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Self-Heating of Pu-238 Anion Exchange Column (U)

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Self-Heating of Pu-238 Anion Exchange Column (U)

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Issued: March 23, 1994

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Summary

Heat and mass transfer calculations were performed to determine the effect of increases in the H-canyon Frames Waste Recovery (FWR) column loading on column temperatures during flow interruptions. The heat transfer calculations are based on a previous analysis of the H Frames columns, and the mass transfer calculations use data from two recent laboratory elutions.

The current Technical Standard (TS) limits the total amount of Pu-238 on the column to 490 g. To meet production goals for NASA's Cassini mission, this limit needs to be increased.

In addition to the loading limit, the TS stipulates that column temperatures cannot exceed 60°C. The temperature limit is set to prevent a thermal excursion due to a nitric acid-resin reaction. Significant column heating occurs only when flow to the column is interrupted. During normal operation, column temperatures are approximately equal to the ambient temperature. The TS limits flow interruptions to 15 min.

Results from the laboratory elutions and the heat and mass transfer analyses show that, for an ambient temperature of 30°C, the maximum column temperature cannot reach the TS limit of 60°C until 80 min. after flow is interrupted during loading or washing or until 50 min. after flow is interrupted during elution. These times are independent of operating conditions. The heating rate for loading and washing was calculated assuming adiabatic heating at a maximum adsorbed plutonium concentration of 45 g/L. The heating rate for elution is based on adiabatic heating at a total plutonium concentration of 71 g/L. The maximum total concentration during elution consists of 45 g/L adsorbed plutonium plus 26 g/L dissolved plutonium in equilibrium with the adsorbed solid.

Based on this results of this study and the previous analysis of the H Frames columns, it is safe to raise the Pu-238 loading of the FWR column from 490 to 800 g or more without violating the TS column temperature limit of 60°C during a 15-min. flow interruption.

Introduction

Historically, the FWR column recovered Pu-238 from dissolved scrap solutions the primary frames and anion columns and recycled it to HB-Line. Currently, this column is used to recover Pu-238 from scrap material to make product for NASA's Cassini mission. To meet expected future production goals for this mission, an increase in column loading above the current TS limit [1] is desired.

The TS limit is set to prevent thermal degradation and disintegration of the resin bed. At low temperatures, resin bed temperatures increase primarily due to decay heat from Pu-238. At temperatures exceeding about 115°C, an exothermic reaction between nitric acid and resin predominates [2,3]. This reaction causes a potentially violent temperature excursion.

The current TS limits the total amount of Pu-238 on the column to 490 g and the source term concentration in H Canyon tanks to 7 g/L Pu-238. In addition, the TS stipulates a maximum column temperature of 60°C to protect against the exothermic nitric acid-resin reaction.

The greatest potential for a resin bed temperature excursion occurs during flow interruptions. If the flow is stopped during loading, washing, or elution, the temperature will rise due to heat from the decay of Pu-238 until conditions for a temperature excursion are met. The temperature rise is nearly adiabatic; previous calculations have shown that natural convection to the ambient air is not effective in cooling the resin bed. To preclude the possibility of a thermal excursion, the TS conservatively limits the duration of flow interruptions to 15 min.

Separations Engineering has requested that the FWR column loading limit be raised from 490 to 800 g Pu-238 and that the maximum feed concentration be increased from 7 to 10 g/L [4]. This report evaluates the effects of increases in column loading on column temperatures during flow interruptions, as a function of time.

Resin Bed Heat Transfer Model

A description of the energy balance used to model heat transfer in the resin bed during flow interruptions follows. Terms in the model equations are defined in the Nomenclature section at the end of this report.

The energy equation includes terms for conduction, natural convection, and heat generation by radiolysis and nitric acid-resin reactions. This equation is

$$\begin{aligned} \rho_{\text{mix}} c_{p,\text{mix}} \frac{\partial T}{\partial t} = & -\rho c_p v_z \frac{\partial T}{\partial z} - \rho c_p v_r \frac{\partial T}{\partial r} + k_{\text{mix}} \left(\frac{\partial^2 T}{\partial z^2} + \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial T}{\partial r} \right) \right) \\ & + q_{\text{rad}} C_{\text{Pu}} + K_{\text{rxn}} \exp \left(\frac{-E_a}{R_g T_a} \right) \end{aligned} \quad (1)$$

Since there is no net flow to the column, the convection terms in this equation represent natural convection. The axial velocity for natural convection is modeled using a form of the Ergun equation for laminar flow [5,6]. This equation takes the form

$$v_z = \frac{d_p^2 \epsilon_o^4 (\rho - \bar{\rho}) g}{200(1 - \epsilon_o)^2 \mu} \quad (2)$$

In this expression, the pressure drop in the Ergun equation is replaced by a buoyancy force proportional to the difference between the local bulk fluid density and the average fluid density at that bed level, which is computed as

$$\bar{\rho} = \frac{2}{R^2} \int_{r=0}^R r \rho dr \quad (3)$$

It may be noted that in Equation 2 $v_z \propto \frac{\epsilon_o^4}{1 - \epsilon_o^2}$, while in the Ergun equation $v_z \propto \frac{\epsilon_o^3}{1 - \epsilon_o^2}$.

The extra void fraction multiplier is added because the buoyant force applies only to the fraction of the total volume occupied by the bulk solution and not to the resin beads.

The radial velocity is calculated using the continuity relation:

$$\frac{1}{r} \frac{\partial r v_r}{\partial r} + \frac{\partial v_z}{\partial z} = 0 \quad (4)$$

For the analysis of flow interruptions during loading and washing, the density of water is used. This does not introduce appreciable errors in density gradients, since virtually all the plutonium is fixed on the resin and the concentration of nitric acid is constant. Errors in the absolute density do not exceed 25%. Data in Reference [7] were fit to obtain the correlation [8]

$$\rho_{H_2O} = 1.0013 - 5.5346 \times 10^{-5} T - 4.5979 \times 10^{-6} T^2 + 8.6533 \times 10^{-9} T^3, \text{ g/cm}^3 \quad (5)$$

For the analysis of flow interruptions during elution, the water density is corrected for the presence of $\text{Pu}(\text{NO}_3)_4$ and HNO_3 using the approximation,

$$\rho = \rho_{H_2O} \left(1 + \frac{\Delta \rho_{\text{Pu}(\text{NO}_3)_4}}{\rho_{H_2O}} + \frac{\Delta \rho_{\text{HNO}_3}}{\rho_{H_2O}} \right) \quad (6)$$

Changes in the density are linearized with respect to the plutonium and nitric acid concentrations. Based on ideal solution approximations and plutonium nitrate and nitric acid density measurements, the maximum increase in the density due to the presence of plutonium is 3.7% [8,9], and the maximum increase for nitric acid is 24.1% [8,10].

The viscosity is set equal to the viscosity of water, given by [11]

$$\mu = 0.01002 \times 10^{\frac{1.3272(20-T) - 0.001053(T-20)^2}{T+105}}, \text{ g/cm/sec} \quad (7)$$

Differences between the viscosity of water and nitric acid solutions are ignored because they are smaller than changes in the viscosity with temperature.

Variations in the bulk density, heat capacity, and thermal conductivity of the resin bed with temperature are not significant. Consequently, these properties are evaluated as constants [2,3]:

$$\rho_{\text{mix}} = 1.23 \text{ g/cm}^3 \quad (8)$$

$$c_{p,\text{mix}} = 0.76 \text{ cal/g}^\circ\text{C} \quad (9)$$

$$k_{\text{mix}} = 0.001 \text{ cal/cm/sec}^\circ\text{C} \quad (10)$$

The heat of reaction for the radiolysis reaction and the heat of reaction and the activation energy for the nitric acid-resin reaction were measured previously [2,3]. These have the values

$$q_{\text{rad}} = 0.13156 \text{ cal/sec/g Pu-238} \quad (11)$$

$$K_{\text{rxn}} = 4.25 \times 10^{-9} \text{ cal/sec/cm}^3 \quad (12)$$

$$\frac{E_a}{R_g} = 10587.2 \text{ }^\circ\text{K} \quad (13)$$

The solution of the energy equation requires boundary conditions for thermal conduction and inlet conditions for natural convection. Mass balances for loading, washing, and elution provide the initial conditions when flow is interrupted.

The boundary condition at the center of the column comes from the requirement that the temperature profile be symmetric. This dictates that

$$\frac{\partial T}{\partial r} = 0 \text{ at } r = 0 \quad (14)$$

Along the column walls, the conduction of heat from the resin bed must equal the rate of natural convection to the ambient air. In other words,

$$-k \frac{\partial T}{\partial r} = h(T - T_{\text{amb}}) \text{ at } r = R \quad (15)$$

where h is the heat transfer coefficient for natural convection [2,3], specified as $0.00027 \text{ cal/cm}^2/\text{sec}^\circ\text{C}$.

It is assumed that there is no heat transfer at the top and bottom of the column. Thus,

$$-k \frac{\partial T}{\partial z} = 0 \text{ at } z = 0 \text{ and } z = L \quad (16)$$

Inlet conditions for natural convection are based on the assumption that the fluid exiting the resin bed due to natural convection becomes well-mixed in small volumes of free-

standing liquid above and below the resin bed and immediately reenters the bed. According to this assumption, at the top of the bed, if R_0 is the radial location where $v_z = 0$, then for $R > R_0$,

$$T_{in} = \frac{\int_0^{R_0} r T v_z dr}{\int_0^{R_0} r v_z dr} \text{ at } z = 0 \quad (17)$$

Similarly, at the bottom of the bed, if R_L is the radial location where $v_z = 0$, then for $R < R_L$,

$$T_{in} = \frac{\int_{R_L}^R r T v_z dr}{\int_{R_L}^R r v_z dr} \text{ at } z = L \quad (18)$$

Mass transfer analyses furnish the initial plutonium concentrations for the heat transfer model. Descriptions of the chemical equilibria and diffusional processes that govern mass transfer and an outline of the mass transfer model follow.

Ion Exchange Chemistry

In the FWR column, plutonium is selectively adsorbed on an anionic resin from an 8 M HNO₃ solution and is eluted with 0.25 M HNO₃. Currently, the column uses Ionac 641[®] macroporous resin especially converted to a nitrate form. The following reaction occurs on the resin surfaces [12], which are assumed to be evenly distributed throughout the resin beads.

where

R = chemically active site on the resin substrate

Equilibrium for this reversible reaction is governed by the solubility product [12]

$$K_1 = [PuNO_3^{+3}] [NO_3^-]^3 \quad (19)$$

where K_1 is an equilibrium constant that depends on the resin type and the plutonium loading on the resin. For fully loaded Dowex-1 X-4 resin, $K_1 = 0.26$.

In solution, the plutonium ions complex with nitrate ions according to [12]:

[®] Ionac is a registered trademark of the Sybron Chemical Corp.

The equilibrium constant for this reaction is given by [12]

$$K_2 = \frac{[\text{PuNO}_3^{+3}]}{[\text{Pu}^{+4}][\text{NO}_3^-]} = 2.9 \pm 0.6 \quad (20)$$

Finally, a requirement of electroneutrality relates the plutonium ion complex concentrations to the nitric acid concentration by [12]

$$[\text{NO}_3^-] = [\text{H}^+] + 3[\text{PuNO}_3^{+3}] + 4[\text{Pu}^{+4}] \quad (21)$$

Solution of Equations 19 through 21 gives the equilibrium solution concentration for plutonium adsorbed on Dowex-1® resin. Figure 1 depicts this concentration as a function of nitric acid molarity.

Adsorption and Elution Processes

The preceding section describes the chemical equilibria at the surfaces where plutonium is adsorbed and desorbed. Diffusion to these surfaces controls the rates of adsorption and elution.

Because the plutonium ionic species react rapidly at the resin surface, adsorption takes place at the outer surfaces of the resin beads before the plutonium can penetrate to the interior of the beads. Consequently, solid-phase, or particle, diffusion controls the rate of adsorption [12]. The particle diffusion model is analogous to a molecular diffusion model, with a particle diffusivity and the bulk adsorbed concentration replacing the ordinary diffusivity and the solution concentration.

A shrinking core approximation describes desorption of plutonium from the resin beads [12]. An examination of the equilibrium relationships controlling the solubility of plutonium nitrate salts shows why the shrinking core model is applicable. As Figure 1 shows, the plutonium solubility decreases as the acid concentration increases. During elution, dilute acid diffuses inward from the resin bead surface to displace more concentrated acid, and plutonium nitrate species diffuse outward toward the surface. Thus, the acid concentration increases and the plutonium nitrate concentration decreases going toward the center of the bead. This implies that a saturated plutonium nitrate solution exists at only one radial location within the bead, provided the adsorbed plutonium concentration is sufficient to locally saturate the pore solution. Plutonium nitrate species diffuse outward from this surface.

Resin Bed Mass Transfer Model

Separate mass transfer models were developed for loading and washing and for elution. Both models use one-dimensional, transient mass conservation equations, with explicit terms to account for adsorption or elution of plutonium into or out of the resin beads. These models divide the total plutonium concentration, C_{Pu} , into a bulk flow concentration, x , a resin bead pore solution concentration, y , and an adsorbed concentration, f :

$$C_{Pu} = x + y + f \quad (22)$$

All concentrations are based on the bulk volume of the resin bed.

The mass balances for adsorption and washing take the form

$$\frac{\partial x}{\partial t} = -v_z \frac{\partial x}{\partial z} + D \frac{\partial^2 x}{\partial z^2} - G \quad (23)$$

and

$$\frac{\partial f}{\partial t} = G \quad (24)$$

where D is the axial dispersion coefficient and G is the rate of adsorption.

The axial dispersion coefficient is calculated using a mixing length of two bead diameters [13]. This gives

$$D = 2d_p v_z \quad (25)$$

The rate of adsorption is calculated using a solid-phase diffusion model [14]. This model generates the following expression.

$$G = f_{feed} \frac{x}{x_{feed}} \frac{\left(\frac{f}{f_{feed}}\right)^2}{\ln\left(\frac{f_{feed} + f}{f_{feed} - f}\right) - 2\frac{f}{f_{feed}} \tau_{part}} \quad (26)$$

where

$$\tau_{part} = \frac{d_p^2}{4\pi^2 D_{part}} \quad (27)$$

and D_{part} is a particle diffusion coefficient.

As $f \rightarrow 0$,

$$G = f_{feed} \frac{x}{x_{feed}} \frac{1.5f_{feed}}{f} \frac{1}{\tau_{part}} \quad (28)$$

The Appendix presents derivations of the adsorption rate equations.

The mass balances for elution are:

$$\frac{\partial c}{\partial t} = \frac{\epsilon_o}{\epsilon_o + \epsilon_{i,1}} \left(-v_z \frac{\partial c}{\partial z} + D \frac{\partial^2 c}{\partial z^2} \right) \quad (29)$$

$$\frac{\partial x}{\partial t} = -v_z \frac{\partial x}{\partial z} + D \frac{\partial^2 x}{\partial z^2} + G_a - G_b \quad (30)$$

$$\frac{\partial f}{\partial t} = -G_a \quad (31)$$

and

$$\frac{\partial y}{\partial t} = G_b \quad (32)$$

where c is the fraction of the bulk solution that is 0.25 M elution acid, G_a is the rate of plutonium desorption, and G_b is the rate of diffusion of plutonium from the bulk solution

into desorbed resin beads. The factor $\frac{\epsilon_o}{\epsilon_o + \epsilon_{i,1}}$, which is the ratio of the bulk solution

volume to the total solution volume before desorption, accounts for interchange of elution acid between the bulk and pore solutions. Use of this factor is based on a quasi-equilibrium approximation. In other words, diffusion of nitric acid is assumed to be rapid compared with diffusion of plutonium nitrate species, so that the pore and bulk solution nitric acid concentrations are equal while plutonium diffuses.

Separate rate models are used for desorption and interchange of plutonium between the bulk and pore solutions, because the desorption model transfers plutonium directly from the adsorbed solid to the bulk solution, without allowing for any plutonium in the pore volume. The Appendix contains derivations for the desorption and solution interchange equations.

As explained previously, a shrinking core model describes desorption. This model yields the rate expression,

$$G_a = \frac{-cf_0 \left(1 - \frac{\frac{x^2}{x_{\max}^2} - \frac{x}{x_{\max}} \sqrt{\frac{cx}{x_{\max}} - \frac{x^2}{x_{\max}^2}}}{2 \frac{x}{x_{\max}} - c} \right)}{\tau_{\text{pore}} \left\{ 1 - \frac{4}{5} \sqrt{\frac{f_0}{f}} - \frac{1}{5} \left(\frac{f_0}{f} \right)^2 \right\}} \quad (33)$$

where

$$\tau_{\text{pore}} = \frac{d_p^2}{24\eta D_{\text{pore}}} \quad (34)$$

The factor η corrects for the difference between the pseudo-steady-state shrinking core approximation and the exact solution to the transient diffusion equation. This factor is 0.75 for the conditions in the FWR column. The analysis for this correction factor is included in the derivation of the shrinking core approximation in the Appendix.

The equations that describe interdiffusion between the bulk and pore solutions are of the same form as the equations for particle diffusion. The rate expression for interdiffusion is

$$G_b = \frac{4\pi^2 D_{\text{pore}} (1 - \epsilon_o)}{d_p^2} \frac{\frac{y^2}{\epsilon_{i,2}^2} \left(\frac{x_{\text{max}} x}{\epsilon_o^2} - \frac{y^2}{\epsilon_{i,2}^2} \right)}{2 \frac{x_{\text{max}} x y}{\epsilon_o^2 \epsilon_{i,2}} - \frac{\sqrt{x_{\text{max}} x}}{\epsilon_o} \left(\frac{x_{\text{max}} x}{\epsilon_o^2} - \frac{y^2}{\epsilon_{i,2}^2} \right) \ln \left(\frac{\frac{\sqrt{x_{\text{max}} x}}{\epsilon_o} + \frac{y}{\epsilon_{i,2}}}{\frac{\sqrt{x_{\text{max}} x}}{\epsilon_o} - \frac{y}{\epsilon_{i,2}}} \right)} \quad (35)$$

where the pore volume fraction, $\epsilon_{i,2}$, is normalized with respect to the plutonium loading at the start of elution:

$$\epsilon_{i,2} = \left(1 - \frac{f}{f_0} \right) \epsilon_{i,2,0} \quad (36)$$

As $\frac{y}{\epsilon_{i,2}} \rightarrow \frac{\sqrt{x_{\text{max}} x}}{\epsilon_o}$, the rate expression reduces to

$$G_b = \frac{4\pi^2 D_{\text{pore}} (1 - \epsilon_o)}{d_p^2} \left(\frac{\sqrt{x_{\text{max}} x}}{\epsilon_o} - \frac{y}{\epsilon_{i,2}} \right) \quad (37)$$

Solution of Mass and Heat Transfer Equations

Finite difference codes were written to solve the one-dimensional mass transfer and two-dimensional heat transfer equations listed in the previous two sections. These codes used explicit time stepping, donor cell differencing for convection terms, and centered-space differencing for diffusion terms. Mass and heat transfer were computed separately, with the output from the mass transfer calculation serving as input to the heat transfer calculation.

The mass and heat transfer codes were written in Fortran and were executed on the LAB1 VAX and Cray computers. Reference [8] contains code listings and documents locations of source code, input, and output files.

Mass Transfer Model Parameter Evaluation

To complete the mass transfer model, values are needed for the resin bead diameter, particle and pore diffusivities, volume fractions for the bulk solution and the pore solution before and after desorption, the maximum plutonium loading on the resin, and the concentration of plutonium in saturated equilibrium with a loaded resin surface. A resin bead diameter of 0.06 cm was used. This corresponds to a 30 mesh size, which is at the small end of the specified range of 20-30 mesh for the Ionac 641® resin. The volume fraction for the bulk solution was estimated to be 0.33, based on void fraction measurements in packed beds of uniform spheres [5]. The remaining variables were evaluated from the results of laboratory elutions and a previous study of the H-frames ion exchange columns conducted by J. A. Wehner [2,3].

Descriptions of Laboratory Elutions

Two laboratory elutions were performed to support this analysis [15]. In the first elution, a short column was nearly fully loaded with plutonium. Results from this elution and from the Wehner study were used to determine the saturated equilibrium plutonium concentration, the maximum plutonium loading, and the particle diffusivity. The second elution, in which a longer column was partially loaded, approximated operating conditions in the FWR column. Results from both elutions were used to estimate the pore diffusivity and volume fractions for the bulk and pore solutions.

Table 1 lists conditions for the laboratory elutions and the Wehner study [2,3] and compares them to FWR column operating conditions [16,17,18].

Table 1. Conditions for Laboratory Elutions, H-Frames Column Study, and FWR Column Operation

	Test Elution 1	Test Elution 2	H-Frames Column	FWR Column
Column diameter (cm)	2.32	1.90	48.0	55.9
Bed length (cm)	9.2	37.5	38.0	35.6
Loading velocity (cm/sec)*	0.0354	0.0526	0.05	0.0469
Column volumes loaded	101.5	18.7	52.1	31.0
Washing velocity (cm/sec)*	0.0354	0.0234	---	0.0197
Bed volumes washed	4.2	6.25	---	10.6
Elution velocity (cm/sec)*	0.0079	0.0073	---	0.0068
Bed volumes eluted	5.1	2.35	---	4.6
Pu feed concentration (g/cm ³)	0.000428	0.000493	0.0004	---

* All velocities are superficial velocities based on flow through the entire cross-section of the column.

The loading, washing, and elution times for Test Elution 2 were shortened so that this elution could be completed in two 8-hour shifts. Although this test was abbreviated, the elution time was sufficient to allow removal of most of the plutonium from the column. During column elutions, the head cut takes 1.2 bed volumes, the heart cut takes 1.5 bed volumes, and the tail cut takes 1.9 bed volumes. The total elution volume for Test Elution 2 is approximately equal to the head plus heart cuts for current column operation.

Results from the Wehner study were not used to determine elution parameters, so washing and elution conditions are not reported.

Analyses of Laboratory Elutions

Figure 2 compares model loading predictions with results reported in the Wehner study. A particle diffusivity of 2×10^{-9} cm²/sec was used to fit the reported data. This diffusivity is the same magnitude as that measured for Dowex X-8 resin [12].

For the Wehner study, it was assumed that the maximum plutonium loading was 40 g/L. From the results of the first test elution, it was determined that the maximum loading at FWR column operating conditions is 45 g/L. As Figure 3 shows, the model accurately predicts the cumulative plutonium discharge with this maximum loading concentration and the particle diffusivity determined from the Wehner study.

Figures 4 and 5 compare model predictions with measured rates of discharge of plutonium during both test elutions. A pore diffusivity of 1.0×10^{-6} cm²/sec and pore volume fractions of 0.132 prior to desorption of plutonium from the resin and 0.160 after desorption were used to fit the model to the test data. The pore diffusivity is about 100 times greater than reported values for anionic resins [12]. The pore volume fractions correspond to resin bead porosities of 0.198 before desorption and 0.240 after desorption. The porosity increases during desorption due to swelling of the resin [12] and loss of $\text{Pu} \cdot 4\text{NO}_3$ by the reaction

The solubility for Ionac 641® resin was estimated from eluate plutonium concentrations measured during Test Elution 1. Before the plutonium concentration spike discharged from the column, the plutonium concentration asymptotically approached a minimum of 0.0106 g/L at a nitric acid concentration of 7.85 M. The plutonium concentration then rapidly peaked at an apparently constant concentration of 26.3 g/L at a nominal elution acid concentration of 0.25 M. (The peak concentration was assumed to reach a plateau, because two successive concentrations, measured when 1.03 and 1.54 bed volumes had eluted, were nearly equal.) The most likely explanation for the asymptotic minimum and constant peak concentrations is that the plutonium in the bulk solution was in equilibrium with the adsorbed plutonium on the resin surfaces. Discharge plutonium concentrations should have approached equilibrium levels during this elution because the bulk solution was in contact with partially loaded resin over the entire length of the column.

The Ionac resin equilibrium saturation was estimated by assuming that equilibrium conditions existed for Test Elution 1. The ratio of the measured equilibrium solubilities for the wash and elution acids was equated to calculated equilibrium values at the measured acid molarities. This calculation yields a solubility constant, K_1 , of 0.63 and a saturated equilibrium concentration of 80.6 g/L at the elution acid concentration of 0.25 M. Figure 6 compares computed solubilities for Ionac resin with solubilities for Dowex 1 resin.

It may be noted that the calculated equilibrium concentration is not the same as the maximum measured discharge concentration. One explanation for this apparent contradiction is that the presence of the resin beads does not change the effective cross-sectional flow area. If the cross-sectional area had changed to the fraction occupied by the bulk solution, then the plutonium would have begun to discharge from the column

well before one bed volume had eluted. The plutonium concentration spike does not appear until about one bed volume has eluted, however. This implies that the plutonium travels down the column at the superficial velocity. From a mass balance, it follows that the plutonium discharge concentration is diluted from the actual bulk solution concentration by the ratio of the cross-sectional area occupied by the bulk solution to the total cross-sectional area, i. e., the volume fraction occupied by the bulk solution. If the plutonium concentration in the bulk solution is in saturated equilibrium with the adsorbed resin, then

$$x = \epsilon_o x_{sat} \quad (38)$$

For $x = 26.3$ g/L and $x_{sat} = 80.6$ g/L,

$$\epsilon_o = 0.326 \quad (39)$$

This value for the bulk solution volume fraction agrees with the assumed value of 0.33 for uniformly sized spheres.

The model accurately calculates the duration of the saturation concentration spike during Test Elution 1. However, the model does not accurately predict the decrease in the plutonium concentration after the saturated concentration spike has passed. The model predictions for the second test elution are accurate, with the exception of the initial measured concentration.

Calculations for FWR Operating Conditions

To determine safe plutonium loading levels, the completed mass and heat transfer models were used to calculate heating rates for flow interruptions during typical FWR column operation. Heating rates were calculated for flow interruptions at the end of the decon wash and at the time during elution when the mass transfer model gave the maximum peak plutonium concentration. These times represent the worst-case conditions for feeding, washing, and elution.

Two cases were evaluated. Both cases used the FWR column conditions listed in Table 1 and an initial temperature of 30°C. In the first case, the plutonium feed concentration was set at the current operating level of 0.2 g/L. In the second case, the feed concentration was increased to 0.7 g/L. This was a convenient hypothetical case, because the plutonium loading profile extended nearly to the bottom of the column. The column loadings for these cases were 513 and 1794 g plutonium, respectively.

Figures 7 and 8 show the plutonium concentration profiles for a feed concentration of 0.7 g/L at the end of the decon wash and at the time of the maximum peak plutonium concentration shortly after the start of elution. The plutonium concentration approaches the fully loaded value of 45 g/L at the column inlet and drops to zero near the outlet, as shown in Figure 7. As Figure 8 illustrates, the plutonium desorbs and transfers to the bulk and pore solutions as the concentration peak descends the column.

Figures 9 and 10 depict centerline and wall temperature profiles for this case. As these figures show, the peak temperature at the end of the decon wash is at the column inlet, and the peak temperature during elution is at the location of the peak plutonium concentration. The temperature drops more precipitously from its peak during elution.

Consequently, thermal conduction moderates the rate of increase of the peak temperature to a greater extent for elution than for feeding or washing.

Figures 11 through 14 compare the heat transfer model calculations of the maximum column temperatures with adiabatic approximations in which thermal conduction and natural convection are ignored. In all cases, the adiabatic approximation conservatively bounds the results of the heat transfer model calculations. The adiabatic calculations more closely approximate the heat transfer model computations for washing, because thermal conduction is more significant for elution.

The adiabatic approximations in Figures 11 through 14 are based on the maximum temperatures calculated by the mass and heat transfer models. Limiting adiabatic approximations can be calculated using maximum possible plutonium concentrations. The maximum concentration for feeding and washing is the maximum adsorbed concentration, which was determined to be about 45 g/L. For elution, the maximum concentration is the sum of the maximum adsorbed concentration and the bulk concentration of solution in equilibrium with adsorbed plutonium, given by the product of the equilibrium concentration and the bulk solution volume fraction. This maximum concentration is $45 + .326 \times 80.6 = 71$ g/L.

Figure 15 depicts the limiting heating rates for loading, washing, and elution. During loading and washing, the TS limit of 60°C will not be exceeded until approximately 80 min. after the flow is interrupted. During elution, it takes about 50 min. for the maximum temperature to reach the TS limit. Both time intervals exceed the maximum flow interruption duration of 15 min. allowed by the TS.

Conclusions

Chemical equilibria set upper bounds for the heating rates during flow interruptions. The maximum concentration of adsorbed plutonium governs the heating rate for loading and washing, and the sum of the maximum adsorbed concentration and the dissolved concentration in equilibrium with the adsorbed resin surface controls the heating rate for elution. Detailed mass and heat transfer calculations indicate that actual heating rates will be somewhat lower than these adiabatic limits.

Neither the heating rate limit for loading and washing nor the limit for elution causes the maximum column temperature to exceed the TS limit in the allowed flow interruption time of 15 min. Therefore, the plutonium loading on the column can be increased without exceeding TS temperature constraints.

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Figure 1. Saturated Equilibria for Dowex-1, X-4, Resin at 60°C

Figure 2. Comparison of Measured and Predicted Resin Loadings after 11 Hours Wash at 0.05 cm/sec with 0.0004 gm/cc Pu Solution

Figure 3. Comparison of Measured and Calculated Cumulative Pu Discharge for Test Elution 1 (assumes 0.045 gm/cc max loading)

Figure 4. Comparison of Measured and Calculated Elution Profiles for Test Elution 1

Figure 5. Comparison of Measured and Calculated Elution Profiles for Test Elution 2

Figure 6. Comparison of Saturation Equilibria for Pu-Loaded Dowex and Ionac Resins in Nitric Acid

Figure 7. Plutonium Concentration Profile at the End of the Decon Wash for a Feed Concentration of 0.7 g/l

Figure 8. Plutonium Concentration Profile 15 min. after the Start of Elution for a Feed Concentration of 0.7 g/l

Figure 9. Temperature Profile after a 60-min. Flow Interruption at the End of the Decon Wash for a Feed Concentration of 0.7 g/l

Figure 10. Temperature Profile after a 60-min. Flow Interruption 30 min. after the Start of Elution for a Feed Concentration of 0.7 g/l

Figure 11. Maximum Temperature Increases after a Flow Interruption during the Decon Wash for a Feed Concentration of 0.2 g/l

Figure 12. Maximum Temperature Increases after a Flow Interruption during Elution for a Feed Concentration of 0.2 g/l

Figure 13. Maximum Temperature Increases after a Flow Interruption during the Decon Wash for a Feed Concentration of 0.7 g/l

Figure 14. Maximum Temperature Increases after a Flow Interruption during Elution for a Feed Concentration of 0.7 g/l

Figure 15. Limiting Temperature Increases after a Flow Interruption during Feeding, Washing, and Elution

Appendix. Derivations of Rate Expressions for Adsorption onto and Elution from Resin Beads

This appendix contains derivations of the rate expressions for adsorption of plutonium onto the resin beads and elution of plutonium from the resin. Definitions of terms may be found in the Nomenclature at the end of this report.

Adsorption of Plutonium onto Resin Beads

As stated in the text, the controlling step in the adsorption of plutonium onto anionic resin beads is particle diffusion [12]. Particle diffusion is modeled using the ordinary Fick's law diffusion equation with a constant particle diffusion coefficient. With a constant diffusivity, Fick's law gives:

$$\frac{\partial f}{\partial t_p} = \frac{D_{\text{part}}}{r_p^2} \frac{\partial}{\partial r_p} \left(r_p^2 \frac{\partial f}{\partial r_p} \right) \quad (\text{A-1})$$

This equation is solved with the boundary conditions

$$f = f_{\text{feed}} \text{ at } r_p = R_p \quad (\text{A-2})$$

and f is finite at $r_p = 0$.

The initial condition is

$$f = 0 \text{ when } t_p = 0 \quad (\text{A-3})$$

An approximate solution to this diffusion problem is [14]:

$$\frac{t_p}{\tau_{\text{part}}} = -\ln \left(1 - \left[\frac{f}{f_{\text{feed}}} \right]^2 \right) \quad (\text{A-4})$$

where

$$\tau_{\text{part}} = \frac{d_p^2}{4\pi^2 D_{\text{part}}} \quad (\text{A-5})$$

The variable t_p represents the time needed for a single resin bead to adsorb a given amount of plutonium. The collective adsorption time for resin beads at a particular bed level, $\bar{t}_p$, is an average of these individual adsorption times, weighted by the adsorbed fraction f . The integral representation of this weighted average is:

$$\bar{t}_p = \frac{f_{\text{feed}}}{f} \int_{t_p=0}^{t_p} \frac{f}{f_{\text{feed}}} dt_p \quad (\text{A-6})$$

This integral is evaluated in terms of the fractional adsorption using integration by parts:

$$\bar{t}_p = t_p - \frac{f_{feed}}{f} \int_{\frac{f}{f_{feed}}=0}^{\frac{f}{f_{feed}}} t_p d \frac{f}{f_{feed}} \quad (A-7)$$

This integration gives

$$\frac{\bar{t}_p}{\tau_{part}} = \frac{f_{feed}}{f} \ln \left(\frac{f_{feed} + f}{f_{feed} - f} \right) - 2 \quad (A-8)$$

The time required for the loading calculation is the average time it takes for a level of the resin bed to adsorb plutonium. The calculation of this loading time is based on the stipulation that the loading profile is fully developed. If the resin beads are in continuous contact with the loading solution, then, for a fully-developed profile, the average adsorption time $\bar{t}_p$ and the loading time t' are related by the characteristic equation,

$$\bar{t}_p \Delta f = f \Delta t' \quad (A-9)$$

At the loading front, however, only a portion of the bulk solution is in saturated equilibrium with the adsorbed plutonium on the resin surfaces. The mixing of saturated and unsaturated solution occurs at a macroscopic rather than a molecular level, because axial dispersion predominates over molecular diffusivity. Consequently, this mixing can be modeled by assuming that the bulk flow is segregated into one fraction that contains dissolved plutonium and another that does not. Under this assumption, the actual loading time, t , and the loading time for continuous contact, t' , are related by

$$\Delta t' = \frac{x}{x_{feed}} \Delta t \quad (A-10)$$

Combination of Equations A-8 through A-10 yields the final expression for the loading mass transfer rate that appears in the overall mass balance.

$$G = \frac{df}{dt} = f_{feed} \frac{x}{x_{feed}} \frac{\left(\frac{f}{f_{feed}} \right)^2}{\ln \left(\frac{f_{feed} + f}{f_{feed} - f} \right) - 2 \frac{f}{f_{feed}}} \frac{1}{\tau_{part}} \quad (A-11)$$

For $f \rightarrow 0$,

$$G = f_{feed} \frac{x}{x_{feed}} \frac{1.5 f_{feed}}{f} \frac{1}{\tau_{part}} \quad (A-12)$$

Transient calculations demonstrate that the adsorbed concentration is approximately proportional to the bulk solution concentration. Then, as an approximation to check this derivation, Equation A-11 can be integrated and $\frac{x}{x_{feed}}$ can be set equal to $\frac{f}{f_{feed}}$ to obtain

$$\frac{t}{\tau_{part}} = \frac{f_{feed}^2}{f^2} \left\{ \left(1 - \frac{f}{f_{feed}} \right) \ln \left(1 - \frac{f}{f_{feed}} \right) - \left(1 + \frac{f}{f_{feed}} \right) \ln \left(1 + \frac{f}{f_{feed}} \right) \right\} + \frac{2f_{feed}}{f} \quad (A-13)$$

When the column is fully loaded ($f = f_{feed}$), this expression gives the mean loading time:

$$\frac{t}{\tau_{part}} = 2 - 2 \ln(2) = 0.614 \quad (A-14)$$

This result is the same as that derived in Ref. [14].

Elution of Plutonium from Resin Beads

As explained in the text, a shrinking core model describes the desorption of plutonium from the resin beads. The derivation of the desorption rate expression follows.

If the pore diffusivity is assumed to be constant, the pore diffusion equation becomes

$$\frac{\partial x_a}{\partial t_{p,a}} = \frac{D'_{pore}}{r_p^2} \frac{\partial}{\partial r_p} \left(r_p^2 \frac{\partial x_a}{\partial r_p} \right) \quad (A-15)$$

A pseudo-steady approximation is applied to eliminate time dependent terms:

$$\frac{d}{dr_p} \left(r_p^2 \frac{dx_a}{dr_p} \right) = 0 \quad (A-16)$$

The steady-state approximation is valid provided that the concentration of plutonium adsorbed on the surface is greater than the bulk concentration in a solution in saturated equilibrium with the adsorbed plutonium. Errors introduced by this approximation are accounted for later in this derivation.

Equation is solved with the boundary conditions

$$x_a = x_{max} \text{ at } r_p = R_{p,1} \quad (A-17)$$

$$\text{and } x_a = 0 \text{ at } r_p = R_p \quad (A-18)$$

The pseudo-steady-state solution is

$$x_a = x_{\max} \frac{R_{p,1}(R_p - r_p)}{r_p(R_p - R_{p,1})} \quad (\text{A-19})$$

This solution is useful only when expressed in terms of a fractional desorption. To convert this result to a useful form, a mass balance is applied to equate the shrinkage of the undissolved core region with the diffusion rate at the bead surface. This takes the form

$$4\pi R_p^2 D'_{\text{pore}} \left. \frac{dx_a}{dr_p} \right|_{r_p=R_p} = f_0 \frac{d}{dt_p} \left(\frac{4}{3} \pi R_{p,1}^3 \right) \quad (\text{A-20})$$

The initial condition for this equation is

$$R_{p,1} = R_p \text{ at } t_{p,a} = 0, \quad (\text{A-21})$$

and the final condition is

$$R_{p,1} = 0 \text{ at } t_{p,a} = \tau_{\text{pore}} \quad (\text{A-22})$$

The fractional desorption is defined by

$$\frac{f}{f_0} = \left(\frac{R_{p,1}}{R_p} \right)^3 \quad (\text{A-23})$$

Solution of Equations A-19 through A-23 yields the following expression for the rate of desorption during elution:

$$\frac{t_{p,a}}{\tau_{\text{pore}}} = 1 + 2 \frac{f}{f_0} - 3 \left(\frac{f}{f_0} \right)^{\frac{2}{3}} \quad (\text{A-24})$$

where

$$\tau_{\text{pore}} = \frac{d_p^2 f_0}{24 D'_{\text{pore}} x_{\max}} \quad (\text{A-25})$$

A modified pore diffusivity is defined to incorporate differences between the adsorbed solid and saturated solution concentrations of plutonium:

$$D_{\text{pore}} = \frac{D'_{\text{pore}} x_{\max}}{f_0} \quad (\text{A-26})$$

In terms of this modified diffusivity,

$$\tau_{\text{pore}} = \frac{d_p^2}{24\eta D_{\text{pore}}} \quad (\text{A-27})$$

An effectiveness factor was added to this equation to account for errors introduced by the pseudo-state-state approximation. To calculate this effectiveness factor, a computer code was written to solve Equation A-17 with boundary conditions given by Equations A-19 and A-20 and the initial condition

$$x = 0 \text{ when } t_{p,a} = 0 \quad (\text{A-28})$$

An effectiveness factor of 0.75 produced agreement between the exact solution and the pseudo-steady-state approximation, as shown by Figure A-1.

As in the previous derivation, the collective adsorption time for resin beads at a particular bed level, $\overline{t_{p,a}}$, is calculated as a weighted average of individual adsorption times, $t_{p,a}$, from the integral,

$$\overline{t_{p,a}} = \frac{f_0}{f} \int_{t_{p,a}=0}^{t_{p,a}} \frac{f}{f_0} dt_{p,a} \quad (\text{A-29})$$

This integral is evaluated using integration by parts:

$$\overline{t_{p,a}} = t_{p,a} - \frac{f_{\text{feed}}}{f} \int_{\frac{f}{f_{\text{feed}}}=0}^{\frac{f}{f_{\text{feed}}}} t_{p,a} d\frac{f}{f_{\text{feed}}} \quad (\text{A-30})$$

which gives

$$\frac{\overline{t_{p,a}}}{\tau_{\text{pore}}} = \frac{f}{f_0} - \frac{6}{5} \left(\frac{f}{f_0} \right)^{\frac{2}{3}} + \frac{f_0}{5f} \quad (\text{A-30})$$

The expression for the rate of desorption is obtained by differentiating Equation A-30. This gives

$$\frac{1}{f_0} \frac{df}{dt_{p,a}} = \frac{1}{\tau_{\text{pore}} \left\{ 1 - \frac{4}{5} \sqrt[3]{\frac{f_0}{f}} - \frac{1}{5} \left(\frac{f_0}{f} \right)^2 \right\}} \quad (\text{A-31})$$

Equation A-31 gives the collective rate of desorption for resin beads continuously in contact with a bulk solution of 0.25 M elution acid that does not contain plutonium.

Correction factors must be added to account for variations in acid and plutonium concentrations in the bulk solution.

To derive a correction factor for acid concentration, it is assumed that during desorption the bulk flow is segregated into one fraction, c , that contains dilute (0.25 M) elution acid and another, $1 - c$, that contains wash (8.0 M) acid. This implies that changes in the collective desorption time and the elapsed time are related by

$$\Delta t_{p,a} = c \Delta t \quad (A-32)$$

To correct Equation A-31 for the plutonium concentration gradient, the average plutonium concentration in the pores at the resin bead surface, $\bar{y}$, must be calculated. This concentration is obtained from a quasi-equilibrium relation, in which the rate of diffusion of plutonium to the bulk solution varies about a mean of zero. To derive this relation, it is assumed that the elution acid is poorly mixed in the bulk solution, so that it

segregates into a fraction $\frac{x}{x_{\max}}$ that is in saturated equilibrium with the adsorbed

plutonium and a fraction $c - \frac{x}{x_{\max}}$ that contains no plutonium. It follows that, if the diffusion resistance of the bulk solution is negligible, plutonium diffuses into the resin bead from a saturated bulk solution a fraction of time $\frac{x}{x_{\max}}$ and diffuses from the resin

bead into elution acid that contains no plutonium a fraction of time $c - \frac{x}{x_{\max}}$. The quasi-equilibrium relation is obtained by integrating the transient diffusion equation. Such an integration shows that the mass transfer is proportional to the concentration difference and the square root of the contact time. In this instance, then,

$$(x_{\max} - \bar{y}) \sqrt{\frac{x}{x_{\max}}} - \bar{y} \sqrt{c - \frac{x}{x_{\max}}} = 0 \quad (A-33)$$

Solution of this equation gives the concentration gradient correction factor,

$$1 - \frac{\bar{y}}{x_{\max}} = 1 - \frac{\frac{x^2}{x_{\max}^2} - \frac{x}{x_{\max}} \sqrt{\frac{cx}{x_{\max}} - \frac{x^2}{x_{\max}^2}}}{2 \frac{x}{x_{\max}} - c} \quad (A-34)$$

The mass transfer rate for desorption, including the correction factors for the acid concentration and the plutonium concentration gradient, is

$$G_a = - \left(1 - \frac{\bar{y}}{x_{\max}} \right) \frac{df}{dt_{p,a}} \frac{dt_{p,a}}{dt} \quad (A-35)$$

Combination of Equations A-31, A-32, A-34, and A-35 yields the mass transfer expression that appears in the elution mass balance:

$$G_a = \frac{-cf_0 \left(1 - \frac{\frac{x^2}{x_{\max}^2} - \frac{x}{x_{\max}} \sqrt{\frac{cx}{x_{\max}} - \frac{x^2}{x_{\max}^2}}}{2 \frac{x}{x_{\max}} - c} \right)}{\tau_{\text{pore}} \left\{ 1 - \frac{4}{5} \sqrt{\frac{f_0}{f}} - \frac{1}{5} \left(\frac{f_0}{f} \right)^2 \right\}} \quad (\text{A-36})$$

As $2 \frac{x}{x_{\max}} \rightarrow c$,

$$G_a = \frac{-cf_0 \left(1 - \frac{c}{4} \right)}{\tau_{\text{pore}} \left\{ 1 - \frac{4}{5} \sqrt{\frac{f_0}{f}} - \frac{1}{5} \left(\frac{f_0}{f} \right)^2 \right\}} \quad (\text{A-37})$$

Interchange of Plutonium between Bulk Solution and Resin Bead Pores during Elution

The desorption model does not account for diffusion of plutonium into and out of the resin bead pores as the elution concentration spike travels down the column. The diffusion equation for this interchange is based on the approximate solution for particle diffusion in a sphere [12], which uses a quadratic concentration gradient. Similarly, pore diffusion between the bulk and pore solutions is modeled with quadratic gradients. Based on a previous argument that the bulk solution is poorly mixed at the molecular level, it is assumed that the bulk solution is segregated into one volume fraction in which the plutonium concentration is in saturated equilibrium with the adsorbed plutonium and another that does not contain any plutonium. The net diffusion for such a segregated mixture can be expressed by

$$\frac{1}{\epsilon_{i,2}^2} \frac{dy^2}{dt_{p,b}} = \frac{1 - \epsilon_o}{\epsilon_{i,2}} \frac{4\pi^2 D_{\text{pore}}}{d_p^2} \left\{ \frac{x}{x_{\max}} \left(\left[\frac{x_{\max}}{\epsilon_o} \right]^2 - \left[\frac{y}{\epsilon_{i,2}} \right]^2 \right) - \left(1 - \frac{x}{x_{\max}} \right) \left[\frac{y}{\epsilon_{i,2}} \right]^2 \right\} \quad (\text{A-38})$$

This simplifies to

$$\frac{1}{\epsilon_{i,2}^2} \frac{dy^2}{dt_{p,b}} = \frac{1 - \epsilon_o}{\epsilon_{i,2}} \frac{4\pi^2 D_{\text{pore}}}{d_p^2} \left(\frac{x_{\max} x}{\epsilon_o^2} - \frac{y^2}{\epsilon_{i,2}^2} \right) \quad (\text{A-39})$$

where the pore liquid concentration is based on the volume fraction in the pores of the eluted portion of the resin beads, $\epsilon_{i,2}$. The factor $\frac{1-\epsilon_o}{\epsilon_{i,2}}$ appears because the pore plutonium concentration is normalized with respect to the pore volume, whereas the pore diffusivity applies to the entire resin bead volume.

The eluted pore volume fraction is related to the pore volume in a completely eluted bead, $\epsilon_{i,2,0}$, by

$$\epsilon_{i,2} = \left(1 - \frac{f}{f_0}\right) \epsilon_{i,2,0} \quad (A-40)$$

The initial loading has been used in place of the full equilibrium loading in this calculation, because it gives the correct initial condition: i. e., the eluted pore volume fraction must be zero at the beginning of the elution.

Time variations of the eluted pore volume fraction have been neglected in Equation A-39. This simplification does not introduce significant errors, since the rate of desorption is slower than the rate of interdiffusion of plutonium between the pores and the bulk liquid.

As in the two previous derivations, the collective adsorption time for resin beads at a particular bed level, $\overline{t_{p,b}}$, is calculated as a weighted average of individual adsorption times, $t_{p,b}$, from the integral,

$$\overline{t_{p,b}} = \frac{f_0}{f} \int_{t_{p,b}=0}^{t_{p,b}} \frac{f}{f_0} dt_{p,b} \quad (A-41)$$

This integral is evaluated using integration by parts:

$$\overline{t_{p,b}} = t_{p,b} - \frac{f_{feed}}{f} \int_{\frac{f}{f_{feed}}=0}^{\frac{f}{f_{feed}}} t_{p,b} d\frac{f}{f_{feed}} \quad (A-42)$$

which gives

$$\overline{t_{p,b}} = \frac{d_p^2}{4\pi^2 D_{pore} \epsilon_{i,2} (1-\epsilon_o)} \left\{ \frac{\epsilon_{i,2} \sqrt{x_{max} x}}{\epsilon_o y} \ln \left(\frac{\frac{\sqrt{x_{max} x}}{\epsilon_o} + \frac{y}{\epsilon_{i,2}}}{\frac{\sqrt{x_{max} x}}{\epsilon_o} - \frac{y}{\epsilon_{i,2}}} \right) - 2 \right\} \quad (A-43)$$

The expression for the rate of desorption is obtained by differentiating Equation A-43 to get

$$\frac{dy}{dt_b} = \frac{4\pi^2 D_{\text{pore}} (1 - \epsilon_o)}{d_p^2} \frac{\frac{y^2}{\epsilon_{i,2}^2} \left(\frac{x_{\text{max}} x}{\epsilon_o^2} - \frac{y^2}{\epsilon_{i,2}^2} \right)}{2 \frac{x_{\text{max}} xy}{\epsilon_o^2 \epsilon_{i,2}} - \frac{\sqrt{x_{\text{max}} x}}{\epsilon_o} \left(\frac{x_{\text{max}} x}{\epsilon_o^2} - \frac{y^2}{\epsilon_{i,2}^2} \right) \ln \left(\frac{\frac{\sqrt{x_{\text{max}} x}}{\epsilon_o} + \frac{y}{\epsilon_{i,2}}}{\frac{\sqrt{x_{\text{max}} x}}{\epsilon_o} - \frac{y}{\epsilon_{i,2}}} \right)} \quad (\text{A-44})$$

As in the previous two models, the mass transfer rate is expressed in terms of the actual elapsed time, so that

$$G_b = \frac{dy}{dt_{p,b}} \frac{dt_{p,b}}{dt} \quad (\text{A-45})$$

In this case, changes in the time for diffusion interchange equal changes in the actual elapsed time:

$$\Delta t_{p,b} = \Delta t \quad (\text{A-46})$$

so that

$$G_b = \frac{4\pi^2 D_{\text{pore}} (1 - \epsilon_o)}{d_p^2} \frac{\frac{y^2}{\epsilon_{i,2}^2} \left(\frac{x_{\text{max}} x}{\epsilon_o^2} - \frac{y^2}{\epsilon_{i,2}^2} \right)}{2 \frac{x_{\text{max}} xy}{\epsilon_o^2 \epsilon_{i,2}} - \frac{\sqrt{x_{\text{max}} x}}{\epsilon_o} \left(\frac{x_{\text{max}} x}{\epsilon_o^2} - \frac{y^2}{\epsilon_{i,2}^2} \right) \ln \left(\frac{\frac{\sqrt{x_{\text{max}} x}}{\epsilon_o} + \frac{y}{\epsilon_{i,2}}}{\frac{\sqrt{x_{\text{max}} x}}{\epsilon_o} - \frac{y}{\epsilon_{i,2}}} \right)} \quad (\text{A-47})$$

As $\frac{y}{\epsilon_{i,2}} \rightarrow \frac{\sqrt{x_{\text{max}} x}}{\epsilon_o}$, this reduces to

$$G_b = \frac{4\pi^2 D_{\text{pore}} (1 - \epsilon_o)}{d_p^2} \left(\frac{\sqrt{x_{\text{max}} x}}{\epsilon_o} - \frac{y}{\epsilon_{i,2}} \right) \quad (\text{A-48})$$

Nomenclature

Variable	Definition
C_{Pu}	total plutonium concentration adsorbed on the resin, in resin pores, and in the bulk solution, g/cm^3
c	normalized concentration of elution (0.25 M) acid, dimensionless
c_p	solution heat capacity, $cal/g^{\circ}C$
$c_{p,mix}$	bulk heat capacity for the resin bed, $cal/g^{\circ}C$
D	axial dispersion coefficient, cm^2/sec
D_{part}	particle diffusivity for diffusion of Pu in the resin bead, cm^2/sec
D_{pore}	bulk pore diffusivity for diffusion of Pu in the resin bead, normalized to account for differences between solid and solution concentrations, cm^2/sec
D'_{pore}	bulk pore diffusivity for diffusion of Pu in the resin bead, cm^2/sec
d_p	average resin bead diameter, cm
E_a	activation energy for the reaction between the resin and nitric acid, $cal/gmole$
f	bulk concentration of plutonium adsorbed onto the resin, g/cm^3
f_{feed}	bulk concentration of plutonium adsorbed onto the resin when the resin is fully loaded, g/cm^3
f_0	bulk concentration of plutonium adsorbed onto the resin at the end of the decon wash, g/cm^3
G	during loading, bulk rate of transfer of plutonium from bulk solution to the resin, $g/cm^3/sec$
G_a	during elution, bulk rate of transfer of plutonium from the resin to the bulk solution due to desorption, $g/cm^3/sec$
G_b	during elution, bulk rate of diffusion of plutonium from the bulk solution to the resin pore solution, $g/cm^3/sec$
g	gravitational acceleration, cm/sec^2
h	heat transfer coefficient for natural convection from the column wall to ambient air, $cal/sqcm/sec/^{\circ}C$
K_{rxn}	coefficient in the expression for the heat of reaction between the resin and nitric acid, $cal/cm^3/sec$
K_1	equilibrium constant for the solubility of plutonium from nitric acid solutions on Ionac 641 resin, $(gmole/L)^4$
K_2	constant governing the equilibrium of plutonium ionic species in nitric acid solutions, $L/gmole$
k_{mix}	bulk thermal conductivity for the resin bed, $cal/cm/sec/^{\circ}C$
L	resin bed length, cm
q_{rad}	heat of reaction for the plutonium radiolysis reaction, $cal/gm/sec$
R	column radius, cm

R_g	gas law constant, cal/gmole/°K
R_L	radial location at the bottom of the column where the axial velocity due to natural convection is zero, cm
R_p	average resin bead radius, cm
$R_{p,1}$	during elution, radius of the undesorbed core of resin bead, cm
R_0	radial location at the top of the column where the axial velocity due to natural convection is zero, cm
r	radial distance from the center of the column, cm
r_p	radial distance from the center of the resin bead, cm
T	bulk temperature, °C
T_{amb}	ambient temperature of the air outside the column, °C
T_{in}	column inlet temperature for natural convection during a flow interruption, °C
T_r	relative temperature for the calculation of the solution viscosity, dimensionless
t	time for heat transfer and mass transfer to bulk solution, sec
t'	characteristic time for adsorption with continuous contact between the loading solution and the resin bead surfaces, sec
t_p	time for adsorption within a resin bead, sec
$\frac{t_p}{t_p}$	average residence time for adsorption at a given axial level, sec
$\frac{t_{p,a}}{t_{p,a}}$	time for desorption within a resin bead, sec
$\frac{t_{p,a}}{t_{p,a}}$	average residence time for desorption at a given axial level, sec
$t_{p,b}$	time for interchange between the bulk solution and resin bead pores, sec
$\frac{t_{p,b}}{t_{p,b}}$	average residence time for interchange between the bulk solution and resin bead pores at a given axial level, sec
v_r	superficial radial velocity in the column, cm/sec
v_z	superficial axial velocity going from the top to the bottom of the column, cm/sec
x	during loading and the decon wash, bulk concentration of plutonium in the bulk solution, g/cm ³
x_a	during desorption, local concentration of plutonium in the resin bead pores, g/cm ³
x_{feed}	concentration of plutonium in the feed solution, g/cm ³
y	during elution, bulk concentration of plutonium in the resin bead pores due to diffusion from the bulk solution, g/cm ³
$\bar{y}$	during desorption, concentration of plutonium in the pores at the resin bead surface, g/cm ³
z	axial distance from the top of the resin bed, cm
$\epsilon_{i,1}$	fraction of the total resin bed volume occupied

	by the resin bead pores before desorption of plutonium, dimensionless
$\epsilon_{i,2}$	fraction of the total resin bed volume occupied by the resin bead pores after desorption of plutonium, dimensionless
$\epsilon_{i,2,0}$	fraction of the total resin bed volume occupied by the resin bead pores after all plutonium has desorbed, dimensionless
ϵ_o	fraction of the total resin bed volume occupied by the bulk solution, dimensionless
η	factor to account for the difference between the pseudo-steady-state shrinking core approximation and the exact shrinking core model solution for the total desorption time, dimensionless
μ	solution dynamic viscosity, g/cm/sec
ρ	solution density, g/cm ³
$\bar{\rho}$	average solution density at a given axial level, g/cm ³
ρ_{H_2O}	density of water, g/cm ³
ρ_{mix}	bulk density of the resin bed, g/cm ³
$\Delta\rho_{HNO_3}$	change in density due to nitric acid in solution, g/cm ³
$\Delta\rho_{Pu(NO_3)_4}$	change in density due to plutonium ionic species in solution, g/cm ³
τ_{part}	time for a resin bead to become fully loaded with plutonium due to particle diffusion, sec
τ_{pore}	time for complete desorption of a resin bead by pore diffusion, sec

Figure A-1. Comparison of the Shrinking Core Approximation with the Transient Solution for Removal of Plutonium from a Resin Bead

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