ION EXCHANGE MODELING OF CRYSTALLINE SILICOTITANATE (IONSIV® IE-911) COLUMN FOR CESIUM REMOVAL FROM ARGENTINE WASTE (U)

Thong Hang

Ion Exchange Column

Argentine Radioactive Waste

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Liquid effluent as low level radioactive waste

June 2003

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CONTENTS

LIST OF FIGURES

LIST OF TABLES

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EXECUTIVE SUMMARY

The U.S. Department of Energy (DOE) and the Nuclear Energy Commission of Argentina (CNEA) have a collaborative project to separate cesium/strontium from waste resulting from the production of Mo-99. The Pacific Northwest National Laboratory (PNNL) is assisting DOE on this joint project by providing technical guidance to CNEA scientists. As part of the collaboration, PNNL staff works with staff at the Savannah River Technology Center (SRTC) to run the VERSE-LC model for removal of cesium from the Mo-99 waste using the crystalline silicotitanate (CST) material (IONSIV® IE-911, UOP LLC, DesPlaines, IL) based on technical data provided by CNEA.

This report discusses the VERSE-LC ion-exchange-column model and the predicted results for CNEA test cases. The major accomplishments of this study include:

- A "best estimate" value of 0.22 is used for (D_p/D_∞) in this report based on a previous study that determined (D_p/D_∞) by utilizing the breakthrough data for several representative column performance tests conducted at SRS, Hanford and Oak Ridge National Laboratory (ORNL). For future use, it is recommended that (D_p/D_∞) be fitted to the breakthrough data of CNEA waste.

- The breakthrough curves for the column tests are established at three different waste flow rates (i.e., 17.8 cm^3/hr, 59.3 cm^3/hr, and 148 cm^3/hr). The results show a faster breakthrough with increasing flow rates. These breakthrough curves provide data for comparison with the test data and with the output from the CNEA model.

- For the plant column system, the VERSE-LC model predicts that the exit cesium concentration reaches the limit imposed by the required decontamination factor of 1040 after ~353.5 hours of operation and 62.57 liters of waste (i.e., 78.2% of the specified 80-liter batch) passed through the system.

- In a preliminary evaluation of the two-column system, a column-length sizing curve is obtained for a column diameter of 1.38 cm. The sizing curve can be expanded for a range of column lengths in the future.

1   INTRODUCTION

The CNEA is investigating the selective removal of cesium and strontium from the Mo-99 production waste stream. Through the Joint Coordinating Committee for Radioactive and Mixed Waste Management between CNEA and DOE, a collaborative proposal was made to study cesium and strontium separations from the Mo-99 waste (Collaboration Agreement, 2001).

Argentine researchers have been conducting experiments to evaluate the performance of an ion exchange column using IONSIV® IE-911 (the engineered form of CST manufactured by UOP LLC, DesPlaines, IL) for cesium removal. The ion exchange technology using CST to remove cesium from radioactive waste has been studied at major DOE sites (Savannah River Site, Hanford), and computer models to calculate CST ion exchange column size and performance were developed at the Savannah River Technology Center (SRTC) using a PC-based version of VERSE-LC software (Walker, 1998; Hamm et al., 2001). VERSE-LC (VErsatile Reaction SEparation simulator for Liquid Chromatography), developed by Professor N.-H. Linda Wang (School of Engineering, Purdue University) to model liquid adsorption, ion exchange and liquid chromatography processes (Whitley and Wang, 1998), has been licensed to SRTC to assist in the column test predictions for both the SRS and Hanford programs. VERSE-LC had been thoroughly verified by SRTC researchers (Hamm et al., 1999).

PNNL is assisting DOE on this joint project by providing technical guidance to CNEA scientists. As part of the collaboration, PNNL staff works with SRTC staff to run the VERSE-LC model for removal of cesium from the Mo-99 wastes based on detailed description of the Mo-99 waste stream provided by CNEA. This report discusses the VERSE-LC ion-exchange-column model, the predicted results of CNEA test cases, and a preliminary evaluation of the two-column system.

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2   VERSE-LC CST ION-EXCHANGE-COLUMN MODEL

2.1   Assumptions

The VERSE-LC model for CST ion exchange column describes the loading of cesium onto the granular CST ion-exchanger fixed bed. The mathematical method applicable to mass transfer in a porous medium is utilized to account for bulk convection, axial dispersion, film mass transfer, pore diffusion, and adsorption. The method involves the following basic assumptions:

1. The solution contains only two components, i.e., a solvent and a single solute (cesium).
2. Plug flow with constant volumetric flow rate through the packed column.
3. No radial concentration gradients in the column.
4. Isothermal process within the column.
5. Solid particles are spherical, uniform in size, and do not swell or shrink.
6. Negligible surface diffusion with Fickian pore diffusion dominating.
7. No angular concentration gradients within a particle.
8. Constant pore diffusivity.
9. Local equilibrium between the solute concentration adsorbed on the solid and the local solute concentration in the solution.

2.2   Governing Equations

A porous particle-diffusion model proposed for simulation of fixed-bed adsorption processes (Berninger et al., 1991) was adopted for the VERSE-LC CST ion-exchange-column model. The porous particle-diffusion model provides the material balance equations in both the mobile phase and the pore phase. An "effective" binary solute-solvent system is assumed. Furthermore, for ionic species modeling, the total ionic strength of the feed solution is assumed to be equal to the native solution within the column.

Mobile phase:

$$\frac{\partial C}{\partial t} = E_b \frac{\partial^2 C}{\partial z^2} - u_o \frac{\partial C}{\partial z} - \frac{3k_f(1-\boldsymbol{e}_b)}{R_p \boldsymbol{e}_b}(C - C_{p,r=R_p}) \tag{1}$$

$$\text{z = 0:} \qquad E_b \frac{\partial C}{\partial z} = u_o(C(t,0) - C_o) \tag{2}$$

$$\text{z = L:} \qquad \frac{\partial C}{\partial z} = 0 \tag{3}$$

$$\text{t = 0:} \qquad C = C(0, z) \tag{4}$$

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Pore phase:

$$\left(\boldsymbol{e}_p + (1-\boldsymbol{e}_p)\frac{\partial Q}{\partial C_p}\right)\frac{\partial C_p}{\partial t} = \boldsymbol{e}_p \frac{D_p}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial C_p}{\partial r}\right) \tag{5}$$

$$r = 0: \qquad \frac{\partial C_p}{\partial r} = 0 \tag{6}$$

$$r = R_p: \qquad \boldsymbol{e}_p D_p \frac{\partial C_p}{\partial r} = k_f (C - C_{p,r=R_p}) \tag{7}$$

$$t = 0: \qquad C_p = C_p(0,r) \tag{8}$$

2.3   Axial Dispersion

Axial dispersion in packed columns is the result of mechanical dispersion added onto molecular diffusion. For practical flowrates, mechanical dispersion dominates. In the low Reynolds number range of interest, axial dispersion coefficient, E_b, is estimated by the Chung and Wen correlation (Chung and Wen, 1968):

$$\frac{u_o L}{E_b} = \frac{L}{2\boldsymbol{e}_b R_p}(0.2 + 0.011\,\mathrm{Re}^{0.48}) \tag{9}$$

The Reynolds number, Re, in Equation 9 is defined as:

$$\mathrm{Re} = \frac{2R_p \boldsymbol{r} u_o \boldsymbol{e}_b}{\boldsymbol{m}} \tag{10}$$

2.4   Film Diffusion

For both the laboratory-scale test column and the plant column proposed by CNEA, with the IONSIV® IE-911 CST particle-size distributions, the Reynolds number is much less than 1. VERSE-LC applies the Wilson and Geankoplis (1966) correlation to determine the film mass transfer coefficient, k_f, in this low Reynolds number range:

$$\left(\frac{k_f}{u_o \boldsymbol{e}_b}\right)Sc^{2/3} = \frac{1.09}{\boldsymbol{e}_b}\mathrm{Re}^{-2/3} \tag{11}$$

With the Schmidt number, Sc, defined as:

WESTINGHOUSE SAVANNAH RIVER COMPANY   REPORT: WSRC-TR-2003-00137
Ion Exchange Modeling of Crystalline Silicotitanate (IONSIV® IE-911) Date: June 2003
Column for Cesium Removal from Argentine Waste (U)   Page: 5 of 16

$$Sc = \left(\frac{m}{rD_\infty} \right) \tag{12}$$

2.5   Molecular Diffusion And Pore Diffusion

CST-packed columns are mass-transfer limited, giving rise to relatively slow "kinetics." Therefore, in predicting cesium-breakthrough behavior for CST packed columns, the pore diffusion coefficient should be an important parameter. The "effective" cesium pore diffusion coefficient D_p can be normalized with respect to the free stream "Brownian" diffusion coefficient D_∞. The inverse of this ratio is referred to as a tortuosity factor that is primarily dependent upon the internal structure of the porous material. For materials with very large pores, a tortuosity factor approaching unity is observed, while for very small pores, factors approaching zero can result. The rate of "kinetics" is inversely related to the tortuosity factor. The "best estimate" value of this ratio (D_p/D_∞) was determined by utilizing the breakthrough data for several representative column performance tests conducted at SRS, Hanford and ORNL. From these test data, the "best estimate" value of 0.22 is obtained for the ratio (D_p/D_∞). The molecular (or Brownian) diffusion coefficient D_∞ is estimated by the Nernst-Haskell equation and then corrected for temperature and viscosity. A detailed discussion of D_p and D_∞ is given elsewhere (Hamm et al., 2001). Although other researchers (Anthony, 2001) suggested a much lower value (i.e., 0.06) for (D_p/D_∞), the value of 0.22 is used in this report. For future use, it is recommended that (D_p/D_∞) be fitted to the breakthrough data of CNEA waste.

2.6   Equilibrium Cesium Isotherm

Solid-phase concentrations Q are related to pore-phase concentrations C_p by isotherms. The non-linear Langmuir isotherm is selected to represent the Q-C_p relationship:

$$Q = \frac{\dfrac{a}{(1-e_b)(1-e_p)} C_p}{1 + bC_p} \tag{13}$$

Langmuir coefficients a and b are obtained by fitting Eq. (13) to CNEA equilibrium loading data at 25°C. The Langmuir isotherm and equilibrium data are shown in Fig. 1.
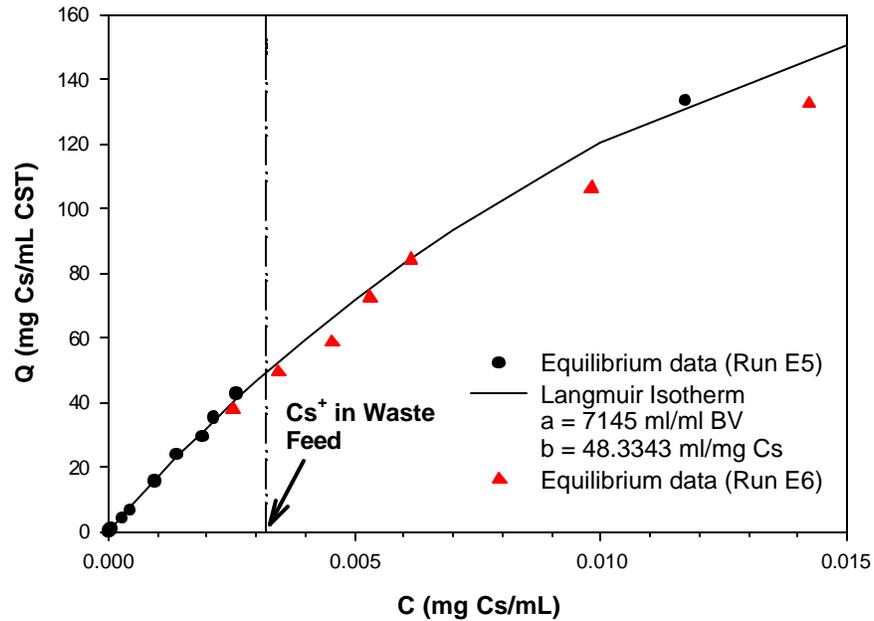
Fig. 1. CNEA Equilibrium Loading Data at 25°C

2.7   Numerical Method

The method of orthogonal collocation on finite elements is applied to numerically solve Eqs. (1) and (8).   The method provides a mathematical technique in which a series of orthogonal polynomials are used as trial functions, the collocation points are taken as the roots to one of those polynomials, and the dependent va riables are the solution values at the collocation points. The entire domain is divided into a set of elements.   Orthogonal polynomials defined for each element are pieced together to provide an approximation over the whole domain (Finlayson, 1980). Fig. 2 below illustrates the grid arrangement in the orthogonal collocation method.
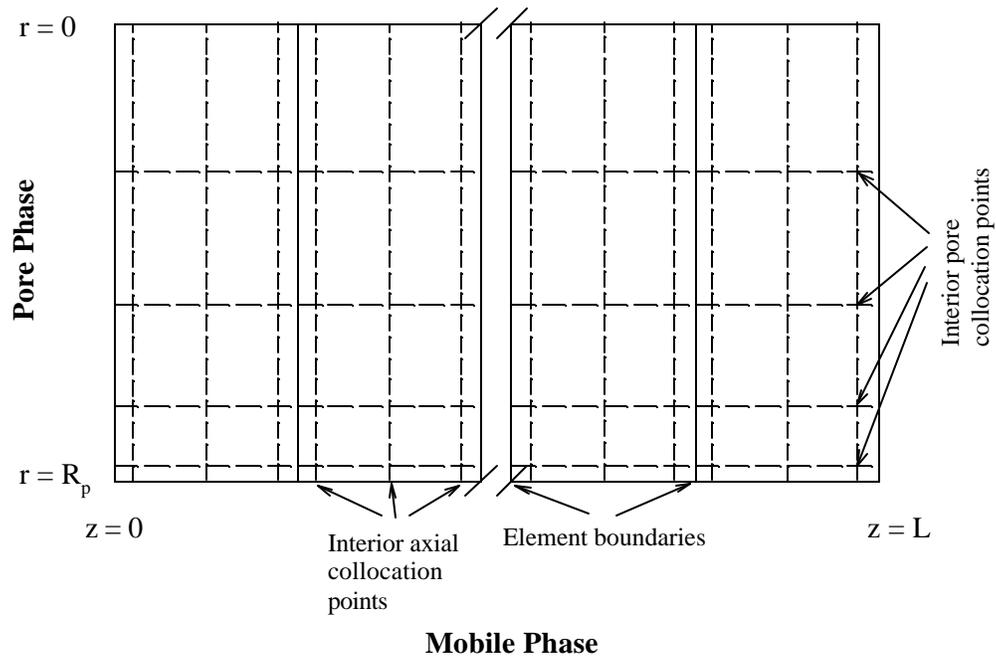
**Fig. 2. Orthogonal Collocation on Finite Elements – Computational Grid
(Example shown: 3 interior collocation points per axial element,
4 interior collocation points in the particle element)**

3   CNEA TEST CASES

CNEA provided data for four test cases to be predicted by the VERSE-LC column model. The first three cases are for the column tests conducted at three different waste feed flow rates. The fourth case is for the plant column test. The four test cases are summarized below:

- Test Case 1: Column test with the waste feed flow rate 17.8 cm^3/hr.
- Test Case 2: Column test with the waste feed flow rate 59.3 cm^3/hr.
- Test Case 3: Column test with the waste feed flow rate 148 cm^3/hr.
- Test Case 4: Plant column with the waste feed flow rate 177 cm^3/hr.

Data on waste feeds for the test cases are given in Table 1 that includes waste composition, viscosity and density. All data were provided by CNEA.

Table 1. CNEA Waste Feeds

	Column Tests (Test Cases 1, 2 and 3)	Plant Column (Test Case 4)
Concentration (M)		
Na^+	3.50	3.50
Cs^+	0.000024	0.000024
Sr^+		0.000003
OH^-	2.76	2.76
AlO_2^-	0.74	0.74
Cl^-		0.004
Viscosity at 20°C (cP)	2.6	2.6
Density at 20°C (g/ml)	1.15	1.15

The parameters employed in the VERSE-LC column model are shown in Table 2. For all test cases, six interior collocation points per axial element and four interior collocation points in the particle element are specified. This discretization scheme seems adequate for the CNEA test cases. The number of axial elements can be varied to achieve the desired accuracy. The effects of theses parameters (i.e. number of axial elements, number of interior axial collocation points, and number of interior particle collocation points) on the convergence of the system and the computational speed have been studied elsewhere (Berninger et al., 1991).

WESTINGHOUSE SAVANNAH RIVER COMPANY   REPORT: WSRC-TR-2003-00137
Ion Exchange Modeling of Crystalline Silicotitanate (IONSIV® IE-911) Date: June 2003
Column for Cesium Removal from Argentine Waste (U)   Page: 9 of 16

Table 2. VERSE-LC Column Model Parameter Settings

Parameters	Test Case 1	Test Case 2	Test Case 3	Test Case 4
Column length L	11.8 cm	11.8 cm	11.8 cm	39.6 cm
Column diameter	0.8 cm	0.8 cm	0.8 cm	1.38 cm
Particle radius R_p	245.25 μm	245.25μm	245.25 μm	245.25 μm
Bed porosity ε_b	0.48	0.48	0.48	0.48
Particle porosity ε_p	0.23	0.23	0.23	0.23
Feed flow rate	0.29667 ml/min (17.8 cm^3/hr)	0.98834 ml/min (59.3 cm^3/hr)	2.4667 ml/min (148 cm^3/hr)	2.95 ml/min (177 cm^3/hr)
Feed viscosity μ	0.026 P	0.026 P	0.026 P	0.026 P
Feed density	1.15 g/ml	1.15 g/ml	1.15 g/ml	1.15 g/ml
Feed cesium concentration	0.00319 mg/ml (0.000024 M)	0.00319 mg/ml (0.000024 M)	0.00319 mg/ml (0.000024 M)	0.00319 mg/ml (0.000024 M)
Brownian diffusivity D_∞	6.34702E-4 cm^2/min	6.34702E-4 cm^2/min	6.34702E-4 cm^2/min	6.34516E-4 cm^2/min
Pore diffusivity D_p	1.39634E-4 cm^2/min	1.39634E-4 cm^2/min	1.39634E-4 cm^2/min	1.39594E-04 cm^2/min
Langmuir coefficient a	7145 mg/ml	7145 mg/ml	7145 mg/ml	7145 mg/ml
Langmuir coefficient b	48.3343 ml/mg	48.3343 ml/mg	48.3343 ml/mg	48.3343 ml/mg
Number of axial elements	25	25	25	100
Number of interior axial collocation points	6	6	6	6
Number of interior particle collocation points	4	4	4	4

3.1 Column Tests

Test cases 1, 2 and 3 deal with the laboratory-scale column tests. The objective for the VERSE-LC column model is to predict the breakthrough curves at specified conditions. These predicted breakthrough curves provide data for comparison with the experimental data and with the output data from the CNEA model. Using parameter settings given in Table 2, three VERSE-LC model runs were made to simulate the three column tests. Fig. 3 displays the predicted relative cesium concentrations at the column outlet vs. time (i.e., breakthrough curves). The results show that the breakthrough is faster with increasing waste feed flow rates.

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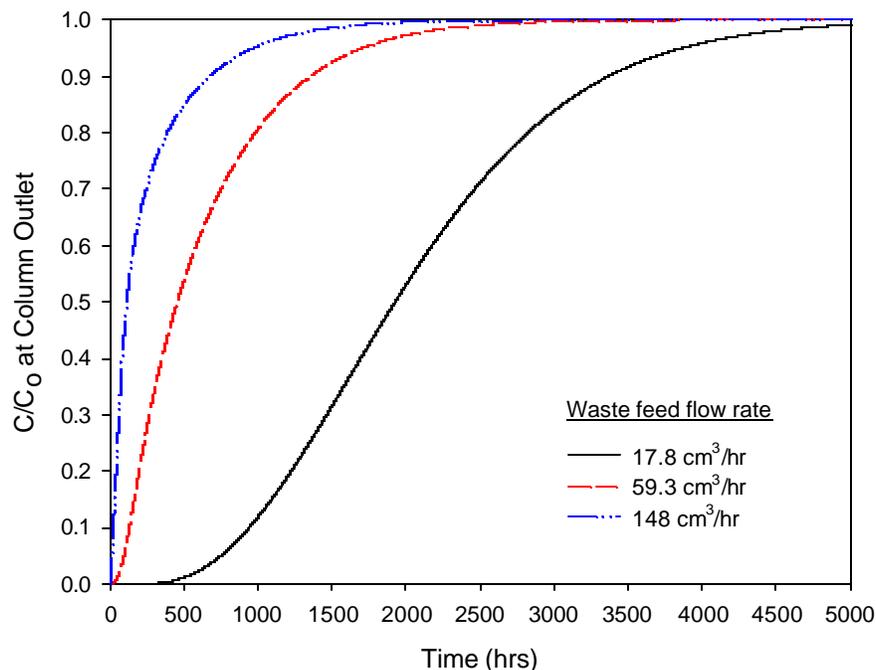
Fig. 3. Relative Exit Cesium Concentration for the Column Tests
(C_o: Cesium concentration in the waste feed)

3.2   Plant Column System

Test case 4 corresponds to the plant column system in which the Mo-99 waste is fed to the ion exchange plant column at 177 cm^3/hr. The required decontamination factor DF for the plant column system is 1040. If DF is defined as the ratio of (C_o/C_f) with C_o and C_f being the feed and exit cesium concentrations, respectively, then C_f cannot exceed 2.3077×10^{-8} M, provided that C_o is 0.000024 M.

Based on CNEA specifications of this test case as listed in Tables 1 and 2, a VERSE-LC run was performed. Fig. 4 shows the calculated result. The VERSE-LC model predicts that the exit cesium concentration reaches the limit after ~353.5 hours of operation and 62.57 liters of waste (i.e., 78.2% of the specified 80-liter batch) passed through the system.
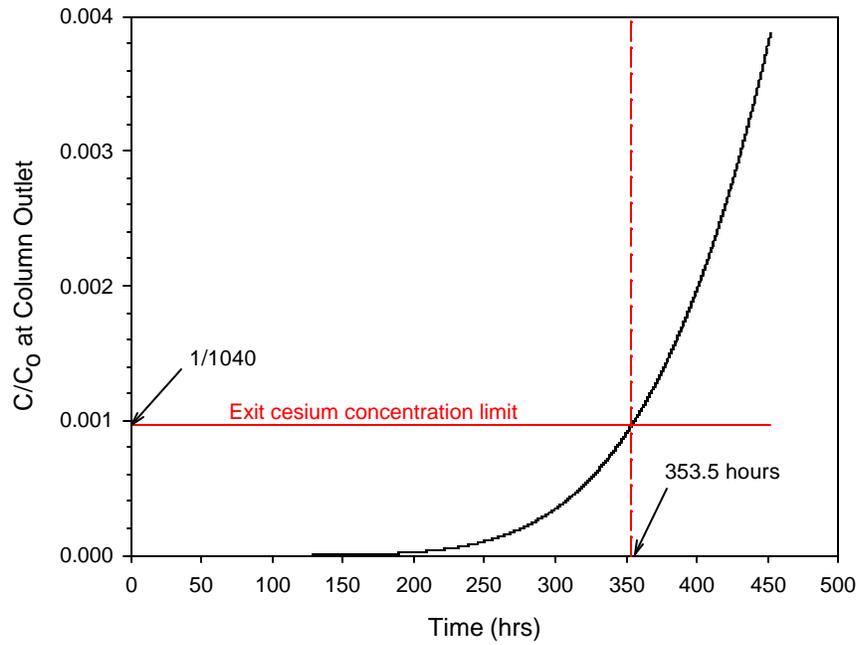
**Fig. 4. Relative Exit Cesium Concentration for the Plant Column System
(C_o: Cesium concentration in the waste feed)**

4 PRELIMINARY EVALUATION OF THE TWO-COLUMN SYSTEM

CNEA has expressed interest in evaluation of a two-column system. The sizes would be chosen in order to hold approximately 90% of the cesium in the first column. This column would be used in the manufacture of cesium sources. The second column, intended to load the remaining 10% of cesium, would be considered solid waste.

Professor Wang at Purdue University proposed the mass transfer zone (MTZ) approach for sizing a system of ion-exchange columns. The MTZ length is a function of isotherm parameters, cesium feed concentrations, mass transfer parameters, and linear velocity. If the isotherm is nonlinear at the concentration level in the waste solution of interest, the concentration waves eventually develop into a constant pattern (Walker, 1998). For demonstration, assuming that (1) the column diameter is specified (e.g., 4ft or 1.2192m), (2) a breakthrough of 90% is desired in the first column, and (3) the exit cesium concentration limit in the second column is $1.3_{x}10^{-6}$ mg/ml (a concentration limit used at SRS), the MTZ is defined as the length of column required to contain the cesium concentration wave from 90% of the feed concentration to $1.3_{x}10^{-3}$ mg/l. In the simulation to determine the MTZ length, a single column is chosen sufficiently long so that the concentration waves can reach a constant pattern. The MTZ length determination is illustrated in Fig. 5 that plots cesium concentration as a function of relative column position (normalized by the simulation column length L_c). If the constant pattern MTZ length, L_{MTZ}, is selected to be the column length, the two-column system will have a total length of $2\,L_{MTZ}$.
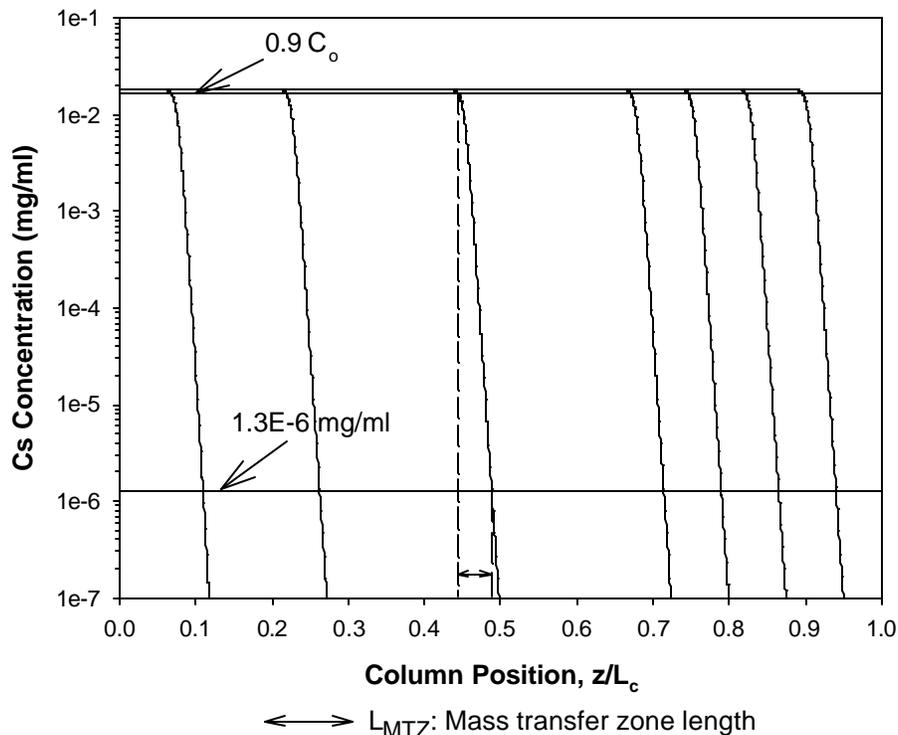
Fig. 5. Mass Transfer Zone Length Determination
(Column Diameter: 4ft or 121.92cm)

Unfortunately, the MTZ approach to sizing ion-exchange columns is not applicable here since the CNEA isotherm displays a high degree of linearity at the cesium concentration level in the Mo-99 waste feed as shown in Fig. 1. In this case, no constant pattern of the concentration waves develops and the MTZ length keeps increasing. Hence, a constant pattern L_{MTZ} cannot be determined.

This preliminary evaluation study assumes that all specifications (with the exception of the column length) and conditions for the plant column also apply to the two-column system. Again, a decontamination factor DF of 1040 is required, resulting in an exit cesium concentration limit of 2.3077_x10^{-8} M (or 3.067_x10^{-6} mg/ml), provided that C_o is 0.000024 M. A series of VERSE-LC runs were made for the selected column diameter of 1.38 cm. In each run, a column length was specified and the run was terminated when the exit cesium concentration in column 2 exceeds the specified limit. Fig. 6 shows the VERSE-LC result for the 80-cm column length. The cesium concentration limit at the column 2 exit is reached at ~3870 hours. The breakthrough in the first column is ~43.5%.
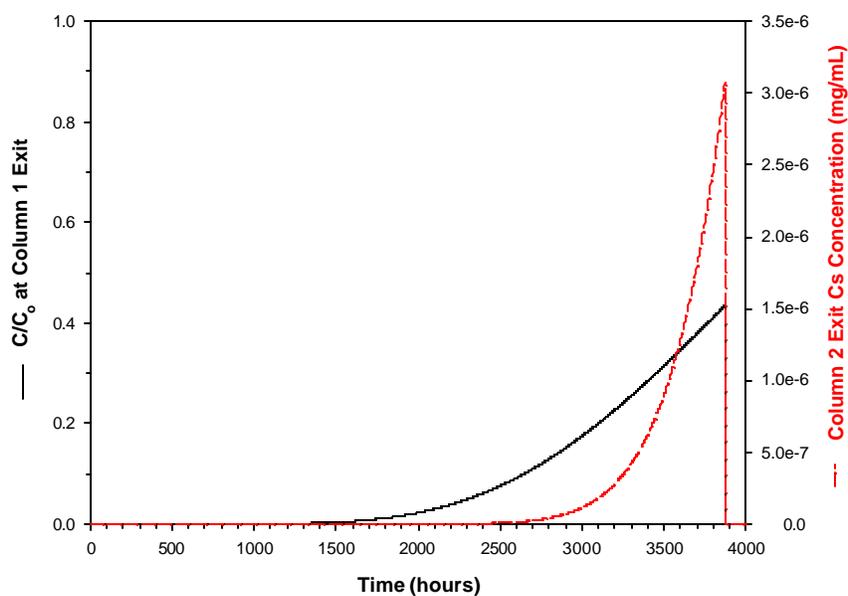
**Fig. 6. Two-Column System
(Column Diameter: 1.38 cm; Column Length: 80 cm)**

The result of all VERSE-LC runs for the two-column system is shown in Fig. 7 that displays the column length as a function of cesium breakthrough in the first column. If desired, this column-length sizing curve can be obtained for a range of column diameters.
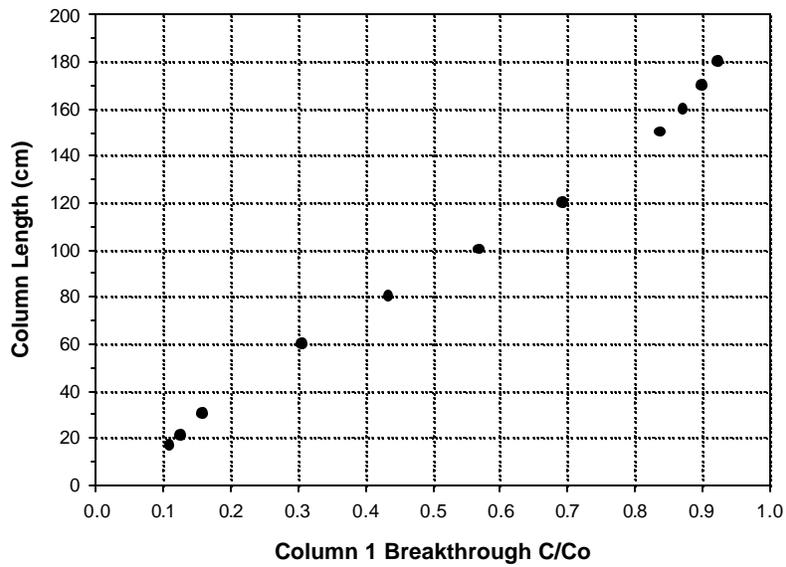
**Fig. 7. Column-Length Sizing Curve for the Two-Column System
(Column Diameter: 1.38 cm)**

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5   NOMENCLATURE

a	Langmuir coefficient, mg/ml B.V. (B.V.: Volume of the fixed bed)
b	Langmuir coefficient, ml/mg
C	Bulk-phase cesium concentration, mg/ml
C_p	Pore-phase cesium concentration, mg/ml
C_o	Column inlet cesium concentration, mg/ml
D_p	Pore diffusivity, cm^2/min
D_∞	Brownian diffusivity, cm^2/min
E_b	Axial dispersion coefficient, cm^2/min
k_f	Film mass transfer coefficient, cm/min
L	Column length, cm
L_{MTZ}	Mass transfer zone length
Q	Solid-phase solute concentration, mg/ml S.V. (S.V.: Volume of the solid phase)
r	Radial position from center of adsorbent particle, cm
Re	Reynolds number
R_p	Adsorbent particle radius, cm
Sc	Schmidt number
t	Time, min
u_o	Linear interstitial velocity, cm/min
z	Position in axial direction, cm
ε_b	Bed porosity
ε_p	Intraparticle porosity
μ	Viscosity, g s^{-1} cm^{-1}
ρ	Density, g/ml

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