APR 15 1964

81691

LADC-6297

PROCESSING OF PLUTONIUM BY ION EXCHANGE, III
KINETIC AND EQUILIBRIUM PARAMETERS
FOR THE CALCULATION OF FIXED-BED COLUMN PERFORMANCE*

by

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ABSTRACT

Parameters and equations are presented which allow the numerical duplication of the sorption of plutonium on nitrate-form Dowex 1x4 from 7M nitric acid. A mass-action description of the two-phase equilibria and an empirical expression for the sorption rate are coupled with the fundamental partial differential equation which describes the operation of a fixed-bed ion-exchange column to produce a system that is only numerically solvable. The calculation and experiment are in good agreement.

The sorption of plutonium by strong-base anion-exchange resin from strong nitrate solution is an excellent purification method since only a few other elements are sorbed to any significant degree. Ryan and Wheelwright⁽¹⁾ studied some of the kinetic and equilibrium parameters of the system and showed that 7M nitric acid is a satisfactory solvent.

Ryan⁽²⁾ demonstrated that plutonium (IV) is sorbed on nitrate-form Dowex 1 x 4 from 7M nitric acid as $\text{Pu}(\text{NO}_3)_6^{-2}$. The equilibrium of this exchange was shown by James⁽³⁾ to be described by a selectivity coefficient,

$$K_{\text{NO}_3}^{\text{Pu}} = \frac{\bar{x}_{\text{Pu}}^* (c_{\text{NO}_3})^2}{c_{\text{Pu}} (\bar{x}_{\text{NO}_3}^*)^2} \quad (1)$$

where $\bar{x}_{\text{Pu}}^*$ and $\bar{x}_{\text{NO}_3}^*$ are the equilibrium concentrations of $\text{Pu}(\text{NO}_3)_6^{-2}$ and NO_3^- respectively in moles per liter of resin bed and c_{Pu} and c_{NO_3} are aqueous concentrations of these species in moles per liter of solution. In 7M nitric acid this coefficient is constant over the entire range of resin loading. With 28.4 percent of the plutonium as the hexanitrate complex in 7M nitric acid⁽²⁾, the value of $K_{\text{NO}_3}^{\text{Pu}}$ is $(4.6 \pm 1.0) \times 10^4$ ⁽³⁾.

Ryan and Wheelwright⁽¹⁾ demonstrated that the sorption of plutonium (IV) by Dowex 1x4 from 7M nitric acid is very slow, controlled by diffusion within the resin particle, and governed by an apparent diffusion coefficient which decreases with increasing degree of resin loading. They suggested that this may be due to a physical blocking of the passageways by the large hexanitrate complex.

EXPERIMENTAL

Reagents: The resin used was Dowex 1 x 4 (100 - 200 mesh) NO_3^- . It was converted from the chloride to the nitrate form and its equivalent capacity for anions determined as described before.⁽³⁾ The nitrate form contained 3.8 milliequivalents per oven-dry gram or about 1.5 milliequivalents per milliliter of resin bed in contact with 7M nitric acid. The impurities in the plutonium used were less than 0.01 weight percent, except for 2.6 percent iron, 0.20 percent uranium, 0.47 percent americium and 0.02 percent aluminum.

Batch Equilibration Experiments: The rate of sorption of plutonium (IV) was followed in a round, four-liter flask with the two phases being rapidly stirred mechanically. A coarse frit at the end of a small tube allowed one milliliter samples to be withdrawn in about ten seconds at a minimum of 100-second intervals.

A weighed amount of oven-dry resin, equilibrated with 7M nitric acid, and filtered "dry" with vacuum was contacted with a 7M nitric acid solution of measured volume and plutonium (IV) concentration at time zero. The mixing time was less than thirty seconds.

The first experiment used 175.0 grams of resin (438 ml) and 2.00 liters of 7M nitric acid, containing 47.6 g Pu/l. The second experiment used 200.0 grams of resin (500 ml) and 1.00 liter of 7M nitric acid, containing 17.3 g Pu/l.

Column Experiment: A 7M nitric acid solution, containing 17.3 g Pu/l, was passed over a column with an inside diameter of 2.20 cm at a flow rate of 6.1 ml/min. The column contained 22.0 grams of oven-dry, nitrate-form resin.

RESULTS AND CONCLUSIONS

The fundamental partial differential equation which describes the sorption of plutonium on a fixed-bed ion-exchange column is

$$\epsilon \frac{\partial c_{\text{Pu}}}{\partial t} + v \frac{\partial c_{\text{Pu}}}{\partial z} = - \frac{\partial \bar{x}_{\text{Pu}}}{\partial t}, \quad (2)$$

where

$\bar{x}_{\text{Pu}}$ = non-equilibrium concentration of plutonium in the resin

phase in moles per liter of resin bed,

t = time in seconds,

v = flow rate in milliliters per second per square centimeter

of column cross section, and

ϵ = fractional interstitial void space about the resin beads.

The exact solution to Ficks law for diffusion into a spherical particle with a constant diffusion coefficient involves an infinite summation. A sufficiently accurate approximation to this solution⁽⁴⁾ is

$$\frac{\partial \bar{x}_{\text{Pu}}}{\partial t} = \frac{\pi^2 D}{2r^2} \frac{(\bar{x}_{\text{Pu}}^*)^2 - (\bar{x}_{\text{Pu}})^2}{\bar{x}_{\text{Pu}}} \quad (3)$$

where

$\bar{D}$ = apparent diffusion coefficient (intra-particle) in square centimeters per second, and

r = average radius of the beads in centimeters.

The results of the first batch equilibration experiment are shown in figure 1. If we define $\bar{X}_{Pu}$ as the maximum capacity of the resin for plutonium in moles per liter of resin bed (one-half the equivalent capacity for anions), the aqueous concentration was such that the system was seeking $\bar{x}_{Pu}^*/\bar{X}_{Pu} = 0.94$ at time zero and $\bar{x}_{Pu}^*/\bar{X}_{Pu} = 0.88$ at equilibrium. A smooth curve drawn through the data in figure 1 was differentiated graphically. A plot of the logarithm of $\frac{\partial \bar{x}_{Pu}}{\partial t} \left\{ \frac{\bar{x}_{Pu}}{(\bar{x}_{Pu}^*)^2} - (\bar{x}_{Pu})^2 \right\}$ versus $\bar{x}_{Pu}/\bar{X}_{Pu}$ was linear for $\bar{x}_{Pu}/\bar{X}_{Pu} < 0.6$. This indicated that an empirical rate law for the system should take the form,

$$\frac{\partial \bar{x}_{Pu}}{\partial t} = \frac{\pi \bar{D}^0}{2r^2} \frac{(\bar{x}_{Pu}^*)^2 - (\bar{x}_{Pu})^2}{\bar{X}_{Pu}} e^{-k\bar{x}_{Pu}/\bar{X}_{Pu}} \quad (4)$$

where $\bar{D}^0$ is the apparent diffusion coefficient for very small $\bar{x}_{Pu}$.

A combination of equations (1) and (4) was integrated numerically⁽⁵⁾ with the appropriate initial and boundary conditions. Good agreement between experiment and calculation was obtained with $\bar{D}^0 = 1.5 \times 10^{-9}$ cm²/sec. and $k = 5.5$. This result is given by the line in figure 1. Two other calculations are included for comparison.

The results of second batch equilibration experiment are shown in figure 2 with the calculation using the above parameters. This experiment was designed so that $\bar{x}_{Pu}^*/\bar{X}_{Pu}$ changed from 0.90 to 0.19 during the

Figure 1.

Sorption of plutonium in the first
batch experiment

	$\bar{D}^0$ (cm ² /secX10 ⁹)	k
A	2.6	6.6
B	1.5	5.5
C	1.0	4.5

Figure 2.

Sorption of plutonium in second
batch experiment

experiment. The experimental data were corrected to discount 4.1 percent of plutonium as plutonium (III). The uncorrected data are shown by the dashed circles.

The preceding paper⁽⁵⁾ gives a numerical method for calculating plutonium loading or breakthrough data for a column operation from equations (1), (2), and (4). The concentration of plutonium in the raffinate from the column experiment is shown in figure 3. The solid line is the calculated result. The disagreement of about eleven percent could be due to uncertainties of this magnitude in ϵ or $\bar{X}_{\text{Pu}}$.

It should be emphasized that equation (4) is strictly empirical. It contains only the average plutonium concentration within the resin beads. Cooper⁽⁵⁾ has solved two diffusion problems in spherical geometry which could apply to this system. Fick's law was solved for the case of a diffusion coefficient which depends exponentially on the local, intra-particle concentration. Also the case of constant diffusion coefficient but immediate reaction and instant local, intra-particle equilibrium was solved (analogous to oxidation of a bead of metal). In neither case could the parameters be varied so as to reproduce the batch equilibration experiments.

It would be of interest to apply these calculations to the sorption of plutonium (IV) from other nitrate solvent systems, such as nitrate salt solutions, other concentrations of nitric acid or mixtures of salt and nitric acid. However the work by James⁽³⁾ for 7M nitric acid is the only system for which the selectivity coefficient (see equation (1)) has been investigated. If one assumes that this coefficient is different but con-

Figure 3.

Breakthrough curve

stant for any high ionic strength, nitrate solvent system, then the equilibrium is easily shown⁽⁶⁾ to be described by

$$\lambda = \lambda^0 (1 - \bar{x}_{\text{Pu}} / \bar{x}_{\text{Pu}})^2 \quad (5)$$

where $\lambda = \bar{x}_{\text{Pu}}^* / c_{\text{Pu}}$ is the distribution coefficient for plutonium and λ approaches λ^0 , the trace-level loading distribution coefficient, as $\bar{x}_{\text{Pu}}^*$ approaches zero. Ryan and Wheelwright⁽²⁾ measured the trace-level loading distribution coefficient of plutonium (IV) from various nitric acid and calcium nitrate solutions on Dowex 1x4(50-100)NO₃⁻. Plotted against molarity of total nitrate in the system, their data for the salt are much higher than those for nitric acid. They suggest protonation of Pu(NO₃)₆⁼ as an explanation. However, if one uses data reported by Harned and Owen⁽⁷⁾ for the concentration of the nitrate ion in nitric acid solutions, the two curves coincide in a plot versus molarity of nitrate ion. The results of this treatment are presented in figure 4 with the data of Ryan and Wheelwright normalized to a value of $\lambda^0 = 978$ ⁽³⁾ for 7M nitric acid.

For any mixture of nitrate salt and nitric acid,

$$c_{\text{NO}_3} = \frac{1}{2} \left[\sqrt{\left(K_{\text{HNO}_3} + T_{\text{HNO}_3} - T_{\text{NO}_3} \right)^2 - 4K_{\text{HNO}_3} T_{\text{NO}_3}} - \left(K_{\text{HNO}_3} + T_{\text{HNO}_3} - T_{\text{HNO}_3} \right) \right] \quad (6)$$

where,

$K_{\text{HNO}_3} = 21.4 = \text{dissociation constant for nitric acid}^{(7)},$

$T_{\text{HNO}_3} = \text{total molar concentration of nitric acid in the aqueous phase},$

$T_{\text{NO}_3} = \text{total molar concentration of nitrate in the aqueous phase}.$

Figure 4.

Trace-level loading distribution coefficient

If one further assumes that the empirical sorption rate law applies and that $\bar{D}^0$ and k are constant for all aqueous nitrate ion concentrations, then equation (6) and figure 4 can be used to apply the numerical calculation to any system for the sorption of plutonium (IV) on Dowex 1x4 from a nitrate solution.

ACKNOWLEDGEMENT

The authors wish to thank the personnel of this laboratory in Group CMB-1, who performed the chemical analyses.

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