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COMPUTERIZED MATHEMATICAL MODEL
FOR THE ANION EXCHANGE PROCESSING OF PLUTONIUM(IV)

James D. Navratil

Stephen G. Proctor

Chemistry Research and Development
CHEMICAL RESEARCH GROUP

Larry L. Kirkby
Dow Chemical U.S.A.
Midland, Michigan
PHYSICAL RESEARCH LABORATORY

Rockwell International

Atomics International Division
Rocky Flats Plant
P.O. Box 464
Golden, Colorado 80401

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SUBJECT DESCRIPTORS

Computer Codes
Ion Exchange
Mathematical Models
Plutonium
Plutonium Recovery

ROCKWELL INTERNATIONAL
ATOMICS INTERNATIONAL DIVISION
ROCKY FLATS PLANT
P.O. BOX 464
GOLDEN, COLORADO 80401

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COMPUTERIZED MATHEMATICAL MODEL FOR THE ANION EXCHANGE PROCESSING OF PLUTONIUM(IV)

James D. Navratil, Stephen G. Proctor, and Larry L. Kirkby

Abstract. A computerized mathematical model for anion exchange processing of plutonium(IV) was adopted from a previously written code. The model was verified to predict, within $\pm 30\%$, a profile of plutonium breakthrough for the sorption process on Dowex 1-X4 anion exchange resin. The program was modified to incorporate column washing and elution logic. Experimental washing and elution data were in satisfactory agreement with predicted data. Provisions for changing the flow rate during the course of a run and for plotting capabilities to aid in better presentation of column breakthrough curves also were incorporated into the model.

INTRODUCTION

Rocky Flats is involved in reprocessing plutonium residues. The current reprocessing method employs an aqueous process that generates reasonably large volumes of both low-level and high-level solutions of plutonium(IV) in 7M nitric acid. These solutions can contain sizable amounts of impurities. The plutonium is capable of forming anionic complexes that are highly sorbed on Dowex® 1-X4 ion exchange resin. Most impurities exhibit low sorption because they exist only in neutral or cationic form. Thus, the ion exchange technique provides a powerful technique for separating plutonium from impurities and for concentrating plutonium in low-level concentration streams.

The importance of ion exchange in plutonium reprocessing has caused considerable interest in the development of computer models for predicting operational behavior of fixed-bed ion exchange columns. With a satisfactory predictive model, it becomes possible to optimize column performance, thus achieving better purification and/or minimizing the volume of low-level waste streams.

Cooper and James of Los Alamos Scientific Laboratory have investigated a number of predictive mathematical models for the sorption, wash, and elution of plutonium(IV) on Dowex 1-X4 resin.¹⁻⁴ Their primary interest, however, centered on the sorption step with only minimal work being done on the wash and elution steps. In the area of wash and elution, James found the observed phenomena complex, thus making it questionable whether or not a satisfactory model could be obtained.⁴ The plutonium sorption model they developed was reported to be reasonably satisfactory; however, they presented only minimal results comparing predicted breakthrough curves with actual column data. Ryan⁵ has been critical not only of the mathematical models of Cooper and James, but also the foundations of some of their work.

Cooper and James developed a computer program to evaluate the behavior of their mathematical models.¹ Their program calculated breakthrough curves and column concentration profiles for the sorption process. The calculations involved empirical rate expressions determined by Cooper and James from kinetic experiments. This original program was then modified and implemented on the Rocky Flats computer by G. Kaes.⁶ The objective of Kaes' effort was to determine if the program would duplicate the findings of Cooper and James, and to apply the program to experimental data from the Rocky Flats Plant.

The objectives of the effort described herein were to modify Kaes' computer program, thus enabling it to handle column wash and elution, and to verify and investigate better empirical models for the sorption step. In addition, it was found desirable to develop plotting capabilities to aid in better presentation of column breakthrough curves.

DESCRIPTION OF MATHEMATICAL MODEL

Sorption, Washing, and Elution Models

Sorption

Ryan and Wheelwright⁷ extensively examined the sorption of plutonium(IV) from nitrate solutions on strong-base anion-exchange resins such as Dowex 1-X4. They found that diffusion within the pores of the resin beads was the rate-limiting step in the process. The diffusion coefficient decreased substantially with plutonium loading because of water loss upon loading. At higher levels of plutonium loading, the diffusion coefficient becomes small, probably approaching the coefficient for solid diffusion. Because of this highly nonlinear diffusion coefficient, the usual analytical solutions of fixed-bed performance are invalidated. This necessitates numerical solution of the column equation.

The approach taken by Cooper and James was to develop an empirical rate expression for plutonium sorption based on batch kinetic-sorption experiments. They then numerically solve the column equations using the empirical, microscopic rate expression to obtain the fixed-bed performance.¹ The optimum rate expression selected by Cooper and James was strictly empirical, without physical justification of the form. Their rate expression is as follows:

$$\frac{\partial \bar{x}}{\partial t} = \frac{\pi^2 \bar{D}^0 \exp(-k\bar{x}/\bar{x}_m)}{2R^2} \left[\frac{(\bar{x}^*)^2 - (\bar{x})^2}{\bar{x}} \right] \quad (1)$$

where

$\bar{x}$ = average concentration of plutonium in resin phase,

$\bar{x}_m$ = maximum capacity of plutonium in the resin phase,

$\bar{x}^*$ = equilibrium concentration of plutonium in the resin phase (corresponding to concentration in adjacent solution),

t = time,

R = average radius of resin particles,

k = empirical constant,

$\bar{D}^0$ = empirical constant representing average plutonium diffusion coefficient at zero loading,

$$\pi = 3.14159$$

The above sorption-rate expression requires the equilibrium concentration of plutonium in the resin phase, $\bar{x}^*$. Neglecting activity coefficients, James^{4, 8} obtains $\bar{x}^*$ from the following isotherms, which he developed:

$$\bar{x}^* = \bar{x}_m \left\{ 1 + U - \sqrt{U(U+2)} \right\}, \quad (2)$$

$$U = \bar{x}_m / 2c\lambda_0 \quad (3)$$

where

c = concentration of plutonium in solution,

λ_0 = distribution coefficient of plutonium at infinite dilution

(i.e., $\lambda_0 = \frac{\bar{x}^*}{c}$ when $\bar{x}^* \rightarrow 0$).

These isotherms have been questioned by Ryan.⁵

Equations 1-3 are employed by the computer program in calculating plutonium mass transfer for those portions of the column undergoing sorption. Coupled with these sorption equations must be those equations describing the macroscopic column behavior and the behavior of other species.

Washing

Using various acid concentrations in the wash solution, James examined the batch washing (desorption) of resin beads with uniform plutonium distributions.⁴ He concluded that desorption for this special situation could be described by the solution of the case where intraparticle diffusion out of the spherical beads was the controlling step. That case assumed a constant diffusion coefficient and constant concentration in the external solution. He employed substantially different diffusion coefficients for each case, depending on initial resin loading. Unfortunately, for the batch kinetic experiments that he performed, neither assumption

appears to have been adequate. Also, in practical cases, one would expect to find substantial concentration gradients in the resin beads, rather than the uniform concentration profiles used in the experiments. The desorption of each resin bead is thus entirely dependent on its past history. James concluded that the washing process is almost hopelessly complex.

Because of the absence of other batch, kinetic data for the washing process, the approach taken here was to develop an empirical model that appeared to provide a reasonable fit to the three, batch, kinetic experiments ($7M$ HNO_3) of James.⁴ The empirical rate expression that produced satisfactory results was Equation 1, which is the equation for the sorption rate. This expression provides a consistent and equivalent mechanism for both the sorption and wash steps. Slightly better washing-rate expressions are certainly possible; however, in the absence of better experimental data, an improved rate expression is not justified.

The washing model is relatively weak (lack of washing data), but its weaknesses is not expected to contribute seriously to the prediction of fixed-bed performance. This is primarily due to the relatively short contact times and the low mass-transfer rates.

Elution

James briefly examined the elution behavior of Dowex 1-X4 resin having uniform plutonium distribution, using low acid strengths ($0.6M$ to $0.3M$ HNO_3).⁴ This work was performed in batch kinetic experiments similar to his washing experiments.

For the several experiments using acid concentrations of approximately $0.35M$ HNO_3 (typical of the Rocky Flats process), the elution was characterized by a rapid release of plutonium (65% release), followed by a much slower rate of release of the remaining plutonium. James suggested that plutonium polymer is formed in the resin at low acid concentrations, and that the slow portion of the elution is caused by dissolution of the polymer. He suggested that the dissolution is first order with respect to the amount of plutonium still in the resin.

The approach taken here was to use the previous sorption and washing rate expression (Equation 1) with a high, constant, diffusion coefficient³ but with the exponential term omitted; i.e.,

$$\frac{\partial \bar{x}}{\partial t} = \frac{\pi^2 \bar{D}^0}{2R^2} \left[\frac{(\bar{x}^*)^2 - (\bar{x})^2}{\bar{x}} \right] \quad (4)$$

The diffusion coefficient used here was the same as that determined by James from a batch elution experiment with concentration gradients in the resin beads.⁴ Based on Rocky Flats processing experience and experimental data, polymer formation does not seem to be significant, in contrast to what James noted. Hence, a diffusion-controlled rate expression appears to adequately describe the typical experience at Rocky Flats. In the absence of experimental data other than that of James, the development of better microscopic elution models is questionable.

Numerical Solutions of Column Equation

The following equation describes the concentration in fixed-bed columns:¹

$$\frac{\partial c}{\partial t} + \frac{v}{\epsilon} \frac{\partial c}{\partial z} = - \frac{1-\epsilon}{\epsilon} \frac{\partial \bar{x}}{\partial t} \quad (5)$$

where

ϵ = void volume fraction of the bed,

v = linear velocity of solution through bed,

z = spatial coordinate.

The initial conditions for the above equation are $c(t=0, z) = f(z)$ and $\bar{x}(t=0, z) = g(z)$ where f and g are known, initial concentration profiles of the solution and resin phases respectively. The boundary condition, $c(t, z=0) = h(t)$, simply implies that the column feed concentration is known as a function of time.

Equation 5 is solved numerically by converting it to a finite difference form in terms of both time and the spatial coordinate. During each time step, the fluid phase in the column is moved one spatial step down the column. Using Equations 1-4 plus an early quadratic approximation,¹ where appropriate, the mass transfer between the fluid phase

TABLE 1. Listing of Job Control Language

```
//KRKBLL1A JOB (3852,1707,,,,,1,N),KIRKBY,
//    TIME=5,
//    CLASS=X
//    EXEC FTG1CG,REGION.GO=160K,TIME.GO=10
//FORT.SYSPRINT DD DUMMY
//FORT.SYSIN DD *                INSERT FORTRAN SOURCE DECK HERE
//GO.SYSLIB DD DSN=SYS1.FORTLIB,DISP=SHR
//    DD DSN=SYS1.GOULD,DISP=SHR
//    DD DSN=SYS1.USERLIB,DISP=SHR
//GO.SYSUT1 DD DSN=&TEMP,DISP=(NEW,PASS),SPACE=(TRK,(10,5)),UNIT=PACK
//GO.SYSUT2 DD UNIT=PACK,SPACE=(TRK,(10,5))
//GO.FT08F001 DD SYSOUT=A,DCB=(LRECL=133,RECFM=FBA,BLKSIZE=1330)
//FT09F001 DD *                PLACE RESTART CARDS HERE
//GO.SYSIN DD *                PLACE DATA CARDS HERE
/*
//STEP5 EXEC PGM=BITSETF
//STEPLIB DD DSN=SYS1.GOULD,DISP=SHR
//SYSUT1 DD DSN=&TEMP,DISP=(OLD,DELETE)
//SYSPL0T DD UNIT=TAPE8,DCB=DCB=2,DSN=GOULD,DISP=(NEW,KEEP)
//
```

and the resin phase is then calculated for each point within the column. The fluid and resin phase concentrations are then adjusted to account for the mass transfer before proceeding to the next time step. Optionally, corrections for film diffusion resistance can be applied to the above calculated mass transfer as suggested by Glueckauf.⁹

Weakly sorbed impurities are handled within the program in the manner described by Cooper.¹⁰ The diffusivities of each of the impurities are assumed to be proportional to the diffusivity of plutonium; hence, they are dependent on the level of plutonium loading. Simple linear isotherms are employed. The kinetic expressions for each of the impurities are the same as those for plutonium.

Program Requirements

The ion-exchange computer program is written in Fortran programming language. It is designed to operate on an IBM 370/158 computer operating under the OS operating system. The main program requires approximately 160K of storage for program execution. For plotting, a Gould electrostatic plotter and its associated software (Calcomp compatible) are required. A listing of the program is given in Appendix 1.

Table 1 presents the Job Control Language required for program execution. The program BITSETF in the second job step is a Dow* program that generates the Gould magnetic tape from plot commands stored in a temporary disk file generated by the main program. Conversion of the program to another computer would necessarily involve modification of this step (with possible elimination) plus modification of calls to the plot subroutines.

Table 2 presents the input and output files associated with the main program.

Program Input

Two different types of input sets are used by the program. The first set consists of experimental breakthrough data for the various components, and is strictly optional. These data, if entered, are simply plotted for comparison with the calculated breakthrough curves. This set of data is indicated by a title card (first card in set) beginning with the word "EXPERIMENTAL." The second type of data consists of all parameters required to define the given problem. This set is indicated by a title card (first card in set) that does *not* begin with the

*The Dow Chemical Company, Midland, Michigan.

TABLE 2. Input and Output Files

File Name	Description
FT05F001	Card input of experimental data and parameter specifications.
FT06F001	Printed output of experimental data reports, parameter specifications reports, and column exit concentration reports.
FT07F001	Punched output of restart cards (column concentration profile reports).
FT08F001	Print output of column concentration profile reports.
FT09F001	Card input of restart cards (column concentration profiles).
SYSUT1	Disk file for output of plot commands.
SYSUT2	Scratch disk file.

word "EXPERIMENTAL." If experimental breakthrough data are to be plotted with the predicted breakthrough curves, then the set of experimental data must be entered just prior to the set of problem parameters.

Free-field input, rather than fixed format input, is used throughout the program for data input. With free-field input, individual data items simply are separated by commas (and/or spaces) without regard to actual column location on the cards. If the default value of a given parameter is to be used, simply omit that item, but use a comma to designate its absence. A slash (/) is used to terminate a free-field input if not all items on that card are present.

Table 3 is an example of the input data for a problem involving sorption only. An example that includes sorption, washing, and elution is given in Table 4.

Experimental Data Input

The beginning of a set of experimental data is indicated by a title card with the characters "EXPE" in Columns 1-4. The experimental data input is organized as follows:

Card 1	Title card (up to 80 characters) beginning with "EXPE" in Columns 1-4.
Card 2	Specification card describing experimental data. 1st item = number of chemical species (1 to 3). 2nd item = column flow rate (liters per hour). 3rd item = column length (cm). 4th item = column diameter (cm). 5th item = void fraction of bed.
Card 3 to N + 2	Specification of N data points describing breakthrough curves. N is limited to 100 data points. 1st item = time of observation (minutes). 2nd item = exit concentration of 1st species (gram per liter). 3rd item = exit concentration of 2nd species (gram per liter) if present. 4th item = exit concentration of 3rd species (gram per liter) if present.
Card N	Set terminator beginning with "*END" in Columns 1-4.

Parameter Specification Input

The beginning of a parameter specification set is indicated by a title card *not* beginning with the characters "EXPE" in Columns 1-4.

Card 1	Title card (up to 80 characters).
Card 2	Specification card. 1st item = Column length (cm). 2nd item = Column diameter (cm). 3rd item = Integer number of column increments to be used in integration (10-200; default = 50). 4th item = Integer spatial print step used during printing of column

TABLE 3. Example of Input Deck for Column Loading Only

```

EXPERIMENTAL DATA FROM ROCKY FLATS RUN NO. 3
2,180,64,15.24,.4/
3. .0043 .000028
8. .0025 .0032
10. 3.27 .0039
11. 5.53 .0041
13. 6.53 .0041
*END
ROCKY FLATS RUN #3 - NOMINAL PARAMETERS
64,15.24,40,1,20,2/
0,0,1,0/
.00696,.76,.4,.1E-5/
8.35,180,.02,3.1,.7E-9,1/
.039,1155,.000017,1/
*END
1,239,.00001,0/
100,241,.00001,0/

```

TABLE 4. Example of Input Deck for Column Loading, Washing, and Elution

```

EXPERIMENTAL DATA FROM ROCKY FLATS RUN NO. 1
1,10.2,64,15.24,.4/
0. .000193 .00004 .00000121
10. .000148 .00004 .000001
20. .000212 .00004 .00000135
30. .000141 .00004 .000000707
40. .000337 .00004 .000139
50. .000379 .00004 .000468
60. .00187 .00004 .0117
70. .00358 .00004 .0204
80. .00619 .00004 .00108
90. .000737 .00004 .00612
100. .00182 .00004 .00842
100. .00976 .0002 .009
105. .00489 .0022 .00315
110. .00837 .0063 .000913
150. .0295 .0025 .000862
195. .00215 .0012 .000107
220. .00115 .00072 .0000258
265. 10.7 .0001 .00022
295. 30.1 .0001 .00062
310. 23.6 .0001 .00048
328. 21.9 .0001 .00045
347. 20.6 .0001 .00042
367. 15.3 .0001 .00032
383. 11.6 .0001 .00023
401. 8.01 .0001 .00017
422. 5.24 .0001 .000125
*END
ROCKY FLATS RUN #1 - NOMINAL PARAMETERS
64,15.24,40,1,20,1/
0,0,1,0/
.00696,.76,.4,.1E-5/
3.64,10.2,.08,3.1,.7E-9,1/
.136,1155/
22.7,53,.08,3.1,.7E-9,0/
0,1155/
5.77,8,.08,0,1.6E-8,-1/
0,4/
*END
1,239,.00001,0/

```

Card 3

- concentration profile (1 to 200; default = 1).
- 5th item = Integer time print step for printing of column concentration profile (default = 100). This item specifies a multiple of the basic exit concentration print interval.
- 6th item = Integer number of chemical species (1 to 3; default = 1).

Option specification card.

- 1st item = Integer column concentration profile punched output option (no punched output if 0; punched output if *not* 0; default = no punched output). The column concentration profiles may be read back into the program for restart. The punched output is generated at the termination of the case.
- 2nd item = Integer option (no restart if 0; restart if *not* 0; default = no restart). If restart is desired, program reads column concentration profiles previously punched out.
- 3rd item = Integer plot option (no plot if 0; plot if *not* 0; default = no plot).
- 4th item = Integer film diffusion resistance option (no film diffusion resistance if 0; film diffusion resistance if *not* 0; default = no film diffusion resistance).

Card 4

Resin specifications.

- 1st item = Resin bead radius in centimeters (default = 0.00696).
- 2nd item = Resin capacity (CMBAR) in moles per liter of wet resin (default = 0.76).
- 3rd item = Column void fraction (default = 0.4).
- 4th item = Liquid diffusion coefficient in cm^2/sec (default = 0.000001).

The next series of cards is employed to describe each of the column operations such as loading, elution, washing, and changes in flow rate. Two cards are required to define each operation. There may be up to 20 separate operations.

Card 5

Operation specification card.

- 1st item = Fraction of bed volumes during this particular operation (default = 1). Bed volumes are based on void volume, not total bed volume.
- 2nd item = Column flow rate in liters per hour (default = 1).
- 3rd item = Bed volume print interval, specifying number of bed volumes between the printout of exit concentration (default = 1). This print interval is also the same interval used to obtain data points if plotting.
- 4th item = Exponential constant used in Cooper-James model to describe changes in diffusion coefficient with loading (default = 3.1).

5th item = Pre-exponential constant used in Cooper-James model to describe changes in diffusion coefficient with loading (default = 0.7×10^{-9}).

6th item = Operation indicator:
 1 = loading
 0 = washing
 -1 = elution

Card 6

Component specification card.

1st item = Feed concentration of plutonium in moles per liter.

2nd item = λ_0 , trace distribution coefficient of plutonium (moles plutonium $\times$ ml solution per moles plutonium $\times$ ml wet resin).

3rd item = Feed concentration of 2nd component (if present) in moles per liter.

4th item = λ_0 , trace distribution coefficient of 2nd component (if present).

5th item = Feed concentration of 3rd component (if present) in moles per liter.

6th item = λ_0 , trace distribution coefficient of 3rd component (if present).

Card Types 5 and 6 are repeated for each operation. The operation set is terminated with the "*END" card.

Card 7

Terminator card beginning with "*END" in Column 1-4.

One card is now entered to describe each of the components. If only one component is present, enter only one card.

Card 8

Component Specification card.

1st item = Diffusion factor to multiply times plutonium diffusion coefficient. This number is always 1.0 for plutonium.

2nd item = Molecular weight

3rd item = Minimum concentration value to be plotted (default = 0.000001).

4th item = Initial solution concentration in column. The resin is assumed to be in equilibrium with the solution.

Program Output

The program generates a variety of types of output that are of interest. The output of primary interest is the plot of the column breakthrough curve that must ultimately be compared with experimental data. Printed reports are provided for the presentation of input parameters, column concentration profiles, pertinent concentrations as a function of time, and experimental data points. Should there be an interest in terminating program execution and then restarting the calculations at a later time, facilities have been provided for punching column concentration profiles on cards.

Plots of Column Breakthrough Curves

The primary output of the program is a plot of the calculated breakthrough curves for each component. Figure 1 is an example of one such computer-generated plot from a case in which both plutonium and silver were present. For this particular run, experimental data were available, as indicated by the two sets of data points, each having different symbols. The ordinate here has units of grams per liter and is plotted on a logarithmic scale to cover the wide range of concentrations normally seen in these problems. The user has control over the minimum concentration values plotted for each component.

FIGURE 1. Example of Computer-Generated Breakthrough Plot

TABLE 5. Report of Experimental Data Points

EXPERIMENTAL DATA FOR ROCKY FLATS RUN NO. 5

NUMBER COMPONENTS= 2 FLOW RATE= 0.60
COL DIA = 2.30 COL LENGTH= 80.00 VOID FRACTION= 0.4000

TIME	BED VOLS	CON1(G/L)	CON2(G/L)	CON3(G/L)
25.00	0.11	0.000015	0.560000	
50.00	0.23	0.000031	1.000000	
75.00	0.34	0.000290	1.000000	
100.00	0.45	0.002700	1.000000	
115.00	0.52	0.005500	1.000000	
125.00	0.56	0.006000	1.000000	
130.00	0.59	0.007600	1.000000	
135.00	0.61	0.007600	1.000000	
140.00	0.63	0.009600	1.000000	
145.00	0.65	0.024000	0.950000	
150.00	0.68	0.300000	0.800000	
155.00	0.70	0.640000	0.840000	
160.00	0.72	1.240000	1.080000	
165.00	0.74	2.000000	1.080000	
168.00	0.76	0.098000	0.240000	
171.00	0.77	0.057000	0.100000	
175.00	0.79	0.046000	0.003000	

TABLE 6. Report of Problem Parameter Specifications

ROCKY FLATS RUN #5 - NOMINAL PARAMETERS

INPUT PARAMETERS:

COL LENGTH= 80.00 COL DIA= 2.30 NO. COL INCREMENTS= 40
CONC PRINT X INTERVAL= 1 CONC SUMMARY STEP= 20 NO. COMPONENTS= 2
PUNCH OPTION= 0 OLD CONC PROFILE OPTION= 0
PLOT OPTION= 1 FILM OPTION= 0

STEP NO. 1

BEDVOL= 12.410 FLOW= 0.60 PRINT INTERVAL= 0.03
ALPHA= 3.100 PU DIFFUSION COEFFICIENT= 0.7000E-09 DUMMY= 1.000
COMPONENT 1 CONC= 0.4350E-01 DVO= 1155.00
COMPONENT 2 CONC= 0.9260E-02 DVO= 0.12

STEP NO. 2

BEDVOL= 13.162 FLOW= 0.60 PRINT INTERVAL= 0.03
ALPHA= 3.100 PU DIFFUSION COEFFICIENT= 0.7000E-09 DUMMY= 0.0
COMPONENT 1 CONC= 0.0 DVO= 1155.00
COMPONENT 2 CONC= 0.0 DVO= 0.12

TIME INCREMENT= 19.94 SEC. SPACE INCREMENT= 2.00 CM.

*** CONCENTRATIONS IN PRINTOUT ARE IN GRAMS/LITER.

PU DIFFUSION COEFF = 0.70000E-09 CM2/SEC

RESIN- RADIUS(CM) = 0.69600E-02 CMBAR(MOLS/L) = 0.76000E+00

VOID FRACTION = 0.4000 LIQUID DIFFUSION COEFF(CM2/SEC) = 0.10000E-05

ALPHA = 3.10

COMPONENT DATA****

COMPONENT	FACTOR	MOL WT	RMIN	CO
1	1.00000	239.00	0.0000100	0.0
2	100.00000	107.00	0.0000100	0.0

Printout of Experimental Data Points

Table 5 is an example of a printout of experimental data points generated whenever experimental data are entered for a particular run. Concentrations here are given in terms of grams per liter.

Report of Problem Parameters

Table 6 is an example of a report giving the parameter specifications for each problem. In this table, input parameters and calculated parameters both are reported for the problem. The items of interest for each column operation step are printed, although this particular example has only one step.

Report of Concentrations Versus Time

Table 7 is an output example giving various concentration quantities as a function of time. This report gives solution concentrations at exit, moles on resin, moles in solution, moles entering column, and moles leaving column.

Report of Column Concentration Profiles

An example of a report showing concentration profiles within the column is given in Table 8. Here, the solution and resin concentration profiles for all components are both given at various points along the column.

Punched Column Profiles (for Restart)

If someone wishes to continue calculations at a later time, cards can be punched showing the resin and solution concentration profiles in the column. These punched cards can then be entered into the program at a later date, and calculations can be resumed. Table 9 is a listing of the cards of one of the restart decks that has been punched.

EXPERIMENTAL

Materials

Dowex 1-X4 anion exchange resin (50-80 mesh), nitrate form, is manufactured by Dow Chemical

U.S.A., Midland, Michigan and was obtained from Bio-Rad Laboratories.* Impure plutonium nitrate feed solutions were used for the ion exchange runs, and the average major impurities in the 7-7.5M HNO_3 feeds, in milligrams per liter, are as follows: aluminum (250), americium (3), boron (10), barium (40), calcium (800), chromium (80), copper (80), fluorine (500), iron (1000), lead (225), magnesium (1000), nickel (100), phosphorus (300), potassium (700), silicon (200), tin (100), and titanium (30).

Plutonium concentrations of the feeds used in the experiments are given in Table 10.

Procedure

The column operating parameters are also given in Table 10. Four different ion exchange columns were used in the tests. All columns were filled with Dowex 1-X4 anion resin and were conditioned with 7M HNO_3 prior to plutonium sorption. The plutonium was sorbed on the anion resin from the nitrate feed solutions (7M HNO_3) at flow rates consistent with the dimensions of the individual ion columns.

After plutonium sorption, the anion resin was washed with 7M HNO_3 to remove the impurities. The columns then were eluted using 0.35M HNO_3 . Samples of each of the exit streams (effluent, wash, and elution) were periodically taken and analyzed for elemental composition.

Analysis

Plutonium and americium concentrations were determined radiometrically. The hydrogen and fluoride ion concentrations were determined by base titration and selective-ion electrode, respectively. A colorimetric method was used to determine iron; silicon was determined by atomic absorption spectrophotometry. Optical emission spectroscopy was used to determine the elemental composition of the feeds, and uranium was determined by fluorometric techniques.

*Bio-Rad Laboratories, Richmond, California.

TABLE 7. Report of Concentrations Versus Time

ROCKY FLATS RUN #5 - NOMINAL PARAMETERS

SUMMARY PRINT

COMPONENT	MOLES IN	MOLES ON RESIN	MOLES IN LIQ	MOLES OUT	CEXIT
TIME =	19.9 SECONDS=	0.33 MINUTES,	VOLUME=	0.00 LITERS=	0.025 COLUMN VOLUMES
1	0.3455589E-01	0.1727793E-01	0.5183383E-01	0.0	0.0
2	0.3293287E-02	0.4173091E-03	0.6169263E-02	0.0	0.0
TIME =	39.9 SECONDS=	0.66 MINUTES,	VOLUME=	0.01 LITERS=	0.050 COLUMN VOLUMES
1	0.6911176E-01	0.4319485E-01	0.6047277E-01	0.0	0.0
2	0.6586574E-02	0.1177297E-02	0.8702561E-02	0.0	0.0
TIME =	59.8 SECONDS=	1.00 MINUTES,	VOLUME=	0.01 LITERS=	0.075 COLUMN VOLUMES
1	0.1036676E+00	0.1343119E-01	0.6479222E-01	0.0	0.0
2	0.9879861E-02	0.1973292E-02	0.1119985E-01	0.0	0.0
TIME =	79.8 SECONDS=	1.33 MINUTES,	VOLUME=	0.01 LITERS=	0.100 COLUMN VOLUMES
1	0.1382235E+00	0.1032234E+00	0.6955570E-01	0.0	0.0
2	0.1317315E-01	0.2787294E-02	0.1367913E-01	0.0	0.0
TIME =	99.7 SECONDS=	1.66 MINUTES,	VOLUME=	0.02 LITERS=	0.125 COLUMN VOLUMES
1	0.1727793E+00	0.1315700E+00	0.7576495E-01	0.0	0.0
2	0.1646644E-01	0.3616324E-02	0.1614339E-01	0.0	0.0
TIME =	119.7 SECONDS=	1.99 MINUTES,	VOLUME=	0.02 LITERS=	0.150 COLUMN VOLUMES
1	0.2073352E+00	0.1611383E+00	0.8075243E-01	0.0	0.0
2	0.1975972E-01	0.4458379E-02	0.1859461E-01	0.0	0.0
TIME =	139.6 SECONDS=	2.33 MINUTES,	VOLUME=	0.02 LITERS=	0.175 COLUMN VOLUMES
1	0.2418910E+00	0.1920087E+00	0.8443773E-01	0.0	0.0
2	0.2305301E-01	0.5310427E-02	0.2103583E-01	0.0	0.0
TIME =	159.5 SECONDS=	2.66 MINUTES,	VOLUME=	0.03 LITERS=	0.200 COLUMN VOLUMES
1	0.2764469E+00	0.2222618E+00	0.8873457E-01	0.0	0.0
2	0.2634630E-01	0.6169505E-02	0.2347004E-01	0.0	0.0
TIME =	179.5 SECONDS=	2.99 MINUTES,	VOLUME=	0.03 LITERS=	0.225 COLUMN VOLUMES
1	0.3110027E+00	0.2513200E+00	0.9423822E-01	0.0	0.0
2	0.2563958E-01	0.7033225E-02	0.2589960E-01	0.0	0.0
TIME =	199.4 SECONDS=	3.32 MINUTES,	VOLUME=	0.03 LITERS=	0.250 COLUMN VOLUMES
1	0.3455586E+00	0.2809350E+00	0.9917909E-01	0.0	0.0
2	0.3293287E-01	0.7899720E-02	0.2832638E-01	0.0	0.0
TIME =	219.4 SECONDS=	3.66 MINUTES,	VOLUME=	0.04 LITERS=	0.275 COLUMN VOLUMES
1	0.3801144E+00	0.3114170E+00	0.1032528E+00	0.0	0.0
2	0.3622616E-01	0.8767627E-02	0.3075174E-01	0.0	0.0
TIME =	239.3 SECONDS=	3.99 MINUTES,	VOLUME=	0.04 LITERS=	0.300 COLUMN VOLUMES
1	0.4146703E+00	0.3426868E+00	0.1065390E+00	0.0	0.0
2	0.3951944E-01	0.9636184E-02	0.3317649E-01	0.0	0.0
TIME =	259.3 SECONDS=	4.32 MINUTES,	VOLUME=	0.04 LITERS=	0.325 COLUMN VOLUMES
1	0.4492261E+00	0.3732553E+00	0.1105261E+00	0.0	0.0
2	0.4281273E-01	0.1050493E-01	0.3560100E-01	0.0	0.0
TIME =	279.2 SECONDS=	4.65 MINUTES,	VOLUME=	0.05 LITERS=	0.350 COLUMN VOLUMES
1	0.4837320E+00	0.4029719E+00	0.1153652E+00	0.0	0.0

TABLE 8. Report of Column Concentration Profiles

ROCKY FLATS RUN #5 - NOMINAL PARAMETERS

TIME = 1994.3 SECONDS= 33.24 MINUTES, VOLUME= 0.33 LITERS= 2.500 COLUMN VOLUMES

CONCENTRATION PROFILE DATA --

C = GRAMS/LITER

CBAR = GRAMS/ LITER RESIN

INCR.	C1	CBAR1	C2	CBAR2	C3	CBAR3
1	0.1039650E+02	0.0	0.9908199E+00	0.0		
2	0.1009149E+02	0.5834204E+02	0.9908198E+00	0.2377967E+00		
3	0.9774390E+01	0.5745674E+02	0.9908195E+00	0.2377966E+00		
4	0.9441809E+01	0.5634564E+02	0.9908190E+00	0.2377965E+00		
5	0.9089859E+01	0.5500815E+02	0.9908186E+00	0.2377964E+00		
6	0.8713810E+01	0.5342934E+02	0.9908183E+00	0.2377963E+00		
7	0.8307804E+01	0.5159453E+02	0.9908178E+00	0.2377962E+00		
8	0.7864014E+01	0.4946371E+02	0.9908174E+00	0.2377961E+00		
9	0.7371824E+01	0.4699644E+02	0.9908171E+00	0.2377961E+00		
10	0.6815395E+01	0.4410326E+02	0.9908167E+00	0.2377959E+00		
11	0.6169963E+01	0.4067088E+02	0.9908162E+00	0.2377959E+00		
12	0.5391415E+01	0.3647676E+02	0.9908159E+00	0.2377958E+00		
13	0.4387012E+01	0.3111545E+02	0.9908155E+00	0.2377957E+00		
14	0.2873184E+01	0.2354364E+02	0.9908150E+00	0.2377956E+00		
15	0.1339753E+01	0.1217918E+02	0.9908147E+00	0.2377955E+00		
16	0.6163008E+00	0.5643003E+01	0.9908143E+00	0.2377954E+00		
17	0.2780772E+00	0.2616068E+01	0.9908139E+00	0.2377953E+00		
18	0.1218234E+00	0.1215342E+01	0.9908134E+00	0.2377952E+00		
19	0.5756850E-01	0.5670630E+00	0.9908131E+00	0.2377951E+00		
20	0.2766897E-01	0.2643420E+00	0.9908127E+00	0.2377950E+00		
21	0.1323736E-01	0.1229480E+00	0.9908122E+00	0.2377949E+00		
22	0.6297171E-02	0.5706156E-01	0.9908118E+00	0.2377948E+00		
23	0.2974291E-02	0.2643172E-01	0.9908115E+00	0.2377947E+00		
24	0.1391359E-02	0.1222443E-01	0.9908110E+00	0.2377946E+00		
25	0.6432829E-03	0.5648259E-02	0.9908106E+00	0.2377944E+00		
26	0.2921484E-03	0.2609703E-02	0.9908102E+00	0.2377942E+00		
27	0.1292427E-03	0.1207469E-02	0.9908096E+00	0.2377939E+00		
28	0.5847542E-04	0.5606534E-03	0.9908090E+00	0.2377936E+00		
29	0.2811049E-04	0.2608348E-03	0.9908077E+00	0.2377930E+00		
30	0.1345044E-04	0.1210473E-03	0.9908058E+00	0.2377921E+00		
31	0.6398800E-05	0.5604017E-04	0.9908031E+00	0.2377910E+00		
32	0.3021935E-05	0.2588714E-04	0.9907991E+00	0.2377895E+00		
33	0.1413709E-05	0.1193625E-04	0.9907944E+00	0.2377874E+00		
34	0.6529148E-06	0.5496888E-05	0.9907876E+00	0.2377844E+00		
35	0.2961102E-06	0.2530805E-05	0.9907773E+00	0.2377805E+00		
36	0.1306400E-06	0.1166699E-05	0.9907649E+00	0.2377750E+00		
37	0.5878469E-07	0.5398031E-06	0.9907475E+00	0.2377675E+00		
38	0.2821894E-07	0.2503066E-06	0.9907232E+00	0.2377572E+00		
39	0.1347688E-07	0.1157470E-06	0.9906895E+00	0.2377431E+00		
40	0.6395144E-08	0.5338121E-07	0.9906436E+00	0.2377239E+00		

RESULTS AND DISCUSSION

Sorption Results

Table 11 compares predicted and experimental results for the loading portion of the experiments.

Here, the percentage difference between the predicted and experimental breakthrough times is presented for breakthrough levels of 1% and 10%. Breakthrough is defined as plutonium concentration in the ion-column effluent divided by plutonium concentration in the feed. Breakthrough did not

TABLE 9. Listing of Punched Column Concentration Profiles for Restart

0.6684E-040.1219E-030.1577E-030.1785E-030.1890E-030.1929E-030.1923E-030.1885E-
 0.1825E-030.1748E-030.1657E-030.1553E-030.1437E-030.1306E-030.1160E-030.9933E-
 0.7960E-040.5428E-040.2713E-040.1356E-040.6775E-050.3386E-050.1692E-050.8457E-
 0.4227E-060.3504E-060.1056E-060.5276E-070.3596E-07
 0.1552E+000.1545E+000.1538E+000.1526E+000.1506E+000.1480E+000.1449E+000.1412E+
 0.1370E+000.1323E+000.1270E+000.1210E+000.1142E+000.1065E+000.9765E-010.8720E-
 0.7438E-010.5758E-010.3317E-010.1658E-001.8284E-020.4140E-020.2069E-020.1034E-
 0.5166E-030.2575E-030.1284E-030.6488E-040.3144E-04
 0.5499E-030.9974E-030.1348E-020.1606E-020.1776E-020.1863E-020.1878E-020.1832E-
 0.1740E-020.1614E-020.1463E-020.1296E-020.1120E-020.9425E-030.7693E-030.6066E-
 0.4590E-030.3301E-030.2215E-030.1367E-030.7657E-040.3882E-040.1844E-040.8745E-
 0.4144E-050.1962E-050.9282E-060.4387E-060.2078E-06
 0.1274E+000.1041E+000.8485E-010.6892E-010.5610E-010.4610E-010.3848E-010.3264E-
 0.2796E-010.2397E-010.2038E-001.1709E-001.1409E-010.1138E-010.8976E-020.6894E-
 0.5135E-020.3691E-020.2546E-020.1605E-020.9140E-030.4733E-030.2283E-030.1081E-
 0.5113E-040.2419E-040.1144E-040.5410E-050.2559E-05

TABLE 10. Properties of Plutonium Nitrate Feeds and Column Operating Parameters

Run Number	Resin Bed (dia x height, cm)	Plutonium Concentration (g/l)	Flow Rate (l/hr)			Column Use
			Loading	Washing	Elution	
1	15.2 x 64.0	32.5	10.2	53.0	8.0	Production
2	15.2 x 64.0	4.9	15.0	136.0	9.3	Production
3	15.2 x 64.0	9.3	180.0	—	—	Production
4	10.2 x 30.5	7.3	9.9	9.9	—	Production
5	2.3 x 80.0	10.4	0.60	0.60	—	Research
6	1.75 x 20.3	2.65	0.30	0.30	0.30	Research
7	15.2 x 64.0	15.4	10.1	—	—	Production
8	15.2 x 64.0	15.4	48.0	—	—	Production
9	1.75 x 19.7	9.3	0.30	0.30	0.30	Research
10	1.75 x 19.7	10.0	0.30	0.30	0.30	Research

occur in four of the ten experiments. In addition, unspecified flow interruptions (15 to 60 minutes) occurred in two more experiments, causing a small increase in resin capacity.

In Appendix 2, figures showing the experimental and predicted breakthrough curves are given for each of 10 runs. Where appropriate, washing and elution results are given on the same figures.

Parameters used by the mathematical models are given in Table 12. The sorption parameters are those used by Cooper and James.¹

The sorption model provides what could be termed satisfactory results, especially considering the uncertainty in the model's parameters as presented in the sensitivity analysis results (vide infra). Moderate differences between the experimental

TABLE 11. Breakthrough Results for Plutonium Sorption

Run Number	Plutonium Concentration (mol/l)	Flow (l/hr/cm ²)	Breakthrough Difference ^a		Comments
			10 Percent Breakthrough ^b	1 Percent Breakthrough	
2	0.02	0.082	-26	-32	Flow interrupted
3	0.04	0.99	-29	-32	Fast flow rate
5	0.04	0.14	- 8	-12	
6	0.01	0.12	+20	+27	
7	0.06	0.055	+ 7	- 1	Flow interrupted
8	0.06	0.26	+18	- 1	

a. Percent difference between computed and experimental breakthrough times at specified breakthrough levels. (Negative values indicate computed breakthrough came before experimental breakthrough.)

b. Breakthrough defined as plutonium concentration in the ion-column effluent divided by plutonium concentration in the feed.

TABLE 12. Mathematical Model Parameters

	Loading	Washing	Elution
Diffusion Coefficient, D_0 (cm ² /sec)	0.7×10^{-9}	0.7×10^{-9}	16×10^{-9}
Coefficient of diffusion constant concentration dependence, α	3.1	3.1	0
Trace distribution coefficient, λ_0 (moles plutonium X ml solution per moles plutonium X ml wet resin)	1155	1155	4
Void Fraction	0.40		
Resin Radius	0.00696 cm		
Liquid Diffusion Coefficient	0.000001 cm ² /sec		
Resin Capacity	0.76 moles per liter wet resin		

parameters and the model's common set of parameters could easily generate the $\pm 30\%$ differences observed between the predicted and experimental breakthrough curves. It should be pointed out that the experiments were performed on four different columns, and vastly different histories were experienced by the different resins.

Deviations between the predicted and experimental results in Table 11 tend to average zero; consequently, it is not possible to suggest that any particular parameter in the mathematical model be adjusted to obtain better agreement. It can be suggested only

that more experiments be run on the same column but in a more controlled manner so as to better establish the adequacy of the Cooper-James mathematical model and its parameters.

As can be noticed from the breakthrough curves in Appendix 2, the experimental curves tend to be steeper than the predicted curves. This results from the step size used in the model. By using a finer step size, one can more closely approximate the experimental curves. A coarser step size of 50 column increments has been used in this study to minimize computing costs.

FIGURE 2. Results of Sensitivity Study

Legend

○ = Experimental Data points for plutonium.

— = Computed data for plutonium.

a = Base Run Number 7 and film diffusion present and +50 percent lambda zero (trace distribution coefficient).

b = +5 percent both linear bed dimensions.

c = +0.05 column void fraction.

d = +10 percent plutonium feed concentration.

e = +15 percent column flow rate.

f = +20 percent trace diffusion coefficient.

g = Column not fully eluted.

h = +20 percent CMBAR (resin capacity).

i = +20 percent ALPHA (coefficient of diffusion constant concentration dependence) and +10 percent resin radius.

j = +100 percent increase in number of column increments.

TABLE 13. Results of Parameter Sensitivity Analysis

	Time (minutes)		Percent Breakthrough Difference ^a	
	10 Percent Breakthrough	1 Percent Breakthrough	10 Percent Breakthrough	1 Percent Breakthrough
Base case (Run Number 7)	246	221	—	—
+0.05 column void fraction	224	202	— 9	— 9
100 percent more column increments	256	243	+ 4	+10
+15 percent column flow rate	204	182	—17	—18
+20 percent trace diffusion coefficient	260	234	+ 6	+ 6
Film diffusion present	246	220	0	0
Column not fully eluted	239	216	— 3	— 2
+20 percent CMBR (resin capacity)	302	272	+23	+23
+20 percent alpha ^b	228	205	— 7	— 7
+50 percent lambda zero ^c	253	224	+ 3	+ 1
+10 percent resin radius	231	207	— 6	— 6
+10 percent plutonium feed concentration	221	198	—10	—10
+5 percent both lineal bed dimensions	299	258	+22	+17

$$\text{a. Percent Breakthrough} = \frac{\text{Plutonium concentration in effluent}}{\text{Plutonium concentration in feed}} \times 100$$

b. Coefficient of diffusion constant concentration dependence.

c. Trace distribution coefficient.

The mathematical model calculations involved the assumption that initial plutonium concentration in the resin and liquid was zero (new resin and 7.0M HNO₃). In reality, the state of the liquid and resin in the column depends on its regeneration history. It would have been possible to much more closely model the pre-breakthrough behavior of the columns by incorporating the initial state of the column into the program.

Some breakthrough curves have been presented in Appendix 2; however, there has been no attempt to optimize the parameters for other species such as silver, uranium, and americium. For that reason, it is not appropriate to discuss the adequacy or inadequacy of the model for handling these species.

Parameter Sensitivity Analysis

Run Number 7 was used as a base case for the parameter sensitivity analysis, and Figure 2 shows

the results of the sensitivity analysis. The adjustment of each parameter from the base case was the estimated error limits of each parameter.

Table 13 lists the breakthrough differences (%) between the adjusted and base cases for each parameter at 1% and 10% breakthrough. The results show that within the error limits of the parameters, CMBR varies the most, followed by bed dimensions and flow rate. All other parameters showed less than 10% difference. Figure 2 also shows the effect of the spatial step size used in the numerical calculations. Note that the finer step size (100 column increments versus 50 column increments) more closely approximates the shape of the experimental breakthrough curve.

Washing Results

Washing results are typified by the curve shown in Figure 3, which shows the washing of silver from

FIGURE 3. Computer Output for Run Number 4 Showing Washing Results

the column. Other results are given in Appendix 2. The washing step was not the major emphasis in this study, which accounts for the lack of controlled washing data and the lack of refined model predictions.

There is considerable room in this study for improving the washing model, particularly for the trace impurities. There was relatively little effort

TABLE 14. Plutonium Elution Results

Run Number	Percent Difference Between Computed and Experimental Elution Times	
	$C/C_o^* = 0.1$	$C/C_o = 0.01$
1	-4	-
2	-19	-22
6	-42	-
9	-13	-
10	0	0

* C/C_o = Plutonium concentration of eluate fraction divided by maximum, experimental, plutonium eluate fraction.

made to develop a model for anything other than plutonium. Because of the large distribution coefficient of plutonium in the 7M HNO_3 wash solution, the current washing model is adequate. Differences between the predicted and the observed washing curves are relatively large, but this is mainly due to differences in the resin loading near the exit of the column. During washing, the mathematical model tends to move plutonium down the column. This results in an increase in the effluent plutonium concentration. The experimental data indicate a decrease in the effluent plutonium concentration with time.

Elution Results

Table 14 compares the predicted and experimental portion of those runs in which valid elution data exist. This table also shows percentage difference between the predicted and observed elution times at two levels of elution: The elution levels selected were 1% and 10% of the maximum concentration that was experimentally observed in the eluate. Figure 4 shows an elution curve for Run Number 10, which provides the best comparison of the observed and predicted elution curves. See Appendix 2 for the other elution curves.

FIGURE 4. Computer Output for Run Number 10 Showing Plutonium Elution Results

The elution model appears reasonably satisfactory despite the lack of a firm microscopic basis as in the case of the sorption model. As indicated by the comparisons in Table 14, the model tends to predict a more rapid elution than is actually observed. This would suggest that a better match might be obtained through a slight reduction in the plutonium diffusion coefficients. This reduction would tend to flatten out the elution tail and more closely match the observed data. The plutonium diffusion coefficient used in the model is based on a single value suggested by Cooper and James;¹ there consequently is ample justification for a slight

modification of the parameter. The nature of the predicted elution curve's overall shape is such that there is probably no justification at this point for changing the model. One must keep in mind that the early part of the elution curve depends largely on the plutonium profile in the column, as produced by the sorption and elution steps.

CONCLUSIONS

A computerized mathematical model for anion exchange processing of plutonium(IV) was adapted from a code written by Cooper and James.¹ The model can predict a profile of plutonium breakthrough on various sizes of columns of Dowex 1-X4 anion exchange resin and with different plutonium feed concentrations and flow rates. The program was modified to incorporate column washing and elution logic in addition to provisions for changing flow rate during the course of a run. Another modification added plotting capabilities toward getting better presentation of column breakthrough curves.

Experimental laboratory-scale and production-scale, ion-exchange column data were obtained for the loading (sorption), washing, and eluting steps of the plutonium-purification, anion-exchange process. In general, the experimental data were in satisfactory agreement with predicted data.

For the plutonium loading step, $\pm 30\%$ difference was observed between the computed and experimental breakthrough curves. Sensitivity analysis, in which the input parameters were varied in relation to their estimated precision, showed that moderate differences could easily generate the $\pm 30\%$ differences observed between the predicted and experimental breakthrough curves.

Since the washing model was not the emphasis of this work, little work was done to demonstrate the predictive ability of the model. The limited washing data available were in satisfactory agreement with predicted data.

The elution model appears to be reasonably satisfactory despite its lack of a firm microscopic basis as in the case of the loading model. The

elution model tends to predict a more rapid elution, an average of 16% earlier, than what is actually observed.

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APPENDIX 1

LISTING OF FORTRAN PROGRAM

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C..... ROCKY FLATS ION EXCHANGE PROGRAM .....
C *** ION EXCHANGE COLUMNS
C *** AN ADAPTATION OF COOPER AND-JAMES PROGRAM -LASL REPORT LA-3046
C *** CODED BY G.L.KAES 10/18/72
C *** MODIFIED BY LARRY KIRKBY 5/21/74
      DOUBLE PRECISION DELCB,CBAR,C,CON,TEST, CEBAR
      DIMENSION CXN(10)
      DIMENSION SCEX(10),CEX(10),CIN(10),SRES(10),RES(10),SOL(10),SSOL(1
10),TITLE(20),AMW(10),CX(10),CINIT(10)
      DIMENSION BMIN(10)
      DIMENSION PTIME(500),PCON(500,3),ETIME(100),ECON(100,3)
      COMMON DVO(10),CEBAR(10),CMBAR,JMAX,C(1000,3),CBAR(1000,3),PIE,R,
1 E,IMAX,DELCB(10),CSTAR(10),CON(10),DELT,DK(10),DO,ALPHA,F(10)
3,VOUT,DL,NOFILM,IELUT,IWASCH
      COMMON ISTATE(1000),$BV(20),$FLOW(20),$PRINT(20),
1 $ALPHA(20),$DO(20),$XTRA(20),$CONC(20,4),$DVO(20,4)
      COMMON TIME
      DATA EXPE,ASK,NEXP,NPLOT /'EXPE','*END',0,0/
      DATA BLANK/' '/
      DATA XFAC,YFAC/.7,.7/
      DATA ANEW/'NEW'/
      PIE = 3.14159
      PI=3.14159

C ***
C *** BEGIN INPUT OF DATA
C ***
1 CONTINUE
  READ(5,1000,END=9999) TITLE
1000 FORMAT(20A4)
  IF((TITLE(1).NE.EXPE).AND.(TITLE(1).NE.ANEW))GOTO 4
  IF(TITLE(1).EQ.ANEW)GOTO 3
C --- WE HAVE DATA POINTS FOR PLOT.
  READ(5,*)NUMEL,FLOWX,CL,CD,E
  IF(NUMEL.GT.3)STOP 88
  BEDVOL=E*PI*CD*CD*CL/4.
  NEXP=0
  WRITE(6,1030)TITLE,NUMEL,FLOWX,CD,CL,E
1030 FORMAT('1',20A4//
1 ' NUMBER COMPONENTS=',I3,' FLOW RATE=',F8.2,/' COL DIA
1=',F8.2,' COL LENGTH=',F8.2,' VOID FRACTION=',F8.4/
3 //' TIME BED VOLS CON1(G/L) CON2(G/L) CON3(G/L)')
2 READ(5,1000)TITLE
C --- TEST IF ALL ODATA POINTS HAVE BEEN ENTERED
  IF(TITLE(1).EQ.ASK)GOTO 1
  BACKSPACE 5
  IF(NEXP.GE.100)WRITE(6,6444)
6444 FORMAT(/' *** TOO MANY EXPERIMENTAL DATA POINTS ***'/)
  IF(NEXP.LT.100)NEXP=NEXP+1
  READ(5,*)TIME,(ECON(NEXP,J),J=1,NUMEL)
  ETIME(NEXP)=TIME
  ETIMEX =TIME*FLOWX/BEDVOL
  WRITE(6,1031)TIME,ETIMEX ,(ECON(NEXP,J),J=1,NUMEL)
1031 FORMAT(F10.2,F10.2,5F12.6)
  GOTO 2
3 READ(5,*)FLOWX
  WRITE(6,1032)FLOWX
1032 FORMAT(/' FLOW RATE CHANGED TO ',F7.2/)
  GOTO 2

```

```

4      CL=40.
      CD=15.26
      NUMX=50
      JMAX=1
      IPUNCH=0
      IOLD=0
      IMW=0
      JPLOT=0
      NOFILM=0
      ISUMRY=100
      ICONC=1
      READ(5,*)CL,CD,NUMX,ICONC,ISUMRY,JMAX
      IF(JMAX.GT.3)STOP 88
      READ(5,*)IPUNCH,IOLD,      JPLOT,NOFILM
      WRITE(6,1033)TITLE,
1      CL,CD,NUMX,ICONC,ISUMRY,JMAX,IPUNCH,IOLD,      JPLOT,NOFILM
1033  FORMAT('1',20A4//' INPUT PARAMETERS: '/
1      ' COL LENGTH=',F8.2,' COL DIA=',F8.2,' NO. COL INCREME
1NTS=',I4/' CONC PRINT X INTERVAL=',I4,' CONC SUMMARY STEP=',
3      I4,' NO. COMPONENTS=',I4/
1      ' PUNCH OPTION=',I3,' OLD CONC PROFILE OPTION=',I3,
1      ' /' PLOT OPTION=',I3,
6      ' FILM OPTION=',I3)
      IF((NUMX.GT.200).OR.(NUMX.LT.10))STOP 66
      IMAX=NUMX
      NSTEP=0
      R=.00696
      CMBAR=.76
      E=.4
      DL=1.E-6
      READ(5,*)R,CMBAR,E,DL
C *** COMPUTE VARIOUS FLOW DATA
C ... GET STEP CHANGE INFORMATION.
40      READ(5,1000)AA
      IF(AA.EQ.ASK)GOTO 50
      BACKSPACE 5
      IF(NSTEP.EQ.20)WRITE(6,6345)
6345  FORMAT(/' *** TOO MANY DISCRETE COLUMN OPERATION STEPS ***'//)
      IF(NSTEP.LT.20)NSTEP=NSTEP+1
      $BV(NSTEP)=1.
      $FLOW(NSTEP)=1.
      $PRINT(NSTEP)=1.
      $ALPHA(NSTEP)=3.1
      $DO(NSTEP)=.7E-9
      $XTRA(NSTEP)=1.
      $DVO(NSTEP,1)=1155.
      READ(5,*)$BV(NSTEP),$FLOW(NSTEP),$PRINT(NSTEP),
1      $ALPHA(NSTEP),$DO(NSTEP),$XTRA(NSTEP)
      READ(5,*)
2      ($CONC(NSTEP,LL),$DVO(NSTEP,LL),LL=1,JMAX)
      IF(NSTEP.NE.1)$BV(NSTEP)=$BV(NSTEP)+$BV(NSTEP-1)
      WRITE(6,6301)NSTEP
6301  FORMAT(/' STEP NO.',I3)
      WRITE(6,6300)$BV(NSTEP),$FLOW(NSTEP),$PRINT(NSTEP),
1      $ALPHA(NSTEP),$DO(NSTEP),$XTRA(NSTEP),
2      (BLANK,LL,$CONC(NSTEP,LL),$DVO(NSTEP,LL),LL=1,JMAX)
6300  FORMAT(' BEDVOL=',F8.3,' FLOW=',F8.2,' PRINT INTERVAL=',
1      F8.2,/' ALPHA=',F8.3,' PU DIFFUSION COEFFICIENT=',
2      E12.4,' DUMMY=',F8.3/(1X,A1,' COMPONENT',I3,' CONC=',
3      E12.4,' DVO=',F9.2))
      GOTO 40

```

```

50  NPTS=0
    A =      PIE *CD*CD / 4.
    BEDVOL=A*CL*E
    DELX=CL/NUMX
    FLH=$FLOW(1)
    FCS = FLH / 3.6
    FLS = .001*FCS
    VOUT = FCS /A
    VIN = VOUT /E
    DELVOL=BEDVOL/NUMX
    DELT=DELX/VIN
    WRITE(6,6036)DELT,DELX
6036 FORMAT(/' TIME INCREMENT=',F8.2,' SEC.      SPACE INCREMENT=',
1    F8.2,' CM.')
    IF(IMW.EQ.0)WRITE(6,10041)
10041 FORMAT(' *** CONCENTRATIONS IN PRINTOUT ARE IN GRAMS/LITER.')
```

DO 5 I=1,JMAX
 CINIT(I)=0.
 BMIN(I)=1.E-5
 AMW(I)=1.
 F(I)=1.
 READ(5,*)F(I),AMW(I),BMIN(I),CINIT(I)
 IF(IMW.NE.0)AMW(I)=1.
 IF(AMW(I).EQ.0.)AMW(I)=1.
 C(1,I)=\$CONC(1,I)
 DVO(I)=\$DVO(1,I)

5 CONTINUE
 F(1) = 1.000
 DO=\$DO(1)
 ALPHA=\$ALPHA(1)

C *** PRINT OUT INPUT DATA AND HEADINGS
 WRITE(6,1005) DO,R,CMBAR,E,DL ,ALPHA
1005 FORMAT('OPU DIFFUSION COEFF =',E12.5,' CM2/SEC' /' RESIN- RADIUS(C
1M) =',E12.5, ' CMBAR(MOLS/L) =',E12.5 / ' VOID FRACTION =',F5.4,
2 ' LIQUID DIFFUSION COEFF(CM2/SEC) =',E12.5,/' ALPHA =',F5.2,/'
 WRITE(6,1006)
1006 FORMAT('OCOMPONENT DATA****' / ' COMPONENT FACTOR ',
1 ' MOL WT BMIN CO')
 DO 10 I=1,JMAX
 WRITE(6,1007)I ,F(I),AMW(I),BMIN(I),CINIT(I)
1007 FORMAT(I11,F10.5,F10.2,2F10.7)
 CINIT(I)=CINIT(I)/AMW(I)
 10 CONTINUE
 WRITE(6,1008) TITLE
1008 FORMAT('1',20A4, // ' SUMMARY PRINT ' // ' COMPONENT',
1 ' MOLES IN MOLES ON RESIN MOLES IN LIQ MOLES OUT' ,
15X,' CEXIT')

C *** SET UP FOR CALCULATIONS
 CEBAR(1)=0.
 IF(CINIT(1).EQ.0.)GOTO 222
 U=CMBAR/(DVO(1)*2.*CINIT(1))
 CEBAR(1)=CMBAR*(1.+U*(1.-SQRT(1.+2./U)))
222 CONTINUE
99 DO 100 J=1,JMAX
 CIN(J)=0.
 SCEX(J) = 0.
 DO 100 I =2,IMAX
337 ISTATE(I)=1
 C(I,J)=CINIT(J)
 IF(J.EQ.1)CBAR(I,J)=CEBAR(J)
 IF(J.NE.1)CBAR(I,J)=CINIT(J)*DVO(J)*2.

```

100  CONTINUE
      DO 1011 I=1,JMAX
      IF(I.EQ.1)CBAR(1,1)=CEBAR(1)
      IF(I.NE.1)CBAR(1,I)=CINIT(I)*DVO(I)*2.
10111 CONTINUE
C *** IF OLD CONC -READ IT IN
      IF(IOLD.EQ.0) GO TO 101
      WRITE(6,1003) TITLE
1003  FORMAT('1',20A4, '// 'OCONCENTRATION PROFILE DATA --', // 'OC = MOLES
      A/LITER', / ' ' CBAR = MOLES/ LITER RESIN' , // 'O INCR.
      1', ' C1 CBAR1 C2 CBAR2 ',
      2 ' C3 CBAR3 C4 CBAR4 ',
      3 /)
      DO 20 J=1,JMAX
      READ(9,4001)(C(I,J),I=2,IMAX)
      20 READ(9,4001)(CBAR(I,J),I=2,IMAX)
      DO 30 I=1,IMAX
      30 WRITE(6,3001) ( I,(C(I,J),CBAR(I,J)),J=1,JMAX)
101  KOUNT2 = 0
      TIME = 0.
      ISTEP=1.
      BVTOT=0.
      IPRINT=0
      TIMVOL=0.
      GOTO 90
C ***
C *** BEGINNING OF TIME LOOP
C ***
102  TIME = TIME + DELT
      TIMEMN=TIME/60.
      TIMVOL=TIMVOL+DELVOL/1000.
      BVTOT=BVTOT+DELVOL/BEDVOL
      COLVOL=BVTOT
C *** MOVE SOLUTION DOWN COLUMN
      DO 120 J=1,JMAX
      CSAVE = C(1,J)
      DO 120 I=2,IMAX
      CT = C(I,J)
      C(I,J) = CSAVE
      CSAVE = CT
      120 CONTINUE
      DO 121 I=2,IMAX
      J=IMAX-I+2
121  ISTATE(J)=ISTATE(J-1)
C ***
C *** PERFORM ION EXCHANGE CALCULATIONS FOR THIS INCREMENT OF TIME AND
C *** CONCENTRATION PROFILE
C ***
      CALL EXCHAN
C ***
C *** PICK UP EFFLUENT CONCENTRATION FOR CONCENTRATION AVERAGE
      DO 130 J=1,JMAX
      CIN(J)=CIN(J)+C(1,J)*AMW(J)*FLS*DELT
      130 SCEX(J) = SCEX(J) + C(IMAX,J)*AMW(J)
      IF(BVTOT.LT.$BV(ISTEP))GOTO 109
      ISTEP=ISTEP+1
      WRITE(6,1050)ISTEP,TIMEMN,BVTOT
1050  FORMAT('// ' ***TRANSITION TO STEP',I3,' AT ',F9.2,' MINUTES OR ',
      1 F6.2,' BED VOLUMES'//)
      WRITE(8,1050)ISTEP,TIMEMN,BVTOT
      IPRINT=100000

```



```

KOUNT2=1000000
IF(ISTEP.GT.NSTEP)GOTO 200
90  ISTATE(1)=ISTEP
    FLH=$FLOW(ISTEP)
    FCS = FLH / 3.6
    FLS = .001*FCS
    VOUT = FCS /A
    VIN = VOUT /E
    DELT=DELX/VIN
    DO 98 J=1,JMAX
98  C(1,J)=$CONC(ISTEP,J)
    MAXPRT=$PRINT(ISTEP)/DELVOL*BEDVOL
    IF(8VOTOT.EQ.0.)GOTO 102
C ... TEST IF TIME TO PRINT.
109  IPRINT=IPRINT+1
    IF(IPRINT.LT.MAXPRT)GOTO 102
C ... CALCULATE CONCENTRATION VALUSE.
    IPRINT=0
C ***
C *** CHECK FOR PRINTOUT OF SUMMARY-NEGATIVE ISUMRY IS NO OF COLUMN
C *** VOLUMES FED
C *** TIME FOR A SUMMARY PRINT
    IF(NPTS.LT.500)NPTS=NPTS+1
    PTIME(NPTS)=TIMEMN
    DO 150 J =1,JMAX
    CX(J)=C(IMAX,J)*AMW(J)
    PCON(NPTS,J)=CX(J)
    CEX(J) = FLS*DELT *SCEX(J)
    SRES(J) = 0.
    SSOL(J) = 0.
    DO 140 I=1,IMAX
    SRES(J) = SRES(J) +CBAR(I,J)*AMW(J)
140  SSOL(J) = SSOL(J) +C(I,J)*AMW(J)
    RES(J) =(FLS*DELT *SRES(J)*(1.-E)/ E )
    SOL(J) = FLS *DELT*SSOL(J)
150  CONTINUE
    WRITE(6,20001)TIME,TIMEMN,TIMVOL,COLVOL
20001 FORMAT('OTIME =',F10.1,' SECONDS=',F8.2,' MINUTES, VOLUME=',
1      F8.2,' LITERS=',F8.3,' COLUMN VOLUMES')
    WRITE(6,2001)((J,CIN(J),RES(J),SOL(J),CEX(J),CX(J)),J=1,JMAX)
2001 FORMAT( I10,5E15.7)
C *** CHECK FOR CONCENTRATION PRINT
    KOUNT2 = KOUNT2 + 1
200  IF(KOUNT2.LT.ISUMRY)GOTO 102
C *** TIME FOR A PRINT OF CONCENTRATIONS
    KOUNT2 = 0
    WRITE(8,1013)TITLE,TIME,TIMEMN,TIMVOL,COLVOL
1013  FORMAT('1',20A4/
1      'OTIME =',F10.1,' SECONDS=',F8.2,' MINUTES, VOLUME=',
1      F8.2,' LITERS=',F8.3,' COLUMN VOLUMES'/
1      / 'OCONCENTRATION PROFILE DATA --',// 'OC = GRAMS
A/LITER',/ ' CBAR = GRAMS/ LITER RESIN' , // 'O INCR.
1', ' C1 CBAR1 C2 CBAR2 ',
2 ' C3 CBAR3')
    DO 210 I=1,IMAX,ICONC
    DO 205 J=1,JMAX
    CXN(J)=AMW(I)*C(I,J)
205  CEX(J)=AMW(J)*CBAR(I,J)
    WRITE(8,3001)I,(CXN(J),CEX(J),J=1,JMAX)
3001 FORMAT(I10,10E15.7)
210  CONTINUE

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```

      IF(ISTEP.GT.NSTEP)GOTO 500
      GO TO 102
C *** END OF CALCULATIONS - DUMP FINAL RESULTS
500  IF(IPUNCH.EQ.0)GOTO 605
      DO 600 J =1,JMAX
      WRITE(7,4001) (C(I,J),I=2,IMAX)
      WRITE(7,4001) (CBAR(I,J),I=2,IMAX)
4001 FORMAT( 8E10.4)
600  CONTINUE
C --- TEST IF PLOTS IS WANTED
605  IF(JPLOT.EQ.0)GOTO 601
      NPLT=NPLT+1
      IF(NPLT.EQ.1)CALL PLOTS(9.,10.)
C --- FIND PLOT MIN AND MAX VALUES
      AMIN=1000.
      AMAX=0.
      DO 604 J=1,JMAX
      IF(NEXP.EQ.0)GOTO 603
      DO 602 I=1,NEXP
      IF(ECON(I,J).GE.AMAX)AMAX=ECON(I,J)
      IF(ECON(I,J).LT.AMIN)AMIN=ECON(I,J)
602  CONTINUE
603  DO 604 I=1,NPTS
      IF(PCON(I,J).GT.AMAX)AMAX=PCON(I,J)
      IF((PCON(I,J).GT.BMIN(J)).AND.
1      (PCON(I,J).LT.AMIN))AMIN=PCON(I,J)
604  CONTINUE
      XMAX=PTIME(NPTS)
      IF((NEXP.GT.0).AND.(ETIME(NEXP).GT.XMAX))XMAX=ETIME(NEXP)
      XLENG=7./XFAC
      YLENG=7./YFAC
      XD=XMAX/XLENG
C --- DO AUTO SCALING OF AXES.
      K=3
      IF(XD.LT.1000.)K=2
      IF(XD.LT.100.)K=1
      IF(XD.LT.10.)K=0
      REM=XD*10.**(-K)
      DX=10.
      IF(REM.LT.8.)DX=8.
      IF(REM.LT.5.)DX=5.
      IF(REM.LT.4.)DX=4.
      IF(REM.LT.2.5)DX=2.5
      IF(REM.LT.2.)DX=2.
      IF(REM.LT.1.5)DX=1.5
      DX=DX*10.**K
      XLENG=IFIX(XMAX/DX+.5)
      MAX=ALOG10(AMAX)+.95
      MIN=ALOG10(AMIN)-.95
      CYCLES=MAX-MIN
      SMIN=10.**MIN
C --- GENERATE PLOT.
      HCHAR=.0875/XFAC
      CALL PLOT(1.,1.,-3)
      QQ=CYCLES/YLENG
      CALL FACTOR(XFAC,YFAC)
      CALL AXIS(0.,0.,'TIME (MINUTES)',-14,XLENG,0.,0.,DX,20.)
      CALL LGAXS(0.,0.,'CONCENTRATION',13,YLENG,90.,SMIN,CYCLES/YLENG)
      CALL SYMBOL(.5,YLENG+.5,HCHAR,TITLE,0.,72)
C --- SET UP TO PLOT POINTS.
      PTIME(NPTS+1)=0.

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        PTIME(NPTS+2)=DX
        ETIME(NEXP+1)=0.
        ETIME(NEXP+2)=DX
        DO 620 J=1,JMAX
C --- ELIMINATE ZEROS.
        DO 610 I=1,NPTS
610    IF(PCON(I,J).LT.SMIN)PCON(I,J)=SMIN
        K=NPTS
        PCON(NPTS+1,J)=SMIN
        PCON(NPTS+2,J)=CYCLES/YLENG
        IF(K.LE.2)GOTO 621
        CALL LGLIN(PTIME(1),PCON(1,J),K,1,0,1,1)
621    IF(NEXP.EQ.0)GOTO 620
        ECON(NEXP+1,J)=SMIN
        ECON(NEXP+2,J)=CYCLES/YLENG
        CALL LGLIN(ETIME,ECON(1,J),NEXP,1,-1,J,1)
620    CONTINUE
        CALL PLOT(0.,0.,999)
601    GOTO 1
9999   IF(NPLOT.NE.0)CALL PLOT(10.,0.,999)
        STOP
        END
        SUBROUTINE EXCHAN
C *** CALCULATES ION EXCHANGE FOR A GIVEN TIME ELEMENT
        DOUBLE PRECISION DELCB,CBAR,C,CON,TEST,CEBAR
        DOUBLE PRECISION DJ
        DOUBLE PRECISION U,FIX
        COMMON DVO(10),CEBAR(10),CMBAR,JMAX,C(1000,3),CBAR(1000,3),PIE,R,
1 E,IMAX,DELCB(10),CSTAR(10),CON(10),DELT,DK(10),DO,ALPHA,F(10),
3 VOUT,DL,NOFILM,IELUT,IWASCH
        COMMON ISTATE(1000),$BV(20),$FLOW(20),$PRINT(20),
1 $ALPHA(20),$DO(20),$XTRA(20),$CONC(20,4),$DVO(20,4)
        COMMON TIME
        DATA KSTATE/0/
        DO 999 I=2,IMAX
C ... TEST IF NEW COLUMN STATE HAS BEN ENTERED.
        IF(KSTATE.EQ.ISTATE(I))GOTO 4
C ... YES
        KSTATE=ISTATE(I)
        ALPHA=$ALPHA(KSTATE)
        DO=$DO(KSTATE)
        XX=$XTRA(KSTATE)
        DO 3 J=1,JMAX
3    DVU(J)=$DVO(KSTATE,J)
C *** FIRST TIME USE CONCENTRATION INTO STAGE
4    KSW=1
        DO 5 J=1,JMAX
5    CON(J)=C(I,J)
C *** START OF CALCULATION LOOP
C *** IS PU CONCENTRATION ZERO OR ESSENTIALLY ZERO
10   IF(CON(1).GT..1E-20)GOTO 15
11   CEBAR(1)=0.
        GO TO 20
C *** COMPUTE ISOTHERM EQUATION FOR PLUTONIUM
C *** REFERENCE JAMES,J.INORG.NUCL.CHEM.,25,711,(1963).
15   U=CMBAR/2./DVO(1)/CON(1)
        DJ=1.+2./U
        CEBAR(1)=CMBAR*(1.+U*(1.-DSQRT(DJ)))
        IF(CEBAR(1).LT.0.)CEBAR(1)=0.
C *** COMPUTE FOR OTHER ELEMENTS(IF THEY ARE PRESENT)
20   IF(JMAX.LE.1) GO TO 40

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DO 30 J=2,JMAX
30  CEBAR(J)=DVO(J)*CON(J)*2.
C *** CALCULATE THE IONS ADSORBED ON THE RESIN WITH THE VERMEULEN EQN
C *** REFERENCE VERMEULEN, I.E.C., 45, 1664 (1953).
C *** THE DIFFUSION COEFFICIENT IS MODIFIED AS SUGGESTED BY JAMES
C *** REFERENCE JAMES & COOPER, LA-2838, LOS ALAMOS (1965).
40  FIX=-ALPHA*CBAR(I,1)/CMBAR
    DK(1)=DO*DEXP(FIX)
    DO 50 J=1,JMAX
    DK(J) = DK(1)*F(J)
C *** CALCULATE DELTA CBAR FOR EACH COMPONENT
    IF (XX.LT.0.) GOTO 42
    IF (XX.EQ.0.) GOTO 46
C - SORPTION
    IF (CBAR(I,J).GT.0.) GO TO 41
C *** FIRST TIME APPROXIMATION
    DKKKK = DK(J)*PIE*PIE/(R*R)
    DELCB(J) = .66*CEBAR(J)*SQRT(DKKKK*DELT)
    GO TO 45
41  DELCB(J) = (PIE*PIE*DK(J)/(2.*R*R)) * DELT
    1  (CEBAR(J)**2 - CBAR(I,J)**2) / CBAR(I,J)
    GO TO 45
C - WASHING
46  IF (CBAR(I,J).GT.0.) GOTO 48
    DKKKK=DK(J)*PIE*PIE/R/R
    DELCB(J)=-.66*CBAR(I,J)*SQRT(DKKKK*DELT)
    GO TO 45
48  DELCB(J) = (PIE*PIE*DK(J)/(2.*R*R)) * DELT
    1  (CEBAR(J)**2 - CBAR(I,J)**2) / CBAR(I,J)
    GO TO 45
C - ELUTION
42  IF (CBAR(I,J).GT.1.E-11) GOTO 43
    DKKKK=DK(J)*PIE*PIE/R/R
    DELCB(J)=-.66*CBAR(I,J)*SQRT(DKKKK*DELT)
    GO TO 45
43  CONTINUE
    DELCB(J) = (PIE*PIE*DK(J)/(2.*R*R)) * DELT
    1  (CEBAR(J)**2 - CBAR(I,J)**2) / CBAR(I,J)
    GO TO 45
431 DELCB(J)=-PIE*PIE/2./R/R*DELT*CBAR(I,J)*DK(J)
    1  /10.
C *** CHECK FOR REASONABLE ION TRANSFER
45  IF (DELCB(J).EQ. 0.) GO TO 50
    IF (DELCB(J).GT. 0.) GO TO 47
C *** NEGATIVE TRANSFER - LIMIT TO 1/2 OF WHAT WAS FED
C *** JERRY - LOOKS LIKE A BAD SIGN
    IF (-DELCB(J).GT..5*CBAR(I,J)) DELCB(J)=-.5*CBAR(I,J)
    GO TO 50
C *** POSITIVE TRANSFER - LIMIT TO 1/2 OF THAT IN FEED
    47 TEST = .5* E * C(I,J) / (1.-E)
    IF (DELCB(J).GT.TEST) DELCB(J) = TEST
50  CONTINUE
C *** IF NO FILM DIFF - SKIP RERUN
    IF (NOFILM.EQ.0) GO TO 100
    IF (KSW.EQ.2) GO TO 100
    KSW = 2
C *** CALCULATE FILM DIFFUSION CORRECTION
C *** REFERENCE GLUECKAUF, ION EXCH. & ITS APPLICATIONS, P34, SOCIETY OF
C ***1 CHEMICAL INDUSTRY, LONDON, 1955 .
C *** CSTAR IS THE SURFACE CONCENTRATION OF THE LIQUID ON THE RESIN
    FILMT = 2.*R / (1.+70.*VOUT*R)

```

```

DO 60 J =1,JMAX
DLC=(DELCB(J)*2.*R*FILMT/(3.*DL*DELT*(1.-E)))*.10
IF(DLC .GT. .5* C(I,J) ) DLC = 0.5* C(I,J)
CSTAR(J) = C(I,J) - DLC
CON(J) =CSTAR(J)
60 CONTINUE
C *** GO BACK AND COMPUTE CBARS WITH DIFFUSION CORRECTED CONCENTRATIONS
GO TO 10.
100 DO 110 J =1,JMAX
C(I,J) = C(I,J) - (1.-E)*DELCB(J)/ E
CBAR(I,J) = CBAR(I,J) + DELCB(J)
110 CONTINUE
C *** END CALCULATION FOR THIS SPACE POINT
999 CONTINUE
C *** END CALCULATION FOR ALL SPACE POINTS
RETURN
END

```

APPENDIX 2

EXPERIMENTAL AND COMPUTED RESULTS

ROCKY FLATS RUN NO. 1 – NOMINAL PARAMETERS

ROCKY FLATS RUN NO. 2 – NOMINAL PARAMETERS

ROCKY FLATS RUN NO. 3 –
NOMINAL PARAMETERS

ROCKY FLATS RUN NO. 4 – NOMINAL PARAMETERS

ROCKY FLATS RUN NO. 5 –
NOMINAL PARAMETERS

ROCKY FLATS RUN NO. 6 –
NOMINAL PARAMETERS

ROCKY FLATS RUN NO. 7 – NOMINAL PARAMETERS

ROCKY FLATS RUN NO. 8 –
NOMINAL PARAMETERS

ROCKY FLATS RUN NO. 9 - NOMINAL PARAMETERS

ROCKY FLATS RUN NO. 10 - NOMINAL PARAMETERS