DEVELOPMENT OF TWO COMPUTER MODELS TO SUPPORT DESIGN OF SELECTIVE ION EXCHANGE SYSTEMS

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ABSTRACT

The Idaho National Engineering and Environmental Laboratory (INEEL) is currently storing approximately 1 million gallons of high activity liquid waste in underground tanks. This material is to be stabilized and packaged for shipment to a disposal site. One of the treatment alternatives under investigation involves separating radioactive cesium by ion exchange so the bulk of the material can be managed as contact-handled waste. Laboratory experimentation has been conducted with several cesium-selective ion exchange materials. Two computer simulation models have been developed for applying experimental results in future design work.

One model solves material balance and mass transfer differential equations using a finite difference method. An iterative approach is applied to obtain agreement between the model output and an experimental breakthrough curve. The second model uses the experimental breakthrough data to estimate an "effective" distribution coefficient, K_d. The ion exchange column is modeled as equilibrium stages in series using this parameter. The value of K_d is held constant, which is reasonable since the isotherm is linear over the range of cesium concentrations of interest at INEEL. Both models accurately describe the results from laboratory experiments.

The models are implemented in a combination of Excel spreadsheets and Visual Basic code. Experimental data are provided as input by the user via a preformatted spreadsheet and through an input screen. The information is then analyzed based on the simulation selected. Two modules are included. The first generates a breakthrough curve that can be compared with laboratory results. Input parameters can be changed (e.g., the estimated mass transfer coefficient or the number of equilibrium stages), until a reasonable fit to the experimental data is obtained. In the second module, the programs estimate the amount of liquid processed and the capacity utilized, based on an effluent concentration endpoint that is provided by the user. The results are written to a separate Excel workbook spreadsheet. The models are currently being used in design studies to predict the performance of multi-column designs.

INTRODUCTION

This document describes two computer models that have been developed to predict the performance of ion exchange (IX) columns – the Equilibrium Stages in Series Model and the Mass Transfer Sorption Model. The goal of each model is to simulate the performance of a column based on laboratory testing. Once the user modifies the input so that the program output effectively mimics the experimental breakthrough curve, the model can be used to evaluate a variety of configurations, including multi-column arrangements.

The two models are independent of each other. That is, either program can be used to model column performance. While the two models provide reasonable good prediction of actual column performance, the Mass Transfer Sorption Model seems to be better at predicting the onset of breakthrough. This is important in designing applications requiring very low solute content in the column effluent.

BACKGROUND

As part of a development program evaluating technologies for radioactive liquid processing, the Idaho National Engineering Laboratory (INEEL) has been testing isotope separation methods, including ion exchange. Cesium-137 accounts for a significant fraction of the exposure rate associated with radioactive liquid wastes stored at the Idaho Nuclear Technology and Engineering Center (INTEC) at the INEEL site. One proposed method of treating the waste includes selectively removing cesium. At that point, the waste technically can be managed as a contact-handled transuranic (CH TRU) waste destined for the Waste Isolation Pilot Plant (WIPP). The result is a substantial reduction in the costs of processing and disposing of the waste versus treatment to borosilicate glass form for disposal at the national high-level waste geologic repository.

Several materials have been investigated for stripping cesium from the waste. These include a proprietary inorganic material, IONSIV® IE911, available from Universal Oil Products (UOP). This is a crystalline silicotitanate (CST) product, supported in a zirconium hydroxide matrix. Because of this, it is not stable in acidic liquids like those at INTEC. However, testing has shown that it performs acceptably if the acidity of the feed material is reduced to 0.5N or less.

Two materials using ammonium moybdophosphate (AMP) have shown promise. The AMP is a microcrystalline compound, so it must be supported on a stable matrix. The AMP has been combined with an organic substrate, polyacrylonitrile (PAN), resulting in a material with high affinity and extremely high capacity for cesium. Unfortunately, the organic substrate presents potential handling problems in high radiation fields. It is expected to generate unacceptably large amounts of hydrogen and volatile organics from radiolytic decomposition of organics when stored.

INEEL and Russian researchers have developed another AMP-based material. The material is combined with inorganic cenospheres, which are small hollow beads of glassy material formed during the combustion of coal. Cenospheres are marketed in large quantities as additives in plastics and engineered products. The spheres are porous and hollow, and a process has been developed to bond AMP to the inside surfaces of the spheres. A patent on the process is pending.

Both AMP-based materials perform well, and neither is susceptible to acid attack. However, neither is commercially available at present.

MODEL THEORY AND DISCUSSION

Equilibrium Stages in Series Methodology

The equilibrium computer program is based on two key assumptions. The first is that an ion exchange column can be modeled as a series of equilibrium stages. This approach is often used for separation processes, such as distillation or liquid-liquid extraction. The program divides a column into a number of segments. In essence, the column is modeled as a series of batch contactors. Mathematically, the process is similar to the stage wise countercurrent model described by Treybal [1]. Mass transfer calculations are based on an aliquot of liquid coming into equilibrium with the solid ion exchange media in a segment. The program then moves that same aliquot of liquid to the next segment, where the same equilibrium and material balance calculations are performed. This process is repeated for all segments.

The second assumption is that the distribution coefficient, Kd, is a constant. The value of Kd is essentially the slope of the isotherm at any point. Typical isotherms are not linear, so Kd varies over the entire range of feed concentrations. However, for exchange of species at very low concentrations, the isotherm is essentially linear. A plot of low concentration values is presented as Figure I.
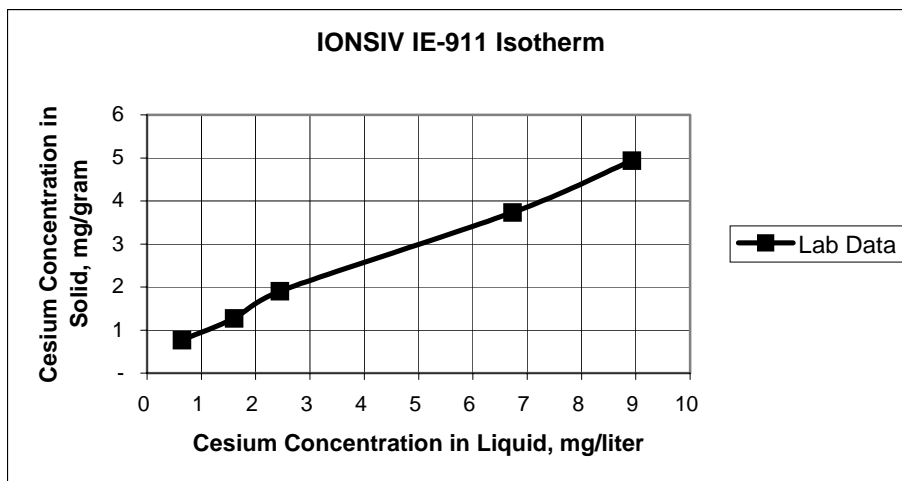
Fig. 1 Typical Isotherm for low concentration liquid

The calculations use the definition of the distribution coefficient along with a material balance. The solute entering a segment of the column is initially all in the liquid phase. At equilibrium, some of this material is adsorbed on the solid media. The remainder is still in the liquid solution. As additional aliquots of liquid pass through a column segment, the solute sorbed from previous aliquots is retained on the solid media.

To describe the approach used in the model, some variables must first be defined.
Let:

V = volume of an aliquot of liquid, liters. An aliquot is the volume of liquid equivalent to the interstitial space in a column segment.

Cin = concentration of solute in liquid entering a segment, mg/liter.

$Ceff$ = equilibrium concentration of solute in the liquid in equilibrium with the solid media in the segment, mg/liter.

Kd = distribution coefficient. This parameter is a proportionality constant relating material sorbed on a solid to the material remaining in solution at equilibrium.

x = incremental mass of solute sorbed onto media in a segment from an aliquot of liquid, mg.

y = mass of solute left in the aliquot of liquid after equilibrium is established in a segment, mg.

$Feed$ = total mass of solute entering a column segment in an aliquot of liquid, mg. ($Feed = x + y$). Also, $Feed = Cin * V$

q_c = current concentration of solute adsorbed onto media, mg/gram.

q_p = concentration of solute sorbed onto media from all previous aliquots of liquid, mg/gram.

m = mass of solid media in a column segment (dry basis), grams.

The distribution coefficient, Kd is defined as follows:

$$Kd = q_c/Ceff \qquad \text{(Eq. 1)}$$
Now $q_c = (x/m) + q_p$ and $Ceff = y/V$, so
$$Kd = ((x/m) + q_p)/(y/V) \qquad \text{(Eq. 2)}$$
Rearranging gives: $y = (V/Kd)*((x/m) + q_p)$
$$= (V/Kd)*(((Feed - y)/m) + q_p) \qquad \text{(Eq. 3)}$$

Further rearranging of the equation for y yields:
$$y = (V/Kd)* (Feed/m + q_p) - (V/(Kd*m))*y$$
$$y*(1 + (V/(Kd*m))) = (V/Kd)*(Feed/m + q_p)$$
$$y = (V/Kd)/(1 + (V/(Kd*m)))*(Feed/m + q_p)$$
$$y = (Feed/m + q_p)/((Kd/V) + V/(V*m))$$
$$y = ((Feed/m) + q_p)/((Kd/V) + (1/m)) \qquad \text{(Eq. 4)}$$
Also, remember that:
$$x = Feed - y \qquad \text{(Eq. 5)}$$

With values of x and y in terms of measured parameters, it is possible to calculate q_c and $Ceff$ and build a model of a breakthrough curve.

Now Ceff is the concentration of the solute in the liquid as it leaves a column segment. This value becomes Cin for the next segment. In fact, the values of q_c, q_p, Cin, and Ceff all relate to a given segment, not to the column as a whole.

The program includes two modules. The first module models the breakthrough curve for a single column. The user can modify input variables to optimize the quality of the fit to experimental data.

The second module models the operation of three columns in series. This is based on an evaluation of the needs for the CsIX process. All three columns have the same dimensions and hold the same amount of media. The effluent from the bottom segment of the first column becomes the feed to the first segment of the second column. Likewise, the effluent from the bottom segment of the second column becomes the feed to the first segment of the third column. Arrays for Cin, Ceff, qp, and qc are used to keep track of values for each segment in a column. A set of these arrays is needed for each column in the series. Thus, it would be relatively simple to modify the source code to add or subtract columns.

The program includes a loop that increments the number of aliquots of liquid applied to the columns. The program keeps track of the mass of solute applied to each column and the total volume of liquid applied. Program output is a data set describing the breakthrough curve for each column. Figure II compares model output to actual laboratory results on a small column. The material tested was a commercial product, IONSIV® IE-911, a crystalline silicotitanate (CST) material. The solute of interest was cesium.
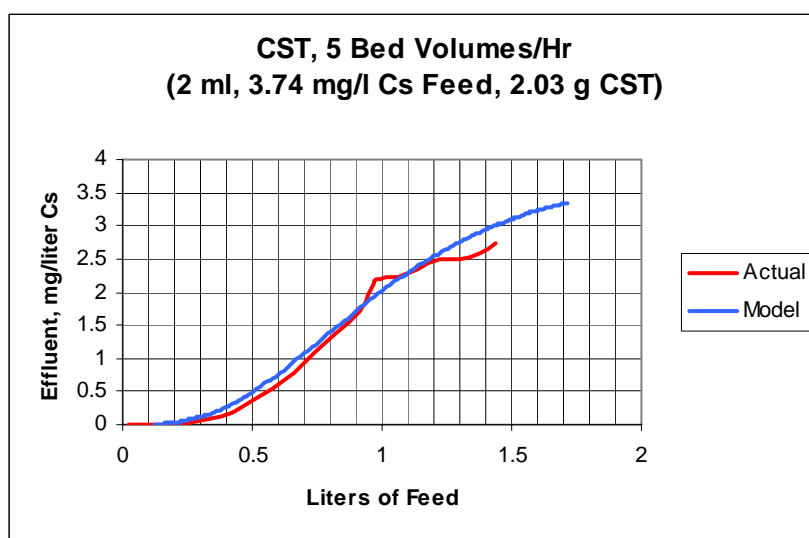

Fig. 2 Comparison of model output to lab test data

This equilibrium-based model includes another module that evaluates the timing and impact of column change out during operation. This module assumes three columns of equal size installed and operated in series. Basically, when a predetermined concentration limit of the solute appears in the effluent of the last column, the first column in the series is ready for change out. Then the following activities are modeled:

- The second column becomes the first (lead column) in the train of three.
- The third column is moved to position 2.
- A brand new column with fresh media is put in position three in the treatment train.

This approach is in keeping with the concept of multiple equilibrium stages discussed by Treybal [1].

The program keeps track of the q and c values for the columns as packets of liquid move from one position to another. Also, the total volume of liquid waste treated between column change outs is included in the program output.

The operation of an ion exchange column does not exactly match the ideal plug flow. Dispersion has the effect of expanding the active zone in the column, where exchange is occurring. This model, based on equilibrium stages in series, addresses dispersion empirically through the selection of the number of segments into which the column is divided. If the user selects a small number of segments, and the model output is a good match for the experimental breakthrough curve, then dispersion is significant. On the other hand, if a large number of segments are needed to accurately model the experimental data, then the column operation is less affected by dispersion [2].

Mass Transfer Based Methodology

This discussion is based in large part on a previously published report by Tranter [3]. The mass transfer model is based on the solutions to partial differential equations (PDEs) for the material balance and the mass transfer rate. The material balance equation is based on a small segment, δz, of the ion exchange column where mass transfer is taking place. In other words, there is a liquid phase concentration gradient across the segment. The material balance equation is:

$(\delta c/\delta t) + v*(\delta c/\delta z) + ((1-\varepsilon)/\varepsilon)*(\delta q/\delta t) = 0$ (Eq. 6)
where:
c = concentration of target solute in liquid, mg/liter
z = distance from column inlet, cm
ε = porosity, dimensionless
v = interstitial fluid velocity, cm/min
q = concentration of target solute in sorbent, mol/ml
t = time, min.

This equation is useful for describing exchange in the portion of the column where mass transfer is taking place. As a column operates the media becomes saturated. Downstream of the saturated zone is an "active" zone, where the bulk of the species of interest is adsorbed onto the solid media. Downstream of the active zone, very little exchange takes place. On either side of the active zone, $\delta c/\delta t$, $\delta c/\delta z$, and $\delta q/\delta t$ are all equal to zero, because there is virtually no net mass transfer. The active zone move further from the liquid entrance as the column operates [4].

It should be noted that the value of q is based on the volume of solid particles, exclusive of the void space between the particles.

There are other versions of this mass balance equation. A term can be added to explicitly deal with dispersion.

The mass transfer equation is:
$\delta q/\delta t = k_p a(q* - q)$ (Eq. 7)
where:

$q*$ = the concentration of the target solute in the solid phase at equilibrium with the liquid phase concentration, c, mol/ml
$k_p a$ = mass transfer coefficient, min^{-1}

For any equilibrium liquid concentration, c, the corresponding value of $q*$ can be obtained from the Langmuir equation:

$$q* = (Q_o Kc)/(1 + Kc) \qquad \text{(Eq. 8)}$$

The mass transfer rate equation and the Langmuir equation together define the relationship between q and c in the active region of the ion exchange column. The values of Q_o and K must be obtained experimentally from batch equilibrium tests.

It is useful to note at this point that these equations can be applied to multi-component ion exchange problems. However, this model and the Kd-based model described above are currently written for a single exchangeable species.

One method for solving these equations involves the transformation of the variables z and t into dimensionless variables as follows:

$$x = z/L \qquad \text{(Eq. 9)}$$
$$tau = L/v \qquad \text{(Eq. 10)}$$
$$\Theta = t/tau \qquad \text{(Eq. 11)}$$

where:
x = dimensionless length
L = overall depth of bed, cm
tau = hydraulic residence time in the bed, min
Θ = dimensionless time of operation.

Now,
$$\delta t/\delta\Theta = tau \text{ and } \delta z/\delta z = tau*v = L. \qquad \text{(Eq. 12)}$$

So converting the time and position relationships to dimensionless variables results in the following:

$$\delta c/\delta t = (1/tau)*(\delta c/\delta\Theta) \qquad \text{(Eq. 13)}$$
$$\delta c/\delta z = (1/tau)*(1/v)*(\delta c/\delta x) \qquad \text{(Eq. 14)}$$
$$\delta q/\delta t = (1/tau)*(\delta q/\delta\Theta) \qquad \text{(Eq. 15)}$$

The differential equations then become:
$$\delta c/\delta\Theta + \delta c/\delta x + ((1 - \varepsilon)/\varepsilon)*\delta q/\delta\Theta = 0 \qquad \text{(Eq. 16)}$$
and
$$\delta q/\delta\Theta = (tau)*k_p a*(q* - q) \qquad \text{(Eq. 17)}$$

In finite difference form these equations are:
$$(c^{k+1}_j - c^k_j) / \Delta\Theta + (c^k_j - c^k_{j-1}) / \Delta x + ((1 - \varepsilon) / \varepsilon) * (q^{k+1}_j - q^k_j) / \Delta\Theta$$
$$= 0 \qquad \text{(Eq. 18)}$$

and

$$(q^{k+1}_j - q^k_j) / \Delta\Theta = tau * k_pa * (q*^k_j - q^k_j) \tag{Eq. 19}$$

Where:

j relates to space or position steps

k relates to time steps

Rearranging allows calculation of liquid concentration at increasing time intervals:

$$c^{k+1}_j = c^k_j + (\Delta\Theta/\Delta x) * (c^k_{j-1} - c^k_j) - ((1 - \varepsilon) / \varepsilon) * (q^{k+1}_j - q^k_j) \tag{Eq. 20}$$

The step-wise changes in sorbent concentration can be obtained from the mass transfer equation:

$$q^{k+1}_j = q^k_j + \Delta\Theta * tau * k_pa * (q^{k*}_j - q^k_j) \tag{Eq. 21}$$

The initial conditions (t = 0) for the ion exchange media are: c = 0; q = 0.

The boundary conditions are: $c = c_0$ at the entrance to the column at all times t, and $\delta c/\delta x = 0$ at the bottom of the column when the media is saturated.

The program divides a column into 20 segments and performs the calculations above for each segment and each time step. The depth of each segment (Δx) is L/20. Testing of the model has shown that $\Delta\Theta/\Delta x$ must be less than 0.5 for stability. A fixed value of 0.25 is used in the model.

This sets the time step, $\Delta\Theta$, for each run.

The user is prompted to input the dimensions of the media in the column, the throughput rate (in bed volumes per hour), and a value for the mass transfer coefficient, k_pa. The program keeps track of the total volume of liquid processed through the column, based on the flow rate and the elapsed time. As with the equilibrium model, the output can be plotted as a breakthrough curve and compared to experimental results. If the output of the model deviates significantly from the experimental data, the program can be rerun using different input values for k_pa until modeled results and experimental results match as closely as possible. Figure III is an example comparison of laboratory results and model output. As with Figure II, the y-axis represents the ratio of column effluent concentration to column influent concentration. It should be noted that small column tests were performed with two ion exchange materials.

SCALE-UP

The programs are intended to be used to support ion exchange column design as indicated in the graphs above, the models have been applied to data from very small columns. It would be risky to design full-scale equipment using information developed from modeling very small-scale tests. To address scale-up, an additional experiment was performed using a 500-ml column of IONSIV® IE-911. The experimental breakthrough data are plotted with equilibrium model output data in Figure IV. A similar plot was obtained using the mass transfer model. It should be noted that the parameters used to determine the best fit to the data were essentially the same as those used to fit the data from the 2-ml column test. Table 1 shows the parameters used to fit the data from both experiments.

USING THE MODELS – AN EXAMPLE

Creating a model for a full-scale column is a twofold process. First experimental data is used to determine the sorption parameters of the equilibrium and mass transfer models (e.g. distribution coefficient, Kd, mass transfer coefficient, "$k_p a$"). Then, using the physical parameters of the actual column, simulations are performed to show how the new column design performs. Here is a walkthrough of the design process using a 2-milliliter column experimental data example.
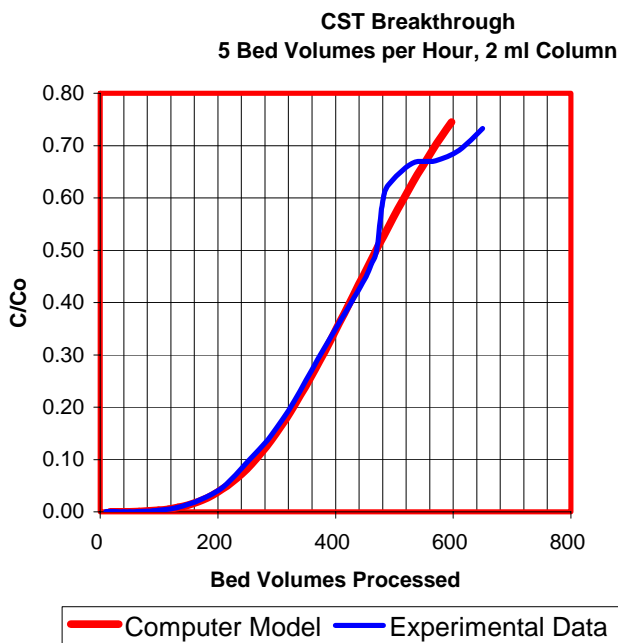

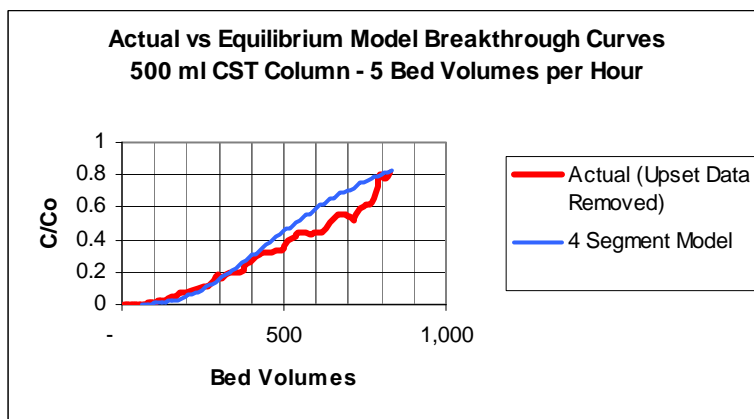Fig. 3 Experimental breakthrough curve vs. mass transfer model output

Fig. 4 Experimental and equilibrium model results for 500-ml column test

Table I Parameters used to model 2-ml and 500-ml experiments

Test	Equilibrium Model	
	Kd, liters/gram	No. of Segments
200-ml Column	0.513	4
500-ml Column	0.497	4
	Mass Transfer Model	
	$k_p a$	
200-ml Column	0.0035	
500-ml Column	0.0035	

Step 1: Run the model, simulating a bench scale experiment.

With the appropriate model, use the experimental data to determine the number of segments, or "$k_p a$" value. Record the final parameters and use them in Step 2 of the model. Be sure to save the results file to a different unique name. Otherwise, multiple runs will over write the data each time.

For the equilibrium model, the key parameter to adjust is the number of segments. The first or "Breakthrough Curves" simulation is used to calculate these data points. One enters the physical parameters and adjusts the number of segments until the simulated computer model data graph matches the experimental data graph as close as possible. The final data for the example are listed in Table II.

For the mass transfer model, the key parameter to adjust is the "$k_p a$" value. One enters the physical parameters of column and media, and adjusts the "$k_p a$" until the computer model data graph matches the experimental data graph as close as possible. The final data for the example are in Table III.

Step 2: Run the model simulating an equipment design.

With the appropriate models and using the parameters determined in step 1, run the model simulations using the inputs reflecting larger scale equipment. The data used for these examples are found in Tables IV and V. The larger scale equipment is modeled as a 681.3-liter (180-gallon) vessel for both models. The column diameter is 45 cm (inside diameter) in each case.

Table II Inputs to equilibrium model for matching experimental breakthrough

Equilibrium Model – Parameter Estimation	
Parameter	Value
Feed in mg / Liter	3.74
Depth of Media in cm	2.5
No. of Segments	4
Volume in cubic centimeters	2
Media Specific Gravity	1.17
Porosity	0.65
Flow Rate, Bed Volumes per Hour	5.2

Table III Inputs to mass transfer model for matching experimental breakthrough

Mass Transfer Model – Parameter Estimation	
Parameter	Value
Langmuir K, milliliters / Mole	931,000
Langmuir Qo, Moles / Milligram	0.0015
Column Length in Centimeters	2.5
Column Volume in Cubic Centimeters	2.0
Column Radius in Centimeters	0.51
Flow Rate in Bed Volumes per Hour	5.2
Feed Concentration in Moles / Milliliter	2.81 E-8
Porosity	0.65
Mass-Transfer Co-efficient Kpa	0.0035

The goal is to estimate the volume of liquid processed when a given end point is reached. In this example, the end point for the both models is set at 0.004 milligrams per liter of cesium in the effluent of the ion exchange system.

The output of the equilibrium model simulation is in units of total bed volumes processed at the end point. The example calculated 63.38 bed volumes for the larger column. Since 1 bed volume (BV) equals 681.3 liters (180 gallons), the total volume of liquid processed at cesium in the effluent (0.004 mg/l) is determined by the following calculation:

63.38 BV * (681.3 liters/ BV) = 43,179 liters of liquid processed end point.

Table IV Inputs for equilibrium model simulation of full-scale column

Equilibrium Model – Simulation of Full-Scale Column	
Parameter	Value
Feed in mg / Liter	3.74
Depth of Media in cm	413.3
No. of Segments	4
Volume in cubic centimeters	681,300
Media Specific Gravity	1.17
Porosity	0.65
Flow Rate in Bed Volumes per Hour	5.2

Table V Inputs for mass transfer model of full-scale column

Mass Transfer Model – Simulation of Full-Scale Column	
Parameter	Value
Langmuir K, milliliters / Mole	931,000
Langmuir Qo, Moles / Milligram	0.0015
Column Length in Centimeters	414.3
Column Volume in Cubic Centimeters	681,300
Column Radius in Centimeters	22.9
Flow Rate in Bed Volumes per Hour	5.2
Feed Concentration in Moles / Milliliter	2.81 E-8
Porosity	0.65

For the mass transfer model, the program's user must locate the predetermined end point on the curve, or from the table of breakthrough data, and perform the following calculation to get the resultant volume of liquid processed.

76 BV * (681.3 liters/ BV) = 51,855 liters of liquid processed at end point.

Based on these results, column change-out would be expected to occur somewhere between 43,200 and 51,900 liters of throughput. A review of Figures II and III shows that the mass transfer model predicts later breakthrough than the equilibrium model at low endpoint concentrations. The model outputs for the large vessel are consistent with this observation. The programs can be run with other design inputs and endpoints to assist the design team in evaluating alternative configurations for ion exchange processes.

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