#, ptscale(1-4) filtering
D
-1, 8400.0, 1, 0.0
D
-1, 14080.0, 1, 0.0
D
-1, 19990.0, 1, 0.0
-
end of commands
20000.0, 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, 1.0d0, 1.0d0 size exclusion factor
3.395d-4, 3.293d-4, 2.566d-4 part-pore diffusivities (cm^2/min)
4.850d-4, 4.704d-4, 3.667d-4 Brownian diffusivities (cm^2/min)
1.1165d-1, 9.2993d-5, 4.8763d-6 Freundlich/Langmuir Hybrid a (moles/L B.V.) rhob=0.335
1.0, 8.3287d-4, 4.3672d-5 Freundlich/Langmuir Hybrid b (1/M)
1.0, 1.0, 1.0 Freundlich/Langmuir Hybrid Ma (-)
1.0, 1.0, 1.0 Freundlich/Langmuir Hybrid Mb (-)
0.0, 0.0, 0.0 Freundlich/Langmuir Hybrid beta (-)

1.2732d-1, 1.0604d-4, 5.5604d-6 Freundlich/Langmuir Hybrid a (moles/L B.V.) rhob=0.382
2.9366d-4, 0.0, 0.0 Freundlich/Langmuir Hybrid beta (-)
```

## VERSE Output for Full-Scale Facility (Ternary Homovalent Model)

```
=====
VERSE v7.80 by R. D. Whitley and N.-H. L. Wang, c1999 PRF
=====
```

Input file: case

[fullscale] Simulation of Cs removal on 1047.74 L Full-Scale Superlig 644 c

3 component (1-Cs, 2-K, 3-Na) isotherms; lead and lag columns with CSTRs

Begin Run: 12:15:23 on 11-29-1999 running under Windows 95/8

Finite elements - axial:100 particle: 1

Collocation points - axial: 3 particle: 6 => Number of eqns: 9657

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)	=	20000.00000 min	dtheta max	=	1.00000 BV
abs. tol.	=	.10000E-06	rel. tol.	=	.10000E-03
Total Length	=	450.00000 cm	D	=	77.00000 cm
Tot. Capacity	=	.00000 eq/L solid	Col. Vol.	=	2095481.56985 mL
F	=	52619.90000 mL/min	Uo (linear)	=	25.11113 cm/min
R	=	332.00000 microns	L/R	=	13554.21687
Bed Void frac.	=	.45000	Pcl. Porosity	=	.61400
Spec. Area	=	49.69880 1/cm	Time/BV	=	8.96017 min
Vol CSTRs	=	1047740.00000 mL			

Component no.	=	1	2	3
Ke [-]	=	.10000E+01	.10000E+01	.10000E+01
Eb [cm ² /min]	=	.35985E+01	.35985E+01	.35985E+01
Dp [cm ² /min]	=	.33950E-03	.32930E-03	.25660E-03
Doc [cm ² /min]	=	.48500E-03	.47040E-03	.36670E-03
kf [cm/min]	=	.20462E+00	.20050E+00	.16983E+00
Ds [cm ² /min]	=	.00000E+00	.00000E+00	.00000E+00

Dimensionless Groups:

Re	=	.58567E+00		
Sc(i)	=	.26415E+04	.27235E+04	.34937E+04
Peb(i)	=	.15701E+04	.15701E+04	.15701E+04
Bi(i)	=	.32590E+02	.32922E+02	.35786E+02
Nf(i)	=	.20249E+03	.19841E+03	.16806E+03
Np(i)	=	.16945E+01	.16436E+01	.12808E+01
Pep(i)	=	.39994E+04	.41233E+04	.52915E+04

Isotherm	=	Freundlich/Langmuir Hybrid		
Iso. Const. 1	=	.11165E+00	.92993E-04	.48763E-05
Iso. Const. 2	=	.10000E+01	.83287E-03	.43672E-04
Iso. Const. 3	=	.10000E+01	.10000E+01	.10000E+01
Iso. Const. 4	=	.10000E+01	.10000E+01	.10000E+01
Iso. Const. 5	=	.00000E+00	.00000E+00	.00000E+00
Init. Conc.	=	.00000E+00	.00000E+00	.25000E+00
Conc. at eqb.	=	.00000E+00	.00000E+00	.25000E+00
Conc. units		M	M	M

=====

COMMAND LIST:

- 1: Step conc. of component 1 at .0000 min to .6089E-04 M
 Execute 1 times, every .0000 mins.
- 2: Step conc. of component 2 at .0000 min to .9000E-01 M
 Execute 1 times, every .0000 mins.
- 3: Step conc. of component 3 at .0000 min to 5.001 M
 Execute 1 times, every .0000 mins.
- 4: User set viscosity to .2613E-01 poise and density to 1.224 g/cm³
- 5: Carousel (conc.). Active between t = .0000 and .2000E+05 min.
 When comp. 1 reaches .8438E-07 M at end of node 100,
 shift 50 axial elements out the feed end
- 6: Monitor conc. history at stream 0. Filename = case.h01
 Output density adjustments:
 1.0 *default abs conc delta, 1.0 *default rel conc delta,
 .25 *default force w/ conc delta, .10 *default force w/o conc delta
- 7: Monitor conc. history at stream 1. Filename = case.h02
 Output density adjustments:
 1.0 *default abs conc delta, 1.0 *default rel conc delta,
 .25 *default force w/ conc delta, .10 *default force w/o conc delta
- 8: Monitor conc. history at stream 2. Filename = case.h03
 Output density adjustments:
 1.0 *default abs conc delta, 1.0 *default rel conc delta,
 .25 *default force w/ conc delta, .10 *default force w/o conc delta
- 9: Monitor conc. history at stream 3. Filename = case.h04
 Output density adjustments:
 1.0 *default abs conc delta, 1.0 *default rel conc delta,
 .25 *default force w/ conc delta, .10 *default force w/o conc delta
- 10: Monitor conc. history at stream 4. Filename = case.h05
 Output density adjustments:
 1.0 *default abs conc delta, 1.0 *default rel conc delta,
 .25 *default force w/ conc delta, .10 *default force w/o conc delta
- 11: Dump full profile file at 8400. min
 Execute 1 times, every .0000 mins.

```

12: Dump full profile file at .1408E+05 min
 Execute 1 times, every .0000 mins.
13: Dump full profile file at .1999E+05 min
 Execute 1 times, every .0000 mins.

```

VERSE Input for Full-Scale Facility (Effective Single Component Model)

```

[fullscale] Simulation of Cs removal on 1047.74 L Full-Scale Superlig 644 column
3 component (1-Cs, 2-K, 3-Na) isotherms; lead and lag columns with CSTRs
1, 100, 3, 6 ncomp, nele, ncol-bed, ncol-part
FCWNA isotherm, axial-disp, film-coef, surf-diff, BC-col FCUNA
NNNNN input-only, perfusable, feed-equil, datafile.yio
MMM comp-conc units
450.0, 77.0, 52619.9, 1.04774d+6 Length(cm), Diam(cm), Q-flow(ml/min), CSTR-vol(ml)
332.0, 0.450, 0.614, 0.0 part-rad(um), bed-void, part-void, sorb-cap()
0.0, 0.0, 0.25 initial concentrations (M)
S COMMAND - conc step change
1, 0.0, 6.089d-5, 1, 0.0 spec id, time(min), conc(M), freq, dt(min)
V COMMAND - viscosity/density change
0.0261255, 1.223549 fluid viscosity(posie), density(g/cm^3)
m COMMAND - subcolumns
50, 100, 0, 1, 3.37528d-7, 0.0, 50000.0 elem-shift, elem-watch, pp-watch, c-watch, c-thresh, t-e, t-ee
h COMMAND - effluent history dump
0, 1.0, 1.0, 0.25, 0.1 unit op#, ptscale(1-4) filtering
h COMMAND - effluent history dump
1, 1.0, 1.0, 0.25, 0.1 unit op#, ptscale(1-4) filtering
h COMMAND - effluent history dump
2, 1.0, 1.0, 0.25, 0.1 unit op#, ptscale(1-4) filtering
h COMMAND - effluent history dump
3, 1.0, 1.0, 0.25, 0.1 unit op#, ptscale(1-4) filtering
h COMMAND - effluent history dump
4, 1.0, 1.0, 0.25, 0.1 unit op#, ptscale(1-4) filtering
D
-1, 8380.0, 1, 0.0
D
-1, 14070.0, 1, 0.0
D
-1, 19970.0, 1, 0.0
D
-1, 25990.0, 1, 0.0
D
-1, 32050.0, 1, 0.0
D
-1, 38140.0, 1, 0.0
-
end of commands
39000.0, 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, 1.0d0, 1.0d0 size exclusion factor
3.395d-4, 4.70d-4, 3.67d-4 part-pore diffusivities (cm^2/min) 4.85d-4
4.85d-4, 4.70d-4, 3.67d-4 Brownian diffusivities (cm^2/min) 4.85d-4
1.1165d-1, 9.2993d-5, 4.8763d-6 Freundlich/Langmuir Hybrid a (moles/L B.V.) rhob=0.335
1.0, 8.3287d-4, 4.3672d-5 Freundlich/Langmuir Hybrid b (1/M)
1.0, 1.0, 1.0 Freundlich/Langmuir Hybrid Ma (-)
1.0, 1.0, 1.0 Freundlich/Langmuir Hybrid Mb (-)
2.9366d-4, 0.0, 0.0 Freundlich/Langmuir Hybrid beta (-)

```

VERSE Output for Full-Scale Facility (Effective Single Component Model)

```

=====
VERSE v7.80 by R. D. Whitley and N.-H. L. Wang, c1999 PRF
=====

```

Input file: case

```

[fullscale] Simulation of Cs removal on 1047.74 L Full-Scale Superlig 644 c
3 component (1-Cs, 2-K, 3-Na) isotherms; lead and lag columns with CSTRs
Begin Run: 14:40:02 on 01-31-2000 running under Windows 95/8

```

Finite elements - axial:100 particle: 1
 Collocation points - axial: 3 particle: 6 => Number of eqns: 3219
 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)	=	39000.00000 min	dtheta max	=	1.00000 BV
abs. tol.	=	.10000E-06	rel. tol.	=	.10000E-03
Total Length	=	450.00000 cm	D	=	77.00000 cm
Tot. Capacity	=	.00000 eq/L solid	Col. Vol.	=	2095481.56985 mL
F	=	52619.90000 mL/min	Uo (linear)	=	25.11113 cm/min
R	=	332.00000 microns	L/R	=	13554.21687
Bed Void frac.	=	.45000	Pcl. Porosity	=	.61400
Spec. Area	=	49.69880 1/cm	Time/BV	=	8.96017 min
Vol CSTRs	=	1047740.00000 mL			

Component no.	=	1
Ke [-]	=	.10000E+01
Eb [cm ² /min]	=	.35985E+01
Dp [cm ² /min]	=	.33950E-03
Doo [cm ² /min]	=	.48500E-03
kf [cm/min]	=	.20462E+00
Ds [cm ² /min]	=	.00000E+00

Dimensionless Groups:

Re	=	.58567E+00
Sc(i)	=	.26415E+04
Peb(i)	=	.15701E+04
Bi(i)	=	.32590E+02
Nf(i)	=	.20249E+03
Np(i)	=	.16945E+01
Pep(i)	=	.39994E+04

Isotherm	=	Freundlich/Langmuir Hybrid
Iso. Const. 1	=	.11165E+00
Iso. Const. 2	=	.10000E+01
Iso. Const. 3	=	.10000E+01
Iso. Const. 4	=	.10000E+01
Iso. Const. 5	=	.29366E-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 .6089E-04 M
 Execute 1 times, every .0000 mins.
- 2: User_set viscosity to .2613E-01 poise and density to 1.224 g/cm³
- 3: Carousel (conc.). Active between t = .0000 and .5000E+05 min.
 When comp. 1 reaches .3375E-06 M at end of node 100,
 shift 50 axial elements out the feed end
- 4: Monitor conc. history at stream 0. Filename = case.h01
 Output density adjustments:
 1.0 *default abs conc delta, 1.0 *default rel conc delta,
 .25 *default force w/ conc delta, .10 *default force w/o conc delta
- 5: Monitor conc. history at stream 1. Filename = case.h02
 Output density adjustments:
 1.0 *default abs conc delta, 1.0 *default rel conc delta,
 .25 *default force w/ conc delta, .10 *default force w/o conc delta
- 6: Monitor conc. history at stream 2. Filename = case.h03
 Output density adjustments:
 1.0 *default abs conc delta, 1.0 *default rel conc delta,
 .25 *default force w/ conc delta, .10 *default force w/o conc delta
- 7: Monitor conc. history at stream 3. Filename = case.h04
 Output density adjustments:
 1.0 *default abs conc delta, 1.0 *default rel conc delta,
 .25 *default force w/ conc delta, .10 *default force w/o conc delta
- 8: Monitor conc. history at stream 4. Filename = case.h05
 Output density adjustments:
 1.0 *default abs conc delta, 1.0 *default rel conc delta,
 .25 *default force w/ conc delta, .10 *default force w/o conc delta
- 9: Dump full profile file at 8380. min
 Execute 1 times, every .0000 mins.

10: Dump full profile file at .1407E+05 min
Execute 1 times, every .0000 mins.
11: Dump full profile file at .1997E+05 min
Execute 1 times, every .0000 mins.
12: Dump full profile file at .2599E+05 min
Execute 1 times, every .0000 mins.
13: Dump full profile file at .3205E+05 min
Execute 1 times, every .0000 mins.
14: Dump full profile file at .3814E+05 min
Execute 1 times, every .0000 mins.

=====

Conc. Carousel caused bed shift at t = 8413. min
Conc. Carousel caused bed shift at t = .1410E+05 min
Conc. Carousel caused bed shift at t = .2000E+05 min
Conc. Carousel caused bed shift at t = .2601E+05 min
Conc. Carousel caused bed shift at t = .3208E+05 min
Conc. Carousel caused bed shift at t = .3816E+05 min
VERSE-LC finished in 4555 steps. Average step size 8.562 minutes
End run: 14:52:05 on 01-31-2000
Integrated Areas in History Files:
case.h01 2.37471
case.h02 2.37195
case.h03 .574635
case.h04 .568776
case.h05 .132965E-02

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