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Processing of Plutonium by Ion Exchange VII.
Plutonium(IV) Desorption Kinetics
from Dowex 1x4 into Nitric Acid Solutions

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**Processing of Plutonium by Ion Exchange VII.
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by

D. B. James

ABSTRACT

The experimental desorption of uniformly-sorbed plutonium(IV) into nitric acid solutions from Dowex 1x4 anion-exchange resin is duplicated by the theory for diffusion in spheres with a constant diffusion coefficient. For the various experiments the diffusion coefficient increases with increasing temperature, decreasing nitric acid in the aqueous phase, and decreasing initial level of plutonium sorption. Desorption into an aqueous phase of less than 0.6M nitric acid, even in the presence of hydroxylamine nitrate, causes the formation of "insoluble" plutonium polymer in the resin phase, and the desorption rate is controlled by the slow rate of polymer "dissolution." One experimental desorption, with the nonuniform initial sorption that results from a short sorption time, indicates that such systems are not duplicated by the simple theory.

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INTRODUCTION

A previous paper in this series¹ dealt with the kinetics of the sorption of plutonium(IV) by the nitrate form of Dowex 1x4 anion-exchange resin from nitrate solutions. It was demonstrated that the particle-diffusion controlled reaction is described by an apparent average diffusion coefficient which decreases exponentially with increasing plutonium concentration. These kinetic results and previously reported² equilibrium parameters were used to duplicate a plant-scale column sorption, and allowed computer optimization of process design.

The work described in this report was conducted in an effort to provide sufficient kinetic data for the desorption process to extend the computer calculations to column washing and stripping cycles.

Fick's law for radial diffusion into spheres is described by

$$\frac{dx(r,t)}{dt} = \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \bar{D}(r,x) \frac{\partial x}{\partial r} \quad (1)$$

where, $x(r,t)$ is the local intraparticle concentration of plutonium, t is time, r is the radial dimension, and $\bar{D}(r,x)$ is the local intraparticle diffusion coefficient. For the case of a diffusion coefficient which is independent of r and with the surface of the bead always at equilibrium, Equation (1) may be integrated throughout the bead to obtain³

$$Y = \frac{\bar{x}^o - \bar{x}}{\bar{x}^o - \bar{x}^*} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp \left(- \frac{\bar{D}t\pi^2 n^2}{R^2} \right), \quad (2)$$

where

Y is the fractional attainment of equilibrium,

$\bar{x}$ is the average concentration of plutonium in the resin phase at time t ,

$\bar{x}^0$ is the initial average concentration in the resin,

$\bar{x}^*$ is the concentration of plutonium in the resin phase when equilibrium is reached,

and

R is the radius of the resin particles.

Values of Y for various values of $\tau = \bar{D}t/R^2$ are tabulated in reference 4 and are shown in Fig. 1.

Of course $\bar{D}$ can be expected to be truly constant only for isotopic or trace exchange systems. The exchange of unlike ions requires equal equivalent fluxes to preserve electrical neutrality. Any excessive charge transfer by a more mobile ion generates a space charge which decreases its mobility. This effect is discussed in reference 5 where it is pointed out that in systems with a large amount of co-ion sorption these electrical effects are greatly reduced.

The sorption of plutonium(IV) from nitric acid solutions is more like solvent extraction than like ion exchange in the usual sense of a Donnan equilibrium. In systems with an aqueous nitric acid concentration greater than several molar, there is considerable penetration of nitric acid into the resin phase. Consequently, there is little "exchange" of nitrate ions with the sorption of plutonium(IV), and the sorption-desorption reaction may be written as

where Z is the resin exchange site.

For this reason the disagreement between sorption data and Equation (2) as described in reference 1 was attributed to changes in the resin composition during sorption, and not to electric field effects.

Fig. 1. Diffusion in Spherical Particles with a Constant Diffusion Coefficient.

Similarly, deviations from Equation (2) during desorption (washing) may be due to resin composition changes.

Of equal interest is desorption into dilute nitric acid (stripping). Resin that has been previously loaded with plutonium from a concentrated nitric acid solution is contacted with a dilute aqueous solution. The nitric acid within the resin phase is rapidly expelled, causing the sorbed plutonium to assume a neutral, or cationic, form. The kinetic problem is again not ion exchange, but simple diffusion in one direction. At least to a first approximation, Equation (2) might be expected to apply.

EXPERIMENTAL

Reagents: The resin used was Dowex 1x4, 100-200 mesh, nitrate form. Its equivalent capacity and range of particle radii have been measured before.¹ The impurities in the plutonium used were less than 100 ppm.

Measurement of λ_0 : The equilibrium, trace-sorption distribution coefficient,

$$\lambda_0 = \frac{\text{amount Pu/g dry resin}}{\text{amount Pu/ml of solution}}, \quad (4)$$

was measured as described before.²

Kinetic Batch Desorption Experiments: In each experiment, 1 gram of "oven-dry" resin was used. Except where specifically noted, this resin was contacted with a 7M HNO₃ solution of appropriate plutonium concentration for sufficient time (several days) to insure a nearly uniform distribution of plutonium within the resin beads. From the initial and final aqueous plutonium concentration $\bar{x}^0$ was calculated. The beads were separated by vacuum filtration, washed free of plutonium solution with a very small volume of 7M nitric acid, and dried by drawing air over them for several hours. The air-dried beads were added to 1 liter of the appropriate nitric acid solution at the

beginning of the experiment. A coarse frit at the end of a small tube allowed 1-ml samples of the aqueous phase to be withdrawn in about 10 seconds at timed intervals. The radiochemical analytical technique has been described before.²

RESULTS AND CONCLUSIONS

To permit calculation of $\bar{x}^*$ in Equation 2, λ_0 was measured in several dilute nitric acid solutions. These results are given by the squares in Fig. 2. The dark circles are data from reference 1, and the open circles are data from reference 6. With less than 5M nitric acid the decrease in λ_0 with decreasing concentration of nitric acid is due to the decrease in the amount of nitrate ion that is available for the sorbable hexanitrate complex. Therefore, the curvature with the more dilute solutions is unexpected. Ryan and Wheelwright⁷ attribute incomplete elution of plutonium from anion-exchange columns by dilute nitric acid solutions to hydrolysis of the plutonium within the resin phase. Certainly as the hydronium ion concentration in the aqueous phase is decreased, the average charge of the plutonium(IV) species must also decrease, and probably to a greater extent in the resin phase with its lower dielectric constant and Donnan exclusion of the hydronium ion. Whether the decreased slope of the curve in Fig. 2 is due to a preference of the resin for some anionic hydrolysis product or to the preferential formation of an "insoluble" hydrated polymer in the resin phase cannot be resolved with equilibrium data alone.

As shown in Fig. 2, λ_0 reaches a maximum with increasing nitric acid concentration at about 7.2M. This led Ryan and Wheelwright⁷ to suggest 7.2M nitric acid as the "optimum" solvent for plutonium processing. While it has been demonstrated¹ that lower concentrations may give higher column capacities because of more favorable kinetics, the kinetics of desorption into 7M nitric acid were studied because this solvent is commonly used as a washing solution.

Fig. 2. Trace-Loading Distribution Coefficients from Nitric Acid.

It has been verified previously² that for the case of sorption from 7M HNO₃, the equilibrium degree of sorption of plutonium(IV) for various aqueous concentrations of plutonium follows a simple mass-action treatment, which assumes a constant exchange quotient and constant activity coefficient ratios between phases. The isotherm takes the form

$$\bar{x}^* = \bar{x}_m \left[1 + U - \sqrt{U(U+2)} \right], \quad (5)$$

$$U = \frac{\bar{x}_m}{2C_{Pu}\lambda_0} \quad (6)$$

over the entire range of resin loading, $0 < \bar{x}^*/\bar{x}_m < 1$. In these equations

$\bar{x}_m$ is the maximum concentration of plutonium in the resin phase (half the equivalent capacity for anions)

and

C_{Pu} is the total molar concentration of plutonium in the aqueous phase.

Equations (5) and (6) were assumed to hold for all aqueous concentrations of nitric acid.

In the desorption experiments C_{Pu} was measured at various times. For each experiment a value of λ_0 was taken from Fig. 2. Then $\bar{x}^*$ was determined at each sampling time. After $\bar{x}^0 - \bar{x}$ was calculated from C_{Pu} , Y was calculated according to Equation (2). The results of these calculations for four desorption experiments into 7M nitric acid are shown in Fig. 3 and described in Table 1. The curves are a best fit of the theory shown in Fig. 1 for the values of $\bar{D}$ shown in Table 1. The three results at 23°C are linear with respect to $\bar{x}^0/\bar{x}_m$, indicating that for $0 < \bar{x}^0/\bar{x}_m < 0.6$,

$$\bar{D} \times 10^{10} = 6.82 - 11.1 \bar{x}^0/\bar{x}_m. \quad (7)$$

Fig. 3. Desorption into 7M Nitric Acid.

Table 1
Desorption into 7M Nitric Acid Solutions

Data Points, Fig. 3	$\frac{\bar{x}^0}{\bar{x}_m}$	T (°C)	$\bar{D} \times 10^{10}$ (cm ² /sec)
0	0.586	23	0.19
●	0.421	23	2.11
□	0.025	23	6.52
■	0.691	60	6.92

The first and last results in Table 1 yield a diffusional activation energy of about 20 kcal/mole which is near what one might expect for solid-state diffusion.

The results of six desorption experiments in different molarities of nitric acid are shown in Fig. 4 and described in Table 2. The correction for varying $\bar{x}^*$ was significant only for the experiments with 2M and 7M nitric acid.

Table 2
Desorption into Nitric Acid Solutions

Data Points, Fig. 4	$\frac{\bar{x}^0}{\bar{x}_m}$	C _{HNO₃} (M)	$\bar{D} \times 10^{10}$ (cm ² /sec)
0	0.586	7.00	0.19
●	0.792	2.00	2.78
□	0.792	0.90	12.6
■	0.785	0.60	18.9
△	0.814	0.45	28.7
▲	0.779	0.30	--

Fig. 4. Desorption into Nitric Acid Solutions.

The increase of $\bar{D}$ with decreasing nitric acid concentration is reasonable, but a value for $1M$ of about 1×10^{-9} , interpolated from Table 2, is an entire order of magnitude lower than that reported by Ryan and Wheelwright.⁷

Data and theory begin to disagree for the 0.45M experiment when Y is about 0.9, and the data for the 0.30M experiment cannot be made to fit any theoretical curve. As suggested by the distribution coefficient data this may be due to the formation of "insoluble" polymer in the resin phase. If it were due to the formation of a less mobile but soluble hydroxyl species, then the data for the 0.30M experiment should fit the theory with a smaller $\bar{D}$. Possibly the Donnan exclusion principle reduces the hydronium ion concentration in the resin phase to a level low enough that polymer formation occurs when the aqueous concentration is below 0.60M. As soon as the beads contact the dilute solution both hydronium and nitrate ions are expelled from the resin. Cationic species of plutonium are formed. These species are also expelled by the resin phase, but probably much more slowly than hydronium and nitrate ions. Some plutonium escapes before the hydronium ions in the resin phase are exhausted, but a portion of the plutonium is trapped as "precipitated" polymer. As plutonium precipitates in the resin phase, the cationic plutonium concentration drops to the solubility limit. However, any fraction of the plutonium that is soluble is continuously expelled from the resin phase. If the polymer dissolution rate is slower than the plutonium diffusion rate, the dissolution of polymer will now control the rate of plutonium desorption.

Elution of plutonium from anion-exchange columns by reduction with hydroxylamine nitrate has been used at Chalk River⁸ and is presently used in this Laboratory. The results of three experiments using hydroxylamine nitrate and the more dilute nitric acid experiments are shown in Fig. 5 and are summarized in Table 3. $\log (1-Y)$ versus time is plotted.

Fig. 5. Desorption into Dilute Solutions.

Table 3
Desorption into Dilute Solutions

Data Points, Fig. 5	$\frac{\bar{x}^0}{\bar{x}_m}$	Composition of Desorption Solution
▲	0.779	0.30M HNO ₃
△	0.814	0.45M HNO ₃
●	0.614	0.44M NH ₂ OH·HNO ₃
○	0.741	0.60M NH ₂ OH·HNO ₃
□	0.888	0.30M NH ₂ OH·HNO ₃ + 0.60M HNO ₃
■	0.785	0.60M HNO ₃

The desorption of the polymer is linear with nearly the same slope for the first four experiments which contain less than 0.60M nitric acid. This may indicate that a first-order dissolution reaction is rate controlling. Since NH₂⁺ is also excluded from the resin, the 0.6M nitric acid experiment with hydroxylamine nitrate shows virtually the same desorption rate as the 0.6M nitric acid experiment without hydroxylamine nitrate.

Diffusion coefficients as a function of initial resin loading for 0.6M nitric acid are shown in Fig. 6. The dark squares are data taken at 23°C, the open squares are data taken at 60°C, and the diamond is a datum at 40°C. A log diffusion coefficient versus reciprocal temperature treatment of these data gives a diffusional activation energy of 9.6 kcal/mole.

All of the kinetic experiments described in Tables 1, 2, and 3 used plutonium-loaded resin which had been previously equilibrated with a 7M nitric acid solution of plutonium long enough to insure that the plutonium concentration within the resin beads was very nearly uniform.¹ One desorption experiment was conducted using resin which had been pre-equilibrated for only one hour. The desorption experiment was commenced 20 minutes after the sorption solution was separated. The results are shown in Fig. 7.

Fig. 6. Diffusion Coefficients for Desorption into 0.6M Nitric Acid Solutions.

Fig. 7. Desorption with Nonuniform Initial Loading.

Reference 1 showed that the kinetic data for sorption agree reasonably well with a computer solution of Equation (1) using $\bar{D}(r,x) = \bar{D}(r,0) (1 - x/\bar{x}_m)$. The solid lines in Fig. 8 are concentration profiles calculated with these assumptions. The dashed line is an estimation of the concentration profile at the time desorption was initiated in the experiment described above.

During the first few minutes of the experiment, plutonium near the surface was moving outward while plutonium in the interior was still moving inward. The data in Fig. 7 cannot be made to fit the theory of Fig. 1 for any value of $\bar{D}$. The first two points seem to fit a curve (solid line) for $\bar{D} = 1.62 \times 10^{-8}$ cm²/sec, but the plutonium is completely removed at a time indicating $\bar{D} = 7.12 \times 10^{-9}$ cm²/sec (dashed line). The initial diffusion coefficient is in reasonable agreement with the value reported by Ryan and Wheelwright.⁷

The desorption diffusion coefficient appears to be strongly dependent upon the intraparticle plutonium concentration. Only for the case of a uniform concentration throughout the beads do the data agree with simple spherical diffusion-theory. The sorption step in conventional plutonium processing equipment is usually of sufficiently short duration that the major portion of the resin does not reach equilibrium. Therefore, when wash or elution cycles are initiated, plutonium concentration profiles (see Fig. 8) are present within the beads. The diffusion-coefficient data presented in this report can be of only qualitative significance in the estimation of equipment performance since these data were determined with a uniform initial plutonium concentration.

The one desorption experiment using nonequilibrium resin indicates that the desorption rate is a strong function of this condition. Apparently the local, intraparticle diffusion coefficient in Equation (1) is dependent upon the local, intraparticle plutonium concentration, $x(r,t)$, for both sorption and desorption processes. It seems hopeless

Fig. 8. Intraparticle Concentration Profiles during Plutonium Sorption.

to attempt to empirically correlate sorption and desorption data. Possibly isotopic diffusion studies or plutonium migration studies on the resin phase alone could yield a diffusion theory which would provide a mathematical description of the interdependence of diffusion coefficient and plutonium concentration. Then Equation (1) could be integrated numerically with any time-dependent boundary condition (aqueous plutonium and nitric acid concentration). This could then be coupled with a numerical integration of the partial differential equations which describe the processing equipment to calculate performance. Only with such an experimentally verified diffusional model could numerical optimization of the design of sorption-desorption cycles be trusted.

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