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Anion-Exchange Processing of Plutonium

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Anion-Exchange Processing of Plutonium

By
Dean B. James





ABSTRACT

A review is presented of the nitrate-solution, anion-exchange technique for the purification and concentration of plutonium, emphasizing the chemical and chemical engineering nature of the process. After a brief introductory chapter the next two chapters review the fundamentals of ion exchange and the solution chemistry of plutonium. The basic chemistry of the nitrate, anion exchange of plutonium is described in Chapter IV. The final two chapters deal with the applied process.

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PREFACE

The credence that plutonium will be bred in and will be a fuel for nuclear power reactors is stimulating a renewed interest in methods for recovery, purification, decontamination, and concentration of plutonium. The most generally applicable, chemical-processing method is anion exchange from nitrate solutions. The technology of this process is diffusely presented in many unclassified government reports, technical journal articles, and abstracts of the proceedings of technical meetings. It has been the intent of this monograph to provide a current reference for this important plutonium-processing operation.

The experimental and applied experience that has been recorded far exceeds that which would be practical to present in this monograph even though much knowledge has been "lost" because

it was never, or very obscurely, recorded. Therefore, I have deliberately based this work on a limited selection of that which has been reported regarding the anion-exchange processing of plutonium. Literature references cite publications which are apt to illustrate the discussion; the choice was made by necessity and does not indicate any personal preferences. To those whom I have not extended due credit I offer my sincere apologies.

I have tried to emphasize the chemical and chemical engineering nature of the process, rather than details regarding plant, operating experience, flow diagrams, equipment design, etc. These details are rather poorly recorded in the literature, but I have attempted to reference what is available.



GLOSSARY OF TERMS

The numbers in parentheses at the end of a definition indicate the defining equation in the text, while the units in parentheses are those which are consistent in the relations given in the text.

PHYSICAL QUANTITIES

A	general chemical species	r	fractional radial dimension in resin particles
a	cross-sectional area (cm ²)	T	temperature (°C)
a _i	chemical activity of species i	t	time (sec)
B	general chemical species	U	dimensionless functional relation (4-17)
C _i	concentration of species i in solution (moles/ℓ)	V _i	volume of solution (ℓ)
D	diffusion coefficient in solution (cm ² /sec)	v	linear flow rate (cm/sec)
\bar{D}	diffusion coefficient of plutonium in the resin phase (cm ² /sec)	v _i	partial molal volume of species i (ℓ)
\bar{D}_i	diffusion coefficient of species i in the resin phase (cm ² /sec)	w	ratio of total amount in resin to total amount in solution
ΔE	diffusional activation energy (kcal/mole)	\bar{X}	equivalent exchange capacity (equivalents/dry g)
f	functional relation (5-3)	x	intraparticle plutonium concentration (moles/dry g)
f _i	fractional concentration of i th species of a class	\bar{x}	average plutonium concentration in resin (moles/dry g)
g	functional relation (5-4)	\bar{x}_m	saturated plutonium capacity of resin (moles/dry g)
H _i	theoretical-plate height of species i (cm) (5-9)	\bar{x}^*	equilibrium plutonium concentration in resin (moles/dry g)
\vec{J}	flux of diffusing species (moles/cm ² /sec)	\bar{x}^o	initial average plutonium concentration in resin (moles/dry g)
K	equilibrium constant	\bar{x}_i	average concentration of species i in resin (moles/dry g)
\bar{K}	selectivity coefficient (2-10)	Y	fraction of equilibrium
K _n	association constant of the n th complex	y	general variable (4-20)
\bar{K}	thermodynamic equilibrium constant (2-8)	Z	column length (cm)
k	dimensionless empirical constant (4-23)	z	axial distance along column (cm)
m	molal concentration (moles/1000 g H ₂ O)	z _i	charge carried by ion i
n	general integer	α _B ^A	separation factor
P	pressure (atm)	β	beta radiation
p	general integer	γ	gamma radiation
R	radius of resin particles (cm) or gas constant (ℓ atm)	γ _i	activity coefficient of species i (2-6)
		δ	film thickness (cm)
		ε	fractional interstitial void volume of resin bed
		θ	pseudo-constant (4-10)
		λ	weight distribution coefficient of plutonium (4-3)

λ° trace-loading weight distribution coefficient of plutonium (4-9)
 λ_i weight distribution coefficient of species i
 λ_i' volume, trace-loading distribution coefficient of species i (5-8)
 μ_i chemical potential of species i
 Π osmotic pressure difference (atm)
 ρ packing density of resin bed (dry g/ml of bed)
 τ dimensionless, time parameter (4-21)
 ϕ_H special function (4-15)
 ϕ_N special function (4-15)

SUPERSCRIPTS

\circ initial, infinitely dilute, or trace amount
 $*$ equilibrium
 overbar resin phase

SUBSCRIPTS

The absence of a subscript on such symbols as x , \bar{x} , \bar{D} , λ , γ , etc., indicates that the symbols refer to plutonium.

i species i
 m maximum

CHAPTER I — INTRODUCTION

Ion exchange has emerged as one of the most important, chemical-engineering, unit operations. It ages whiskey and purifies water; it provides electric power for space craft; it separates adjacent, rare-earth elements and isotopes of the same element on an industrial scale; and it made possible the separation and identification of four atoms of mendelevium.

Plutonium is a unique element in that its existence and utility are entirely the result of man's labor and ingenuity. It was born of science. Plutonium and its neighboring elements have given a new life to science that has led man into the atomic age. Atomic power could carry man to other worlds or it could obliterate him from this one.

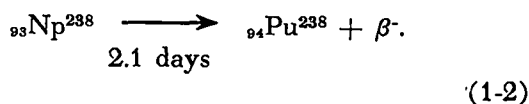
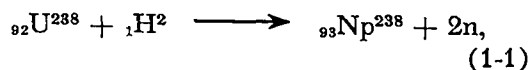
With the establishment of thermal nuclear reactors as competitive civilian power sources and the credence that breeding, fast-neutron, power reactors are important future power sources, plutonium fuel processing and reprocessing have received increased interest. The feasibility of processing plutonium by anion exchange is well established. The success of this process is due to its high specificity. Only a few elements are sorbed to any significant degree by anion-exchange resin from nitric acid solutions, while plutonium(IV) is very strongly sorbed. The process is inherently simple from an engineering standpoint; it generates a small, salt-free waste volume and a pure, concentrated, salt-free product in one or two cycles; and radiation degradation of the resin, while significant, is not prohibitive.

Recorded evidence of ion-exchange phenomena dates from Moses,⁽¹⁾ who desalinated brackish water with the foliage of a tree. Aristotle⁽²⁾ described the desalination of sea water by its

percolation through sand. The first systematic studies concerned the base exchange of the minerals present in soil.⁽³⁾ Exchange of ammonia for calcium was described long before concepts of ionic solutions and crystal structure were established.

Adams and Holmes⁽⁴⁾ in 1935 demonstrated that crushed phonograph records possess ion-exchange properties. This marked the beginning of the development and application of synthetic, organic, ion-exchange resins during and immediately following World War II. A series of patents by Holmes^(4,5) marks the first synthesis of organic anion exchangers. These were polymerized amines. The copolymers of styrene and divinylbenzene, containing quaternary ammonium groups, were first prepared in 1948.⁽⁶⁾

Plutonium was first produced in 1940 by Seaborg, McMillan, Kennedy, and Wahl⁽⁷⁾ by the deuteron bombardment of uranium:



The fissionable isotope plutonium-239 was discovered in the same laboratory in 1941.⁽⁸⁾ Plutonium was first isolated by a lanthanum fluoride cycle by Cunningham and Werner⁽⁹⁾ in 1942, and it occurs naturally in uranium and thorium ores to an extent of $< 1 \times 10^{-14}$ to 9×10^{-13} parts.⁽¹⁰⁾

It is generally agreed that ion exchange emerged as an important analytical-, physical-,

and engineering-chemical tool as a result of the Plutonium Project in the United States during and just after World War II. Workers, such as A. W. Adamson, G. E. Boyd, C. D. Coryell, W. E. Cohn, J. A. Marinsky, J. Schubert, E. R. Tompkins, and others, began with an interest in chromatographic separation of the actinides, lanthanides, and other fission products.

This work stimulated an interest in the use of ion exchange for processing applications. During the middle 1940's anion-exchange resins were not yet commercially available, so interest was entirely directed toward cation exchange. A cation-exchange process for the concentration of plutonium-product solutions from Purex was developed at Oak Ridge. Most of the earliest work concerning plutonium, cation-exchange properties is rather obscurely hidden in progress reports. A few representative references will be cited here;⁽¹¹⁻¹⁴⁾ but these are only intended to serve as an introduction and are by no means a comprehensive list. The cation-exchange process has been applied on a plant scale at Oak Ridge,⁽¹⁵⁾ Savannah River,⁽¹⁶⁾ Los Alamos,⁽¹⁷⁾ Fontenay-aux-Roses,⁽¹⁸⁾ and elsewhere. There are several, excellent, summary descriptions of the process.⁽¹⁹⁻²³⁾

In acidic solutions less than 2M plutonium can exist in the (III), (IV), (V), and (VI) valence states, all of which are sorbed by cation resins. However, plutonium(III) is the most favorable valence for cation-exchange processing because plutonium(V) and (VI) are difficult to maintain and because plutonium(IV) is eluted by the dilute sulfuric acid used to remove uranium(VI) contamination. Plutonium(III) shows greater resin capacity and better elution characteristics than plutonium(IV). Sorption to 60 to 70 percent of theoretical capacity for Pu⁺³ is accomplished from feed solutions containing 0.025

to 0.05M hydroxylamine sulfate and 0.2 to 0.6M nitric acid.⁽²²⁾ After a dilute, sulfuric acid wash the plutonium is eluted with 5.7M nitric acid, containing 0.3M sulfamic acid. This cation-exchange process finds its greatest application in the concentration of plutonium solutions; but rather poor decontamination from such common impurities as iron, aluminum, rare earths, etc., makes it rather impractical as a general purification process.

In the late 1940's, when strong-base, anion-exchange resins, stable in strong, nitric acid solutions, became commercially available, their application to plutonium processing was investigated. The anion-exchange properties of the four valences of plutonium with hydrochloric and nitric acid solutions are summarized by Hardy⁽²⁴⁾ and by Prevot and Regnaut.⁽²⁵⁾ Because of its high sorbability plutonium(IV) is the optimum valence. Nitric acid provides much better separations from impurities than does hydrochloric acid. The most significant, early, development work was a concentrated effort by the Canadians. References to this work are cited by Nishimura.⁽²⁶⁾ The process emerged as an extremely important, general, plutonium-processing technique when its plant-scale feasibility was demonstrated by Aikin^(27,28) and when Ryan and Wheelwright⁽²⁹⁾ established much of the basic process chemistry.

This monograph will describe the nature and application of this nitrate anion-exchange process for the concentration, purification, and decontamination of plutonium. To provide a foundation for this discussion the fundamentals of ion exchange and plutonium, aqueous-solution chemistry will be reviewed in Chapters II and III. The chemistry of the plutonium(IV), nitrate, anion-exchange system will be presented in Chapter IV and the final two chapters will deal with specific, process applications.

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CHAPTER II — FUNDAMENTALS OF ION EXCHANGE

Ion-exchange substances may be defined as insoluble solid materials which have ions that can be stoichiometrically exchanged with other ions of the same sign in a solution. Ion exchange is a particular class of sorptive process characterized by the requirement for stoichiometric exchange that arises from the structure of these materials.

A. Nature of Crosslinked Polystyrene Ion-Exchange Resins

The solid exchanger is composed of a microporous framework, held together by chemical bonds. This framework carries rigidly affixed ionic sites, which are neutralized by oppositely charged mobile ions called *counter ions*.

This monograph will be concerned with the synthetic, organic ion-exchange resins. These substances are water-swollen gels with a framework or matrix of hydrocarbon chains which are interconnected or *crosslinked*. This hydrophobic matrix is rendered hydrophilic by the introduction of ionic groups along the hydrocarbon chains. A common ionic group which is incorporated in synthetic cation exchangers is $-\text{SO}_3^-$; a common group for anion exchangers is $-\text{N}(\text{alkyl})_3^+$. Therefore, the matrix is a macromolecular polyanion or polycation. A schematic representation of an anion exchanger is shown in Figure II-1.

When the exchanger is immersed in a polar solvent, such as water, the counter ions become mobile and exchangeable. Counteracting the energy necessary to separate the counter ions from the fixed ionic sites is the energy of solvation of these ions. The entropy decrease that is due to the ordering of the polar solvent molecules in solvation shells about the fixed ionic sites can be reduced by the uptake of more solvent to render the ions more dilute. Furthermore, the electrostatic

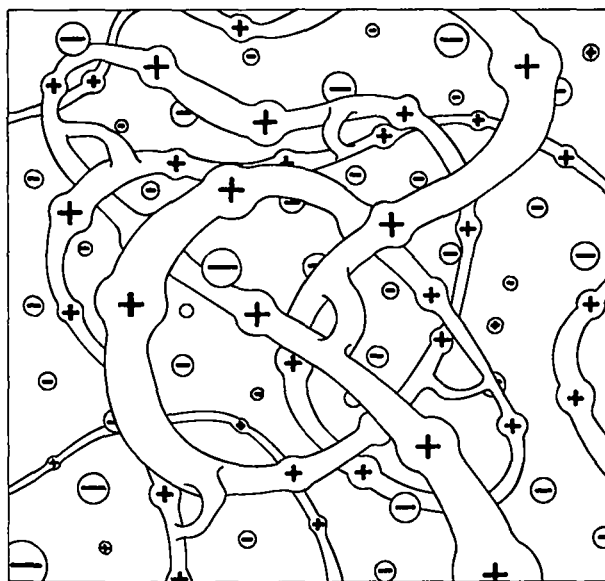


Fig. II-1. Schematic representation of anion-exchange resin.

repulsion of the neighboring, fixed ionic groups can be lessened by dispersing the charge. In macroscopic models this solvent uptake is due to the osmotic pressure difference between the solution within the matrix and the external solution, while in microscopic considerations the free energy of solvent uptake is represented by the free energy of mixing.

All of these forces which tend to expand the solid by the uptake of solvent are constrained by the elastic, crosslinked matrix. An equilibrium is established when the expanding forces are balanced by the constraining forces. In the absence of crosslinks, i.e. linear polystyrene sulfonic acid, the sorption of water proceeds to the point of complete solubility of the polymer. In crosslinked materials the matrix chains cannot separate com-

pletely. Therefore, these materials swell but do not dissolve.

A common synthetic hydrocarbon matrix is that formed from the copolymerization of styrene and divinylbenzene. The polymer is formed into tiny spheres which are sized. The anion-exchange resins commonly used for plutonium processing are of this type. A schematic representation of this resin is shown in Figure II-2. The quaternary ammonium groups are highly ionized at all pH's, and these resins are *strong-base* anion exchangers. The stability of these materials is discussed in Chapter V.

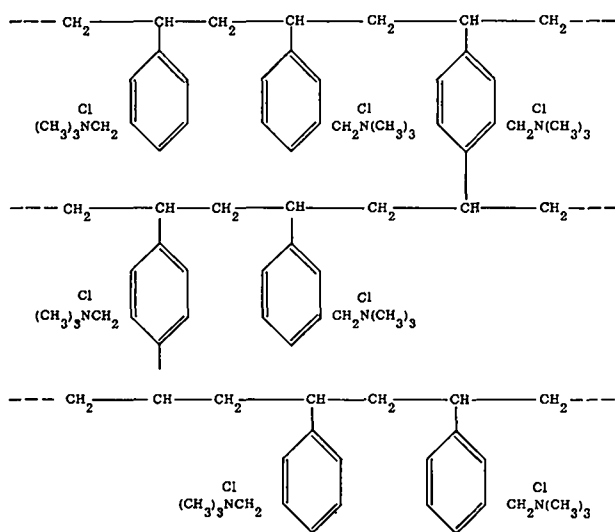


Fig. II-2. Schematic representation of a copolymer of styrene and divinylbenzene with quaternary ammonium functional groups.

B. Ion-Exchange Equilibria

The only entirely rigorous means of describing equilibria is thermodynamics, and ion-exchange equilibria can be accurately described by means of Gibbsian thermodynamics. A rigorous development of this thermodynamic treatment is beyond the scope of this monograph, and the reader is referred to the literature.⁽¹⁻¹⁰⁾ Particular attention should be drawn to the excellent book by Helfferich⁽¹⁾ that treats both the theoretical and applied aspects of ion exchange in a very complete, yet understandable, manner.

Of course, ion-exchange resins sorb nonelectrolytes in much the same way as do conventional sorbents. The sorption of electrolytes is influenced by electrostatic forces. When an ion exchanger is

placed in a dilute solution of a strong electrolyte, there are great concentration differences between the two phases. Diffusion would tend to level these differences if it were not for the fact that there are immobile ions affixed to the matrix in the exchanger. Ions of either sign cannot enter the resin phase without equivalent exchange for this would produce an excess of charge. The only way for mobile ions, which carry charges of the same sign as the fixed ions and are called co-ions, to enter the resin phase is for them to bring along counter ions. But this increases the resin-phase, counter ion concentration which is already much higher than the aqueous counter ion concentration. The effect is analogous to the common-ion effect on the solubility of a sparingly soluble electrolyte. This exclusion of electrolyte is called Donnan exclusion after F. G. Donnan,⁽¹¹⁾ who described analogous ion-selective membrane systems.

With a dilute aqueous phase the only ions that are free to diffuse between the two phases are the counter ions, and they are limited by the requirement for preservation of electroneutrality. There is also a further limitation in that the exchanger always, although sometimes only slightly, prefers one counter ion over another. This selectivity can be due to the Donnan potential causing a preference for the more highly charged ion; it can be due to differences in interactions between the counter ions and the fixed ions, i.e. ion pairs or covalent complexes; and it can be due to a preference for the smaller, equivalent, solvated ion because of the osmotic pressure difference between the two phases.

Treatment of ion-exchange equilibria with thermodynamics is universally applicable but does not allow prediction of behavior from fundamental data. The introduction of specific models removes the latter disadvantage at the expense of the former advantage. In thermodynamic treatments activity coefficients can be introduced to cover nonideal behavior, and these coefficients depend upon the standard and reference states chosen. Activity coefficients indicate extent and direction of deviation from a particular solution model, the ideal solution, but in the absence of a nonideal model, indicate nothing as to the cause of deviations.

Equilibrium between two different phases

may be regarded as the condition of equality of the chemical potential of every transferable component i between the phases:

$$\mu_i = \bar{\mu}_i, \quad (2-1)$$

where the bar refers to the resin phase. The liquid within the resin matrix is influenced by the contractive forces of the elastic matrix and, therefore, is at a much higher pressure than the aqueous phase. If it is assumed that this contribution to the chemical potential is entirely additive and independent of the chemical contributions, then the chemical potential of i at pressure P and total concentration m is

$$\mu_i(P,m) = \mu_i(P^0,m) + (P-P^0)v_i, \quad (2-2)$$

where P^0 is a standard reference pressure, usually 1 atm, and v_i is the partial molal volume of component i .

The activity of component i , a_i , is defined by

$$\mu_i(P,m) = \mu_i^0(P) + RT \ln a_i \quad (2-3a)$$

or by

$$\mu_i(P,M) = \mu_i^0(P^0) + RT \ln a_i, \quad (2-3b)$$

where μ_i^0 is the chemical potential of component i in some arbitrary standard state. These definitions in combination with equation (2-2) yield

$$\mu_i(P,m) = \mu_i^0(P^0) + RT \ln a_i + (P - P^0)v_i \quad (2-4a)$$

or

$$\mu_i(P,m) = \mu_i^0(P^0) + RT \ln a_i, \quad (2-4b)$$

respectively. If we choose the standard state to be the same for all components in both phases, substitution into the equilibrium condition yields (assuming $\bar{v}_i = v_i$)

$$\ln \frac{a_i}{\bar{a}_i} = (P - P^0)v_i = \Pi v_i \quad (2-5a)$$

or

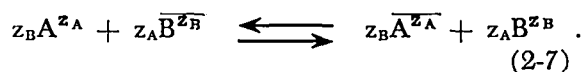
$$a_i = \bar{a}_i. \quad (2-5b)$$

Whether one chooses definition (2-3a) or (2-3b) is entirely arbitrary, and the choice is usually made in a manner so as best to describe the ion-exchange system of interest. With definition (2-3b) the simpler relation between activities at equilibrium, equation (2-5b), results; but pressure-volume effects become incorporated in the activity coefficients γ_i . These are defined by

$$\gamma_i = \frac{a_i}{m_i}, \quad (2-6)$$

where m_i is some unit of concentration, usually molal.

Consider the exchange of counter ion A^{z_A} for counter ion B^{z_B} ;



The thermodynamic equilibrium constant,

$$\bar{K}_B^A = \left(\frac{\bar{a}_A}{a_A} \right)^{z_B} \left(\frac{a_B}{\bar{a}_B} \right)^{z_A}, \quad (2-8)$$

with result (2-5a) becomes

$$RT \ln \bar{K}_B^A = z_B \Pi_{AV} - z_A \Pi_{BV}, \quad (2-9a)$$

or with result (2-5b) becomes

$$RT \ln \bar{K}_B^A = 0. \quad (2-9b)$$

By defining the selectivity coefficient,

$$\bar{K}_B^A = \left(\frac{\bar{m}_A}{m_A} \right)^{z_B} \left(\frac{m_B}{\bar{m}_B} \right)^{z_A}, \quad (2-10)$$

and using definitions (2-6) and (2-8), equations (2-9a) and (2-9b) become

$$\begin{aligned} z_B \ln \left(\frac{\bar{m}_A}{m_A} \right) - z_A \ln \left(\frac{\bar{m}_B}{m_B} \right) &= \\ &= z_A \ln \frac{\bar{\gamma}_B}{\gamma_B} - z_B \ln \frac{\bar{\gamma}_A}{\gamma_A} - \\ &\quad - \Pi_B^A (z_B v_A - z_A v_B) \end{aligned} \quad (2-11a)$$

and

$$\begin{aligned}
 z_B \ln \left(\frac{\bar{m}_A}{m_A} \right) - z_A \ln \left(\frac{\bar{m}_B}{m_B} \right) &= \\
 = z_A \ln \left(\frac{\bar{\gamma}_B}{\gamma_B} \right) - z_B \ln \left(\frac{\bar{\gamma}_A}{\gamma_A} \right), & \\
 & \quad (2-11b)
 \end{aligned}$$

where we have assumed $\Pi_A = \Pi_B = \Pi_B^A$.

Both forms of the equilibrium expression have been derived here in order to emphasize that both are present in the literature on ion exchange. If activity is defined by (2-3b) rather than (2-3a), the third term on the right of equation (2-11a) is contained in the activity coefficients on the right of equation (2-11b). Claims in the literature for constancy of activity coefficients ratios, $\bar{\gamma}_B/\gamma_B$ and $\bar{\gamma}_A/\gamma_A$, under definition (2-3b) should be viewed with considerable scepticism if v_A and v_B are quite different or if the resin shrinks or swells as it is converted from the A form to the B form.

C. Ion-Exchange Kinetics

Ion-exchange resins are used to effect a redistribution of ions between a solution and the resin. This exchange will proceed until the equilibrium condition of the system is reached. Usually this process of reaching equilibrium takes a significant amount of time. In many chemical operations time can be an important parameter. Therefore, kinetics can play an important role in any ion-exchange process.

This redistribution of counter ions is accomplished by the mechanism of diffusion. To effect this redistribution a sequence of processes is necessary. For the exchange given by equation (2-7) ions A must diffuse from the solution phase and into the resin phase while ions B must diffuse from the resin phase into the solution phase. However, the total counter ion concentration in either phase must remain constant in order to preserve electrical neutrality. The fluxes of the counter ions must be the same, even though their mobilities are quite different.

In the bulk of the solution phase any concentration differences are usually very rapidly removed by some form of agitation. However, no matter how rapid this agitation, there will always remain a layer of unstirred liquid around each resin sphere. The transport of ions through this adherent film, called a Nernst film, and through the resin phase can be accomplished only by diffusion.

In any time-dependent phenomena which occurs in a sequence of steps, if one step in the sequence is much slower than all the rest, the rate of this step will determine the rate of the entire process. We cannot eliminate a priori the possibility that the actual chemical exchange of counter ions at the fixed ionic site could be sufficiently slow to influence the overall rate of the process, but there are no known ion-exchange processes where this step is rate controlling.

Studies of ion-exchange kinetics ordinarily involve the comparison of diffusional theory with experimental data for fractional distance from equilibrium versus time. However, ion-exchange systems where solid-phase diffusion is rate influencing are complicated by the electrical coupling of the diffusing ions, by specific chemical interactions, and by changes in the swelling of the resin phase with changes in resin composition. These complications generally produce nonlinear, differential rate equations. Such complications can be eliminated from the experimental data by studying systems in which the chemical composition of neither phase changes during the process, that is, by using systems in equilibrium except for isotopic composition. Just as these complications make analysis of experimental data difficult, a lack of experimental knowledge of their effects may make it unrealistic to apply easily determined isotopic-diffusion parameters to complex exchange systems.

In order that the diffusion of ions through the Nernst film be the slow step, the exchanger must be of high capacity, low crosslinking, and small particle size; the aqueous phase should be dilute and poorly stirred. Of these criteria only high capacity is realized in the anion-exchange processing of plutonium, so very rarely is film diffusion sufficiently slow to be significant. The

criteria for the determination of which process will be rate controlling is given by (see reference 1, p. 255)

$$\frac{\bar{X} \bar{D} \delta}{C D R} (5 + 2 \alpha_B^A). \quad (2-12)$$

If this dimensionless group is considerably less than unity, resin-phase diffusion will control; if it is considerably greater than unity, film diffusion will control; if it is approximately unity, both processes will influence the rate. For most plutonium processing operations \bar{X} , the exchange capacity is about one equivalent per cubic centimeter; \bar{D} , the solid diffusion coefficient, is less than 10^{-9} cm²/sec; δ , the film thickness, is 10^{-3} cm; C , the total anionic aqueous concentration, is about $7M$; D , the aqueous diffusion coefficient, is greater than 10^{-6} cm²/sec; R , the particle radius, is about 10^{-2} cm; and α_B^A , the separation factor, is greater than 10^2 . This gives a value to (2-12) of about 10^{-3} , so that resin-phase diffusion should control.

This work will not deal further with the process of film diffusion. Reference 1, Chapter 6, may be consulted for further information.

All diffusional processes are governed by Fick's First Law,

$$\vec{J} = -D \text{grad } m, \quad (2-13)$$

where \vec{J} is the flux of the diffusing species (amount per unit time per unit cross section), D is the diffusion coefficient, and m is the concentration of the diffusing species (amount per unit volume). In systems where no other processes or changes are occurring the flux must be proportional and normal to the concentration gradient, so D must be constant.

A material balance gives the relation between change in concentration with time t and the flux,

$$\frac{\partial m}{\partial t} = -\text{div } \vec{J}. \quad (2-14)$$

This is Fick's Second Law.

For radial diffusion in spherical particles, equations (2-13) and (2-14) may be combined with spherical geometry to yield

$$\frac{\partial x(r)}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \bar{D}(r, x) \frac{\partial x(r)}{\partial r}, \quad (2-15)$$

where x is local concentration in the resin phase, $\bar{D}(r, x)$ is the local diffusion coefficient, and r is the fractional radial dimension. Except for \bar{D} , independent of r and x , usually only realized in isotopic exchange systems, equation (2-15) is not linear; it must be integrated numerically. With constant \bar{D} equation (2-15) has been solved for nearly all the more important boundary conditions. With an infinite solution volume, so that the concentration of the solution phase is constant, the result^(12,18) is

$$\gamma(t) = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp \left(- \frac{\bar{D} t \pi^2 n^2}{R^2} \right), \quad (2-16)$$

where $\gamma(t)$ is the fraction of equilibrium and R is the radius of the spheres. This function is tabulated in reference 1, p. 584. Vermeulen⁽¹⁴⁾ has given a good approximation to this function in the form of the rate expression

$$\frac{d\gamma}{dt} = \frac{\pi^2 \bar{D}}{R^2} \frac{1 - \gamma^2}{2\gamma}. \quad (2-17)$$

With a finite solution volume the solution of (2-15) with constant \bar{D} is given by Paterson⁽¹⁵⁾ for heat transfer. An approximation to this solution, also given by Paterson, is also tabulated in reference 1, p. 585.

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CHAPTER III — AQUEOUS CHEMISTRY OF PLUTONIUM

The chemical behavior of plutonium in aqueous solutions is very complex. Four oxidation states, (III), (IV), (V), and (VI), are stable in aqueous solutions. Because the formal reduction potentials between each of the successive states are about 1 V, all four states can exist simultaneously in finite concentrations in equilibrium in the same solution. With a formal charge of +3 or more for all four of these oxidation states, there is extensive interaction of these ions with the solvent and any anions which may be present in the solution. Therefore, plutonium exhibits nearly all the chemical properties of all cations in aqueous solution.

Fortunately, the optical absorption spectra of these ions show many weak, but sharp, bands. These bands are due to forbidden transitions in the shielded 5f orbital. Because these transitions are only slightly perturbed by coordination reactions, absorption spectra can give only qualitative information as to the stability of complexes. However, the spectra of the different oxidation states are sufficiently different to allow quantitative determination of oxidation-reduction equilibria and kinetics.

A. Hydrolytic Interactions of Plutonium

Because of its small radius the hydroxide ion is one of the strongest of the complexing anions. Since in water it is the anion of an extremely weak acid, hydroxide complexes may be easily destroyed by supplying hydrogen ions to the solution. Early work on the hydrolytic behavior of plutonium was reviewed by Hindman,⁽¹⁾ Kraus,⁽²⁾ and Katz and Seaborg.⁽³⁾ The reader is also referred to English translations of recently published monographs by Russian authors.^(4,5)

With increasing formal charge, the interaction with water is stronger. Therefore, in slightly acidic solutions plutonium(III) forms a hydrated cation, while plutonium(IV) forms a hydroxide and plutonium(V) and (VI) form oxyanions.

The hydrolytic behavior of plutonium(III) is similar to that of the light rare-earth elements. The solubility product of $\text{Pu}(\text{OH})_3$ is 2×10^{-20} .⁽⁶⁾

The hydrolytic behavior of plutonium(IV) is similar to cerium(IV). The most striking feature is the irreversible formation of plutonium(IV) polymer. It can have a very high molecular weight and requires drastic conditions for its destruction. It can form in hot solutions of acidity as high as 0.3M. Possibly the chains are held together and crosslinked by oxide and hydroxide bridges. If the hydrolysis is carried to the limit, insoluble $\text{Pu}(\text{OH})_4$ precipitates with a solubility product of 7×10^{-56} .⁽⁶⁾ Treating this precipitate with a solution of insufficient acidity also results in the formation of polymer.

Plutonium(V) in aqueous solution is apparently in the form of PuO_2^+ ; but it is less acidic than NpO_2^+ , indicating that it is not just a simple, singly charged ion. It has only a slight tendency to undergo any type of complex formation. PuO_2^+ begins to hydrolyze only above a pH of nine.

Kraus and Dam⁽⁶⁾ and Russian authors^(6,7) have investigated the hydrolysis of plutonium(VI) solutions. The results of their calculations of hydrolysis constants and solubility products from their data are in considerable disagreement. However, these calculations do not account for poly-

merization reactions, which must be occurring if the hydrolytic behavior of PuO_2^{+2} is anything like UO_2^{+2} .

B. Complex Ions of Plutonium

As with the trivalent rare-earth elements, plutonium(III) does not exhibit a strong tendency to form complex ions. Because the 5f shell, which is responsible for its absorption spectra, is shielded from perturbations due to complexing ligands, spectrophotometric observations are of little qualitative value for measuring the extent of complex formation.

Diamond, Street, and Seaborg⁽⁸⁾ attribute to stronger chloride complexes the more rapid elution of the trivalent actinides than the lanthanides from Dowex 50 by high concentration hydrochloric acid solutions. Ward and Welch⁽⁹⁾ used the cation-exchange technique to determine a dissociation constant for PuCl^{+2} of 0.58.

Spectrophotometric evidence for nitrate complexes of plutonium(III) are also qualitative. The fact that the amount of plutonium(III) extracted by tributyl phosphate⁽¹⁰⁾ and by anion-exchange resin⁽¹¹⁾ increases with increasing, nitrate ion concentration can only be regarded as qualitative evidence for nitrate complexes in aqueous, nitrate solutions. A value of 0.77 for the first association constant is given by Shevchenko, Timoshev, and Volkova.⁽¹²⁾

Plutonium(III) also forms cationic and anionic complexes with sulfate,^(10,13) carbonate,^(13,14) oxalate,^(5,13) ethylenediaminetetraacetate,⁽¹⁵⁻¹⁷⁾ and citrate.^(13,14)

Plutonium(IV) forms stepwise chloride complexes with increasing chloride concentration. Values for the first three stability constants in 4M perchlorate are given by Grenthe⁽¹⁷⁾ and by Danesi, Orlandini, and Scibona.⁽¹⁸⁾

There is evidence for cationic, but not anionic, fluoride complexes of plutonium(IV).^(1,3) There is also evidence for plutonium(IV) complexing by acetate,⁽¹⁾ acetylacetonate,⁽¹⁹⁾ salicylate,⁽²⁰⁾ sulfite,⁽¹⁾ oxalate,^(1,5,21) carbonate,^(1,5) peroxide,^(1,3,22) phosphate,^(1,23,24) citrate,^(1,3)

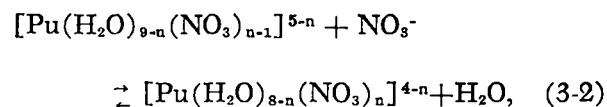
and ethylenediaminetetraacetate.^(14,25) There is considerable evidence for the existence of sulfate complexes, PuSO_4^{+2} , $\text{Pu}(\text{SO}_4)_2$, and $\text{Pu}(\text{SO}_4)_3^{-2}$, but the quantitative data are somewhat conflicting.⁽²⁶⁻²⁹⁾

Since nitrate solutions of plutonium(IV) are employed in the Purex, Redox, Butex, and the anion-exchange processes for plutonium fuel processing, there has been considerable investigation of the nitrate complexes of plutonium(IV) in aqueous solutions of nitric acid and nitrate salts. Hindman⁽¹⁾ gives a value of 2.9 ± 0.6 for the first association constant in 2M nitric acid, based on changes in the absorption spectrum. The change in the potential of the plutonium(III)/plutonium(IV) couple with changing nitrate ion concentration led Rabideau and Lemons⁽²⁶⁾ to a value of 3.48 ± 0.06 at an ionic strength of unity. However, the calculation was not corrected for the complexing of plutonium(III). Grenthe⁽¹⁷⁾ gives values to the first three association constants,

$$K_n = \frac{[\text{Pu}(\text{NO}_3)_n^{4-n}]}{[\text{Pu}(\text{NO}_3)_{n-1}^{3-n}] [\text{NO}_3^{-1}]}, \quad (3-1)$$

of 5.5 ± 0.2 , 4.3 ± 0.2 , and 0.6 ± 0.4 for $n = 1, 2$, and 3 , respectively, with an ionic strength of four. Solvent extraction data of Zebroski and Neumann⁽³⁰⁾ yield values of 4.7, 0.96, and 0.33 at an ionic strength of six. Values of the first four association constants are given by Laxminarayanan, et al.⁽²⁹⁾ for ionic strengths of 1.02, 1.9, and 4.7. A comparison of these results is given in reference 18.

Lipis, et al.⁽³¹⁾ studied the absorption spectra of nitric acid solutions of plutonium(IV). By assuming a coordination number of eight⁽¹⁾ they postulate



and that changes in the spectra are due to 5f-orbital perturbations, caused by the nitrate ions replacing the water molecules in the coordination sphere of the ion.

Brothers, et al.⁽³²⁾ investigated the solvent extraction of plutonium(IV) by liquid amines from sodium nitrate solutions containing 0.2M nitric acid and sufficient sodium perchlorate to keep the ionic strength at 6.7. These experiments, conducted in a manner to minimize activity coefficient effects, indicate that in a nitrate ion concentration ranging from 3.0 to 5.5M the predominant species of plutonium is $\text{Pu}(\text{NO}_3)_4$. The anion and cation exchange data of Tuck and Welch⁽³³⁾ indicate that $\text{Pu}(\text{NO}_3)_4$ is the dominant species in the intermediate nitrate ion concentrations and that higher concentrations give a preponderance of $\text{H}_2\text{Pu}(\text{NO}_3)_6$. This is in qualitative agreement with earlier electromigration studies⁽³⁴⁾ which show that in the range of 4 to 8M nitric acid the plutonium(IV) complex changes from being almost completely cationic to predominantly anionic. The transition is nearly complete in 10M nitric acid.

Ryan⁽³⁵⁾ investigated the anion-exchange behavior, the absorption spectra, and the solubility of various compounds of the type $\text{X}_2\text{Pu}(\text{NO}_3)_6$ in nitric acid, calcium nitrate solutions, and various organic solvents. The absorption spectra of solutions of $(\text{C}_2\text{H}_5)_4\text{N}_2\text{Pu}(\text{NO}_3)_6$ in acetone, acetic anhydride, acetonitrile, nitromethane, and solutions of $(\text{C}_4\text{H}_9)_4\text{N}_2\text{Pu}(\text{NO}_3)_6$ in methyl isobutyl ketone and nitromethane were essentially the same as the spectra of plutonium(IV) in greater than 13M nitric acid solutions. The addition of $(\text{C}_2\text{H}_5)_4\text{HNO}_3$ to the acetone solution did not change the spectrum. These spectra were also essentially identical to the spectra of plutonium(IV), sorbed in Dowex 1X1 anion exchange resin in equilibrium with 4 and 8M nitric acid and with 4M calcium nitrate-0.2M nitric acid. These results indicated that the species of plutonium in these solutions is the hexanitrate complex, but cannot give any indication of the degree of protonation of the complex.

Analysis of isobestic points in these spectra led Ryan to two possible conclusions. In 4 to 15M nitric acid only two complexes of plutonium(IV) exist, or the complexes other than the hexanitrate complex have identical spectra. In view of results of Brothers, et al.⁽³²⁾ and Tuck and Welch⁽³³⁾ one might tentatively conclude that the only predominant, higher nitrate complexes in nitrate solutions are the neutral tetranitrate and the hexanitrate complex.

The literature makes references to complex formation of plutonium(V) with chloride,⁽³⁶⁾ oxalate,⁽⁵⁾ and ethylenediaminetetraacetate.^(16,37,38)

Krevinskaya, et al.^(7,39,40) investigated the nitrate complexes of plutonium(VI) with measurements of solubility and absorption spectra in nitric acid. The solubility of pink $\text{PuO}_2(\text{NO}_3)_2 \cdot n\text{H}_2\text{O}$ shows the expected decrease with increasing nitric acid concentration. At about 13M the deep red trinitrate acid $\text{HPuO}_2(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$ appears and shows a lesser solubility. These authors gave values of 72, 36, and 7 to the first three nitrate association constants.

The first two chloride association constants⁽⁴¹⁾ of plutonium(VI) are 0.8 and 3.6. Plutonium(VI) also forms complexes with sulfate,⁽³⁾ acetate,⁽⁵⁾ carbonate,⁽⁵⁾ oxalate,⁽⁵⁾ and ethylenediaminetetraacetate.⁽¹⁴⁾

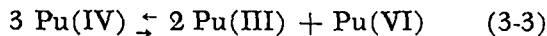
C. Oxidation and Reduction of Plutonium

The existence in aqueous solution of several oxidation states of an element is not an uncommon phenomenon. However, plutonium has four oxidation states which are stable in aqueous solution, a quite uncommon condition. That all four of these states can exist together in the same aqueous solution is unique.

An extensive and critical review of the oxidation-reduction behavior of plutonium in solution was given by Connick.⁽⁴²⁾ This work covers the literature through about 1951. Less comprehensive, but more recent, reviews are given as sections in references 3, 4, and 5.

Since it is difficult with the (III), (V), and (VI) states and impossible with the (IV) state to obtain dilute plutonium solutions without the complications of hydrolysis and disproportionation, the electrochemical potentials between these states are usually measured in more concentrated electrolyte solutions; extrapolation to zero ionic strength is impossible. Values reported in the literature are for a specific solution and are not readily comparable. Unfortunately for the process chemist, nearly all the quantitative work has been done with perchloric and hydrochloric acid solutions. There is little quantitative data for more concentrated nitric and sulfuric acid solutions.

The intermediate oxidation states of plutonium can undergo self-oxidation and reduction reactions. The disproportionation of plutonium(IV) can be represented formally by

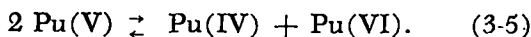


for solutions of acidity greater than about 1.0*M*, where plutonium(V) cannot exist to an appreciable extent. The equilibrium constant for this reaction has been found experimentally to have a fourth-power dependence upon hydrogen ion concentration.⁽⁴³⁾ At unit ionic strength this constant,

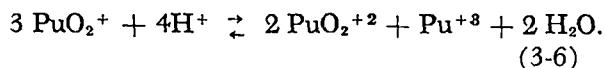
$$K = \frac{[\text{Pu}^{+3}]^2 [\text{PuO}_2^{+2}] [\text{H}^+]^4}{[\text{Pu}^{+4}]^3 [\text{H}_2\text{O}]^2}, \quad (3-4)$$

has a value of 8.9×10^{-8} in perchloric acid solution. The fourth-power dependence upon hydrogen ion concentration is also present in hydrochloric acid solutions, but *K* at unit ionic strength is 1.9×10^{-8} . In either system *K* increases rapidly with increasing temperature. Connick⁽⁴²⁾ estimates from the data of Hindman⁽¹⁾ a value of 4×10^{-7} for *K* in 1*M* nitric acid. Its value is also very low in sulfuric acid.⁽⁴²⁾ This decrease in *K* is probably due to increased complex formation with the resulting stabilization of plutonium(IV). In solutions of acidity less than about 0.2*M*, *K* is also decreased, due to hydrolysis of plutonium(IV).

In solutions of less than 1*M* acidity plutonium(V) can exist in appreciable quantities in plutonium solutions. Its disproportionation can be written formally as



However, the plutonium(IV) reacts with another mole of plutonium(V) to produce plutonium(III) and more plutonium(VI). Hence, in solutions of acidity $0.2M < [\text{H}^+] < 1M$ the important disproportionation equilibrium is



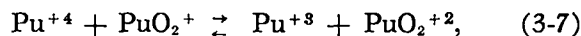
In solutions less than 0.2*M* and greater than 1*M* the stable species are hydrolytic or complex species

of plutonium(IV) so that disproportionation stops with the formation of plutonium(IV).

Plutonium-239 has a half-life of 24,360 years with an alpha-particle energy of 5.15 MeV. This rate of production and magnitude of energy can produce significant changes in the distribution of plutonium oxidation states after a period of several days. Rabideau and co-workers⁽⁴³⁻⁴⁵⁾ have investigated this phenomenon in perchloric and hydrochloric acid solutions. In perchloric acid a steady-state mixture of 0.9 plutonium(III) and 0.1 plutonium(IV) is achieved. Reduction is probably caused by the alpha-particle production of free radicals and hydrogen peroxide. Plutonium(IV) and (VI) are not reduced by the effect of alpha radiation in molar hydrochloric acid solutions,^(44,45) but plutonium(III) solutions are oxidized.

The chemical and electrolytic oxidation and reduction of plutonium in aqueous solution have received considerable qualitative attention. The literature was extensively reviewed by Connick,⁽⁴²⁾ and his results are summarized by Katz and Seaborg.⁽³⁾ As with the disproportionation reactions these reactions are greatly influenced by the complexing power of the medium. Those oxidation-reduction reactions with process significance are discussed in Chapter V; no detailed discussion of these reactions will be attempted in this chapter.

The kinetics of the oxidation, reduction, and disproportionation reactions of plutonium in solution has also received considerable attention.⁽⁴³⁻⁴⁶⁾ Reactions involving the formation of oxygen bonds, such as reaction (3-6), are usually slow, irreversible, and involve hydrolytic intermediates. Reactions involving only the exchange of an electron, such as



are usually fast and reversible. The chemical oxidation or reduction of plutonium solutions can proceed via direct reaction with the reagent or by reaction of disproportionation products with the reagent.

CHAPTER III — REFERENCES

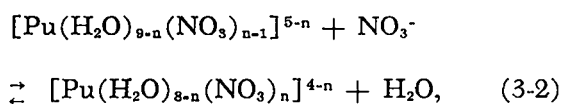
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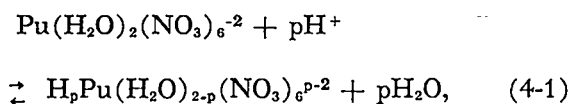
CHAPTER IV — PRINCIPLES OF THE ANION EXCHANGE OF PLUTONIUM

Because of the Donnan exclusion cationic metal ions are usually not sorbed by strong-base anion exchangers. The anion associated with the metallic salt may be exchanged, but the metal ion remains in the aqueous phase.

However, if the metal cation is capable of forming anionic complexes with the ligand anion, these complexes can be sorbed by an anion-exchange resin. As was described in Chapter III, in nitrate solutions of considerable strength, plutonium(IV) forms stepwise nitrate complexes, probably of the form⁽¹⁾.



where n is a positive integer ranging from one to six. Qualitative data⁽²⁻⁵⁾ indicate that in solutions greater than about $3M$ the predominant species are the quadra- and hexanitrate forms, $\text{Pu}(\text{H}_2\text{O})_4(\text{NO}_3)_4$ and $\text{Pu}(\text{H}_2\text{O})_2(\text{NO}_3)_6^{-2}$. In nitric acid solutions protonation of the hexanitrate complex is probably significant:



where p is either one or two.

A. Equilibria of the Anion Exchange of Plutonium

Spectrophotometric data⁽⁵⁾ have indicated that the only significant species sorbed by anion-

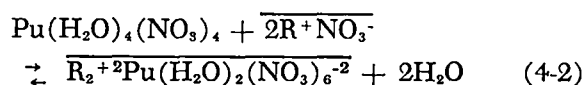
exchange resin is the hexanitrate complex. Furthermore, the amount of plutonium(IV) sorbed from increasingly more concentrated plutonium(IV) nitrate solutions approaches, but does not exceed, the limit calculated from the anion-exchange capacity of the resin, assuming a charge of minus two.⁽⁶⁻⁸⁾

This indicates that the species of plutonium(IV) within the resin phase contains six nitrate ligands, but it does not answer the riddle of its exact chemical character. We might speculate that the species is $\text{Pu}(\text{H}_2\text{O})_2(\text{NO}_3)_6^{-2}$, or possibly $\text{H}_2\text{Pu}(\text{NO}_3)_6$, or even $\text{R}_2\text{Pu}(\text{NO}_3)_6$, where R represents the quaternary ammonium site affixed to the resin matrix. The strong affinity of the resin phase for plutonium(IV) nitrate could be explained by the formation of an "ion pair" between the hexanitrate complex and the quaternary ammonium cation.

Even a semiquantitative, thermodynamic treatment of this complex heterogeneous system is very difficult. The thermodynamics of concentrated aqueous solutions of electrolytes are not well understood; and when one introduces the mystery of the anion-exchange resin, the problem becomes labyrinthine.

When anion-exchange resin is immersed in an aqueous solution of an electrolyte, some of the electrolyte penetrates into the resin phase. This penetration increases with increasing aqueous concentration. The sorption of electrolytes by anion exchangers has been studied by several authors.⁽⁹⁻¹³⁾ As electrolyte is sorbed, water is expelled from the resin. Danon⁽¹³⁾ studied the sorption of nitric acid by Dowex 1X8 immersed in solutions of nitric acid.

It is of little consequence which aqueous species we consider as being sorbed by the resin. The actual species that is physically transferred and the mechanism of its transport will be the subject of the next section. Let us consider the equilibrium between the aqueous neutral complex and the hexanitrate ion pair:



where the overbar indicates a species in the resin phase. We will assume that the plutonium species on the right is the only significant species of plutonium in the resin phase. The other plutonium species in the aqueous phase are related by equations (3-2) and (4-1). We could write sorption equilibria similar to equation (4-2) for any of these species.

The experimentally determinable parameter which can be related to equation (4-2) is the distribution coefficient λ which will be defined by

$$\lambda = \frac{\text{total Pu in resin phase per gram of dry resin}}{\text{total Pu in aqueous phase per milliliter of solution}} \quad (4-3)$$

The total amount of plutonium in each phase may be given in any consistent unit, such as moles. By defining \bar{x}^* as the total moles of plutonium per kilogram of dry resin at equilibrium and C_{Pu} as the total molar concentration of plutonium in the aqueous phase, we obtain

$$\lambda = \frac{\bar{x}^*}{C_{\text{Pu}}} \quad (4-4)$$

With the above assumption

$$\bar{x}^* = [\overline{\text{R}_2^{+2}\text{Pu}(\text{H}_2\text{O})_2(\text{NO}_3)_6^{-2}}], \quad (4-5)$$

where the brackets indicate concentration in moles per dry gram. Also

$$C_{\text{Pu}} = \sum_{n=0}^6 [\text{Pu}(\text{H}_2\text{O})_{8-n}(\text{NO}_3)_n^{4-n}] + \sum_{p=1}^2 [\text{H}_p\text{Pu}(\text{H}_2\text{O})_{2-p}(\text{NO}_3)_6^{p-2}], \quad (4-6)$$

where the brackets indicate molar concentration.

With the inclusion of pressure-volume effects in the activity coefficients (see Chapter II) the thermodynamic equilibrium constant for the sorption described by equation (4-2) is

$$\bar{K}_4 = \frac{[\overline{\text{R}_2^{+2}\text{Pu}(\text{H}_2\text{O})_2(\text{NO}_3)_6^{-2}}] \bar{\gamma}_6 a_{\text{H}_2\text{O}}^2}{[\text{Pu}(\text{H}_2\text{O})_4(\text{NO}_3)_4] [\overline{\text{R}^+\text{NO}_3^-}]^2 \bar{\gamma}_R^2 \gamma_4} \quad (4-7)$$

where $\bar{\gamma}_6$ is the activity coefficient for $\overline{\text{R}_2^{+2}\text{Pu}(\text{H}_2\text{O})_2(\text{NO}_3)_6^{-2}}$, $a_{\text{H}_2\text{O}}^2$ is the activity of water in the aqueous phase, $\bar{\gamma}_R$ is the activity coefficient for $\overline{\text{R}^+\text{NO}_3^-}$, and γ_4 is the activity coefficient for the neutral complex in the aqueous phase.

We shall define the fraction of plutonium in the aqueous phase in the form of neutral complex \mathfrak{F}_4 by the relation,

$$\mathfrak{F}_4 = \frac{[\text{Pu}(\text{H}_2\text{O})_4(\text{NO}_3)_4]}{C_{\text{Pu}}} \quad (4-8)$$

1. Trace-Sorption Distribution Coefficients.

Let us consider first only systems where the sorption of plutonium is so slight that $[\overline{\text{R}^+\text{NO}_3^-}]$ is nearly constant and equal to the equivalent capacity of the resin for anions. Under these conditions \bar{x}^* is very nearly zero, and we define

$$\lambda = \lambda^0, \quad \bar{x}^* \rightarrow 0. \quad (4-9)$$

Then it is easily shown that

$$\log \theta = \log \frac{\lambda^0 a_{\text{H}_2\text{O}}^2}{\gamma_4 \mathfrak{F}_4} = \log \bar{K}_4 [\overline{\text{R}^+\text{NO}_3^-}]^2 + \log \frac{\bar{\gamma}_R^2}{\bar{\gamma}_6} \quad (4-10)$$

where θ is a pseudo-constant given by $\lambda^0 a_{\text{H}_2\text{O}} / \gamma_4 \mathfrak{F}_4$.

All the quantities on the left of equation (4-10) have been measured experimentally. Various authors^(6,7,14) have measured λ^0 for Dowex 1X4 resin as a function of total molarity of nitric

acid in the aqueous phase, C_{HNO_3} . A generalization of their results is shown in Figure IV-1. Figure IV-2 gives λ^0 versus C_{HNO_3} , normalized

to a value of $\lambda^0 = 28.4$ for unit C_{HNO_3} , as given in reference 14. Davis and de Bruin⁽¹⁵⁾ have recently made an extensive study of the activity of nitric acid solutions, and they give $a_{\text{H}_2\text{O}}$ as a function of C_{HNO_3} . Their data, also normalized to unit C_{HNO_3} , are represented by the dashed line in Figure IV-2. The activity coefficient for the neutral plutonium complex is given as a function of ionic strength by Hart, Brothers, and Allam.⁽¹⁶⁾ Combining these data with the data for the degree of dissociation of nitric acid,⁽¹⁵⁾ one obtains γ_4 as a function of C_{HNO_3} , again normalized to unit C_{HNO_3} . This is shown by the dotted line in Figure IV-2. Data for the fraction of plutonium as the hexanitrate complex \mathcal{F}_6 , as a function of C_{HNO_3} , is given by Ryan.⁽⁵⁾ We might assume, as qualitatively argued in Chapter III, that at higher concentrations of nitric acid the only significant species of plutonium(IV) are the neutral complex and the hexanitrate complex. The curve for $1-\mathcal{F}_6$ versus C_{HNO_3} is shown by the dash-dot line in Figure IV-2. The equality of $1-\mathcal{F}_6$ with \mathcal{F}_4 is obviously incorrect as C_{HNO_3} approaches unity.

That γ_4 is the major contributor to the increase in λ^0 is apparent from Figure IV-2. The constancy of γ_4 in the more concentrated nitric acid solutions reflects the broad maximum in the ionic strength in these solutions. That θ is very nearly unity over the large change in nitric acid concentration indicates that the ratio of activity coefficients in the resin phase, $\bar{\gamma}_R^2/\bar{\gamma}_0$, does not change appreciably even though the ionic strength, water content, degree of swelling, etc., of this phase are changing greatly. One might expect that the changes in $\bar{\gamma}_R^2$ and $\bar{\gamma}_0$ are quite appreciable over this region. However, it is their relative change that is important in the sorption equilibrium, and this is apparently not great.

Ryan and Wheelwright⁽⁷⁾ also investigated λ^0 for sorption from calcium nitrate solutions containing 0.5M nitric acid. These results (dark squares) are compared with their results for nitric acid (dark circles) in Figure IV-3. This comparison is plotted against the upper abscissa, total nitrate concentration in moles per liter. These authors attribute the large difference in these two curves to the formation in the nitric acid solutions of protonated hexanitrate complex, as in reaction (4-1). This would reduce the amount of $\text{Pu}(\text{H}_2\text{O})_4(\text{NO}_3)_4$ available for sorption because of the relation

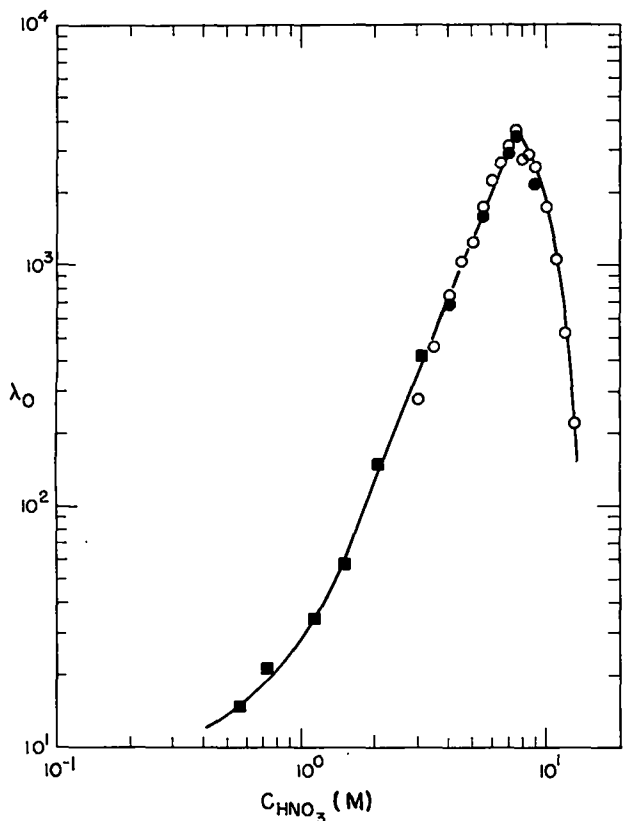


Fig. IV-1. Distribution coefficients with nitric acid⁽¹⁴⁾ [open circles,⁽⁵⁾ dark circles,⁽²¹⁾ squares⁽¹⁴⁾].

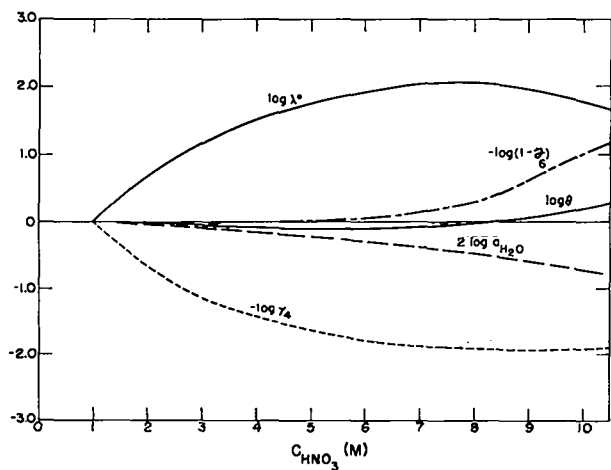


Fig. IV-2. Anion-exchange equilibria with nitric acid.

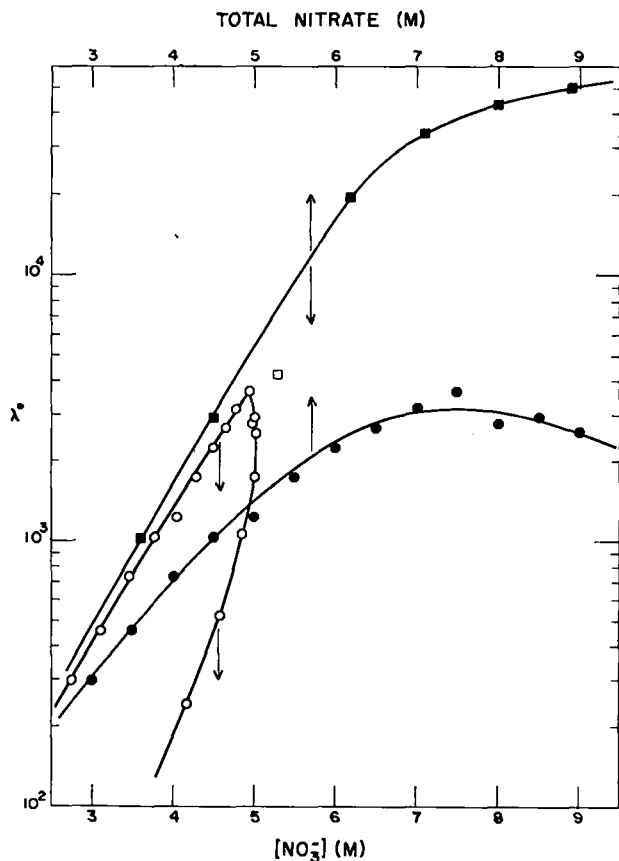
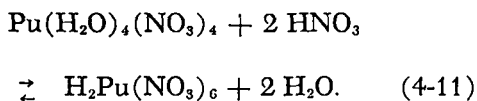


Figure IV-3. Distribution coefficients with nitrate solutions (data from reference 5).



Ryan and Wheelwright⁽⁷⁾ did not consider the appreciable difference in the nitrate ion concentration between calcium nitrate and nitric acid solutions of the same total nitrate concentration. In more concentrated solutions nitric acid is a fairly weak acid, and it is associated to a considerable extent. Data of Davis and de Bruin⁽¹⁵⁾ for the degree of dissociation of nitric acid were used to establish the curve for nitric acid (open circles), plotted in Figure IV-3 against the lower abscissa, molar nitrate ion concentration. In the absence of data for activity coefficients for $\text{Pu}(\text{H}_2\text{O})_2(\text{NO}_3)_6^{-2}$ we can gain some insight into the real difference between calcium nitrate and nitric acid solutions by plotting λ° against $[\text{NO}_3^-]$ rather than total nitrate concentration. The doubling back of the data for nitric acid is caused

by the maximum in $[\text{NO}_3^-]$, as shown in Figure IV-4. With this treatment the difference between the curves is significant, but not great until about $5M$ $[\text{NO}_3^-]$. Protonation of the hexanitrate anion may be the reason that the nitric acid data do not double back exactly coincident. However, the chemical character of 6 and $12M$ nitric acid cannot be the same even though the nitrate ion concentration is the same in these solutions. The "activity" of the nitrate ion could be considerably different, due to large differences in the concentrations of water and undissociated nitric acid. This could easily cause the lack of coincidence. A complete understanding of the contribution which the formation of $\text{H}_2\text{Pu}(\text{NO}_3)_6$ makes to the difference between nitrate salt solutions and nitric acid awaits an independent method for the measurement of the aqueous concentration of $\text{H}_2\text{Pu}(\text{NO}_3)_6$.

A semiquantitative study of λ° with aluminum nitrate and mixed aluminum nitrate-nitric acid solutions has also been described.⁽¹⁷⁾ Representing the exchange by the sorption of hexanitrate anion and neglecting activity coefficient ratios, the equilibrium quotient with trace sorption of plutonium is

$$\begin{aligned} \bar{K}_G &= \frac{[\overline{\text{R}_2^{+2}\text{Pu}(\text{H}_2\text{O})_2(\text{NO}_3)_6^{-2}}] [\text{NO}_3^-]^2}{[\text{Pu}(\text{H}_2\text{O})_2(\text{NO}_3)_6^{-2}] [\text{R}^+\text{NO}_3^-]^2} = \\ &= \frac{\lambda^\circ [\text{NO}_3^-]^2}{\mathcal{F}_{6-2} \bar{X}^2}. \quad (4-12) \end{aligned}$$

With a trace amount of sorbed plutonium $[\overline{\text{R}^+\text{NO}_3^-}]$ becomes \bar{X} , the equivalent capacity of the resin for anions. Previously, we defined \mathcal{F}_6 as the fraction of the plutonium in the hexanitrate form,

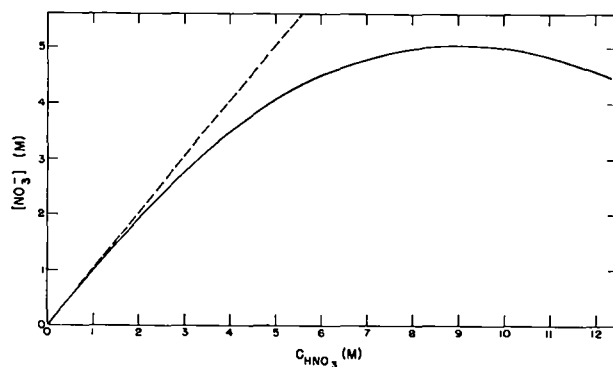


Fig. IV-4. Dissociation of nitric acid.

$$\mathcal{F}_6 = \frac{[\text{H}_2\text{Pu}(\text{NO}_3)_6] + [\text{H Pu}(\text{H}_2\text{O})(\text{NO}_3)_6] + [\text{Pu}(\text{H}_2\text{O})_2(\text{NO}_3)_6]^{-2}}{C_{\text{Pu}}} \quad (4-13)$$

In equation (4-12) we have used the fraction of plutonium as the hexanitrate anion,

$$\mathcal{F}_{6-2} = \frac{[\text{Pu}(\text{H}_2\text{O})_2(\text{NO}_3)_6]^{-2}}{C_{\text{Pu}}} \quad (4-14)$$

Again neglecting activity coefficient ratios, it can be shown that the complicated expression for C_{Pu} , when substituted in equation (4-12), yields

$$\frac{1}{\lambda^\circ [\text{NO}_3^-]^2} = \phi_H + \phi_N, \quad (4-15)$$

where ϕ_H and ϕ_N are functions only of $[\text{H}_3\text{O}^+]/[\text{H}_2\text{O}]$ and $[\text{NO}_3^-]$, respectively. Using the values of Ryan⁽⁵⁾ for λ° in calcium nitrate solutions, and assuming the contribution due to ϕ_H is negligible in these solutions, a graphical relation between ϕ_N and $[\text{NO}_3^-]$ was obtained. Then a graphical relation between ϕ_H and $[\text{H}_3\text{O}^+]/[\text{H}_2\text{O}]$ was determined by calculating, at constant $[\text{NO}_3^-]$ so that ϕ_N is constant, the difference between ϕ_N and $1/\lambda^\circ [\text{NO}_3^-]^2$, using Ryan's data⁽⁵⁾ for λ° in nitric acid solutions. Values of $[\text{H}_3\text{O}^+]/[\text{H}_2\text{O}]$ and $[\text{NO}_3^-]$ in nitric acid solutions were calculated from the degree of dissociation and specific gravity of these solutions. Axtmann, et al.^(18,19) give a method for calculating these concentrations in mixed aluminum nitrate-nitric acid solutions. This allows ϕ_H and ϕ_N to be estimated for the mixed solutions and λ° to be calculated according to equation (4-15). Comparison of these calculated values of λ° with experimental values showed greater reliability than a simple weighted average of distribution coefficients for pure salt and acid solutions of appropriate concentration.⁽¹⁷⁾

All of the work described above was done with Dowex 1X4 resin. Mazumdar, Namboodii, and Sharma⁽²⁰⁾ compare λ° versus C_{HNO_3} for several resins. James⁽²¹⁾ has measured λ° with $C_{\text{HNO}_3} = 7.0M$ for Dowex 1X2 and Dowex 1X10.

The effect of temperature on λ° has been considered by several authors. Ryan and Wheelwright⁽⁷⁾ show λ° against total nitrate molarity for calcium nitrate and nitric acid solutions at 25 and 60°C for Dowex 1X4. James⁽²¹⁾ plots $R \ln(\lambda^\circ [\text{NO}_3^-]^2)$ versus reciprocal temperature to obtain -4.1 kcal/mole for the sum of enthalpies for complex formation and for sorption. The negative temperature coefficient probably reflects a weakening with increasing temperature of either the complexing in the aqueous phase, the ion-pair formation in the resin phase, or both.

2. The Distribution Isotherm. In the last section we considered the effect of various aqueous parameters and temperature on the tranceloading distribution coefficient λ° . We shall now turn our attention to the sorption isotherm. This is the equilibrium relation between the concentrations of plutonium in the two phases λ , as a function of the fraction of resin exchange sites occupied by plutonium. In order to simplify the problem we will now hold constant the temperature and concentrations of everything in both phases but plutonium and R^+NO_3^- .

Returning to equation (4-7),

$$\bar{K}_4 = \frac{[\text{R}_2^{+2}\text{Pu}(\text{H}_2\text{O})_2(\text{NO}_3)_6]^{-2} \bar{\gamma}_6 a_{\text{H}_2\text{O}}^2}{[\text{Pu}(\text{H}_2\text{O})_4(\text{NO}_3)_4] [\text{R}^+\text{NO}_3^-]^2 \bar{\gamma}_R^2 \gamma_4}, \quad (4-7)$$

the quantity $[\text{R}^+\text{NO}_3^-]$ is now no longer constant and equal to \bar{X} . Since we are not varying the aqueous phase except for C_{Pu} , which is very small compared to C_{HNO_3} , it is not too unreasonable to assume that γ_4 and $a_{\text{H}_2\text{O}}$ are constant. It was shown earlier that $\bar{\gamma}_6/\bar{\gamma}_R^2$ is not a strong function of aqueous composition. Since there is considerable penetration of nitric acid into the resin phase, the "ionic strength" of this phase may also be nearly constant even though \bar{x}^* varies. We shall assume that $\bar{\gamma}_6/\bar{\gamma}_R^2$ is constant also. With these assumptions

$$\frac{\bar{K}_4 \bar{\gamma}_R^2 \gamma_4 \bar{\mathcal{F}}_4}{\bar{\gamma}_6 a_{\text{H}_2\text{O}}} = \lambda^\circ = \frac{\lambda}{(1 - \bar{x}^*/\bar{x}_m)^2}, \quad (4-16)$$

where \bar{x}^*/\bar{x}_m is the fraction of resin exchange sites occupied by plutonium. We shall continue to as-

sume that $R_2^{+2}Pu(H_2O)_2(NO_2)_6^{-2}$ is the only significant species of plutonium in the resin phase so that $\bar{x}_m = \bar{X}/2$. Rearranged, equation (4-16) becomes⁽⁶⁾

$$\frac{\bar{x}^*}{\bar{x}_m} = 1 - U + \sqrt{U(U+2)}, \quad U = \frac{\bar{X}}{4C_{Pu}\lambda^0} \quad (4-17)$$

Measurements of λ versus C_{Pu} from 7M nitric acid solutions have been described.⁽⁶⁾ These data, plotted with \bar{x}^*/\bar{x}_m versus $\log C_{Pu}$, are shown in Figure IV-5. The solid line is the curve calculated from equation (4-17), using the datum where \bar{x}^*/\bar{x}_m is the smallest to calculate λ^0 according to (4-16).

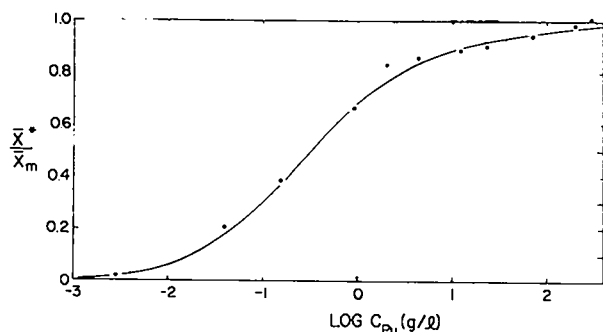


Fig. IV-5. Plutonium, anion-exchange, distribution isotherm.

Unfortunately, equation (4-17) has not been experimentally verified in any solvent other than $C_{HNO_3} = 7M$ or with any resin other than Dowex 1X4. However, considerable random experiments at Los Alamos with other C_{HNO_3} , with mixed aluminum nitrate-nitric acid solutions, and with other crosslinkages of Dowex 1 have not contradicted these mass-action descriptions of the sorption isotherm. Of course, λ^0 is a strong function of the aqueous composition; but we have found no experimental evidence to indicate that, after measuring λ^0 for the solution of interest, λ at higher levels of plutonium sorption cannot be approximately described by equation (4-16).

It should be recalled that equation (4-7) was derived by incorporating pressure-volume effects in the activity coefficients. As \bar{x}^*/\bar{x}_m increases, Dowex 1X4 shrinks quite markedly.⁽⁷⁾ Therefore, one would expect both $\bar{\gamma}_R^2$ and $\bar{\gamma}_6$ to be functions

of \bar{x}^*/\bar{x}_m . Nevertheless, it appears from Figure IV-5 that the ratio $\bar{\gamma}_R^2/\bar{\gamma}_6$ is not a function of \bar{x}^*/\bar{x}_m .

B. Kinetics of the Anion Exchange of Plutonium

The fundamentals of the kinetics of the ion-exchange process were discussed in Chapter II. The partial differential equation (2-15) was derived to describe the radial diffusion of a substance in a spherical resin phase:

$$\frac{\partial x(r)}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \bar{D}(r,x) \frac{\partial x(r)}{\partial r} \quad (2-15)$$

The concentration of the diffusing plutonium at fractional radial distance r is $x(r)$; and $\bar{D}(r,x)$ is the local, intraspherical diffusion coefficient at r , as defined by equation (2-13).

It would be a very difficult experimental problem to directly measure $x(r)$ as a function of t . Even if one changes to other geometries, such as rods or slabs, large pieces of ion-exchange resin are usually not homogeneous. Schlogl⁽²²⁾ has studied ion-exchange kinetics by using a stack of discs which are physically separated and analyzed at t .

A much simpler, but less direct, experimental problem is to measure the total concentration in the resin phase,

$$\bar{x} = \int_0^1 x(r) dr, \quad (4-18)$$

as a function of t .

This can be done by either direct analysis of the resin phase or by measuring a concentration change in the solution phase. Resin-phase analysis is complicated by the problem of instantaneous separation of a portion of the solid phase from all of the liquid phase. This is generally a more difficult problem than the reverse, which is necessary with analysis of the solution phase. However, direct analysis of the resin phase allows the use of an "infinite" volume of solution in which the plutonium concentration does not vary. A varying

aqueous concentration complicates the boundary conditions for the integration of equation (2-15). With the advent of numerical analysis this complication is no longer limiting.

1. *Isotopic Diffusion of Plutonium.* The only particle-diffusion controlled, ion-exchange systems where equation (2-15) has been integrated exactly are those where it has been assumed that $\bar{D}(r,x)$ is independent of r and x and constant throughout the process. This condition can be realized experimentally by studying systems in chemical equilibrium where the only concentration gradient is that of isotopic composition.

Experiments of this type, using a plutonium-239-rich resin phase and a plutonium-238-rich aqueous phase, have been carried out in our laboratory.⁽²³⁾ Some of the results are shown in Figure IV-6. With a finite volume of aqueous phase an approximation to the exact solution of equation (2-15) is given by⁽²⁴⁾

$$\gamma(t) = \frac{w+1}{w} \left\{ 1 - \frac{1}{\alpha - \beta} [\alpha \exp(\alpha^2 \tau) (1 + \operatorname{erf} \alpha \tau^{1/2}) - \beta \exp(\beta^2 \tau) (1 + \operatorname{erf} \beta \tau^{1/2})] \right\} \quad (4-19)$$

where α and β are the roots of the equation

$$y^2 + 3wy + 3w = 0, \quad (4-20)$$

w is the ratio of the total amount of material in the resin phase to that in solution phase, and

$$\tau \equiv \frac{\bar{D}t}{R^2} \quad (4-21)$$

is a dimensionless time parameter. The function (4-19) is tabulated in reference 24. Values of \bar{D} are extracted from experimental determinations of γ versus the logarithm of t by obtaining a best fit with theoretical γ plotted versus the logarithm of τ .

A strong dependence of \bar{D} upon the fractional degree of loading, \bar{x}^*/\bar{x}_m , is apparent from Figure IV-6. Since equilibrium is reached at about $\tau = 1$ and R^2 is about $5 \times 10^{-5} \text{ cm}^2$, with $\bar{D} = 10^{-13}$

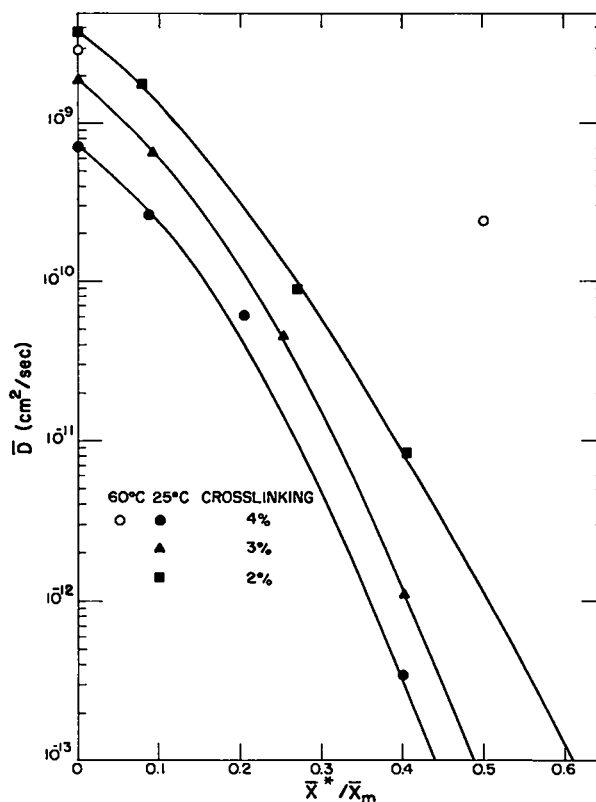


Fig. IV-6. Self-diffusion coefficient of plutonium in anion-exchange resin.

cm^2/sec , which corresponds to about $\bar{x}^*/\bar{x}_m = 0.5$, equilibrium will not be reached for 5×10^8 sec. This is more than a year.

The open circle in Figure IV-6 corresponds to a measurement made at 60°C. A log \bar{D} versus reciprocal temperature treatment of this point and an extrapolation of the data at 25°C indicate that at an equilibrium, fractional loading of about a half, the diffusional activation energy is over 50 kcal/mole.

The results shown in Figure IV-6 would seem to indicate that it would be impossible to obtain in a reasonable time the high equilibrium loadings described in Figure IV-5. However, these data represent sorptions at 25°C over about 50 hr. We shall return to this seeming contradiction after the kinetics of sorption and desorption of plutonium by anion-exchange resin is discussed in the next section.

2. *Sorption Kinetics of Plutonium.* The kinetics of the sorption of plutonium(IV) by

strong-base, anion-exchange resin were first investigated in a quantitative fashion by Ryan and Wheelwright.⁽⁷⁾ They studied sorption by Dowex 1X1, 1X4, and 1X8 and also Dowex 21K, Dowex 3, Permutit SK, Permutit S-1, Duolite A-42 LC, Duolite A-101, and by Amberlite 1RA-400 and 401. These studies showed that the sorption rate was controlled by diffusion within the resin and that the apparent diffusion coefficient decreases with increasing sorption.

The sorption isotherm⁽⁶⁾ was not available to these authors, so qualitative estimates of \bar{x}^* were necessary for the comparison of sorption data with equation (2-16),

$$\frac{\bar{x}}{\bar{x}^*} = \gamma(t) = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{\bar{D}t\pi^2 n^2}{R^2}\right) \quad (2-16)$$

With Dowex 1X1 $\bar{D} = 1.2 \times 10^{-8} \text{cm}^2/\text{sec}$ and was independent of \bar{x} . However, this resin is very soft and shrinks markedly with increasing \bar{x} , making it impractical for plutonium processing. Both Dowex 1X4 and Dowex 1X8 at 25 and 60°C showed an effective diffusion coefficient, as calculated by (2-16), which decreased with increasing \bar{x} . Treatment of the data by comparison with equation (2-16) yields average $\bar{D}(\bar{x})$ from $\bar{x} = 0$ to \bar{x} , rather than instantaneous \bar{D} at \bar{x} , so the values reported by Ryan and Wheelwright⁽⁷⁾ are of little value for quantitative calculations of sorption rates. Comparison of the data at the two temperatures at constant \bar{x} gave a diffusional activation energy,

$$\Delta E = - \frac{R}{T_1 - T_2} \ln \frac{D_1}{D_2} \quad (4-22)$$

of about 7 kcal/mole as $\bar{x} \rightarrow 0$; ΔE increased slightly with \bar{x} .⁽⁷⁾

Ryan and Wheelwright⁽⁷⁾ postulated that the decrease in $\bar{D}(\bar{x})$ with \bar{x} for the higher crosslinked resins was due to increased physical drag by the resin matrix on the diffusing plutonium species, which they asserted is $\text{Pu}(\text{NO}_3)_6^{-2}$. They attributed

the increased friction to the loss of imbibed water because of ion-pair interaction of the sorbed plutonium with the fixed charges on the matrix.

James and Cooper⁽²⁵⁾ provided an empirical relation to describe the rate of sorption of plutonium by Dowex 1X4,

$$\frac{\partial \gamma}{\partial t} = \frac{\pi^2 \bar{D}^0}{2 R^2} \frac{1 - \gamma^2}{\gamma} \exp\left(-\frac{k\bar{x}}{\bar{x}_m}\right) \quad (4-23)$$

where $\bar{D} = \bar{D}^0$, $\bar{x} \rightarrow 0$. With $k = 0$ equation (4-23) reduces to Vermeulen's⁽²⁶⁾ approximation of equation (2-17), as described in Chapter II. For Dowex 1X4 James and Cooper⁽²⁵⁾ assigned a value of about six for k , but a much more extensive subsequent study⁽²¹⁾ fixed the value of k at 3.1 and showed it to be independent of the composition of the aqueous phase.

The strong dependence of \bar{D}^0 upon the composition of the aqueous phase was also studied.⁽²¹⁾ In nitric acid solutions \bar{D}^0 decreases rapidly with increasing C_{HNO_3} with a minimum at about 8M. A qualitative proportionality between \bar{D}^0 and $[\text{H}_2\text{O}]/\lambda^0[\text{H}_3\text{O}^+]$ was demonstrated and was compared to experimentally determined \bar{D}^0 in mixed aluminum nitrate-nitric acid solutions. This is consistent with the suggestion of Boyd, et al.⁽²⁷⁾ that in systems with high λ^0 most of the counterions are bound to the resin matrix, leaving only a few free to diffuse in the liquid within the bead. Since λ^0 is a qualitative measure of this affinity for the matrix, \bar{D}^0 should be inversely proportional to λ^0 . The inverse proportionality to $[\text{H}_3\text{O}^+]/[\text{H}_2\text{O}]$ may indicate the formation of a protonated diffusing species which is less mobile.

The trace-loading, diffusion coefficient \bar{D}^0 is also dependent upon crosslinking. Values from references 21 and 23 and extrapolated values from data in reference 7 are shown in Figure IV-7. The empirical k in equation (4-26) is a function of crosslinking below four nominal percent, but it is independent of temperature.⁽²¹⁾ A trace-loading, diffusional activation energy of 8.7 kcal/mole for Dowex 1X4 in 7M HNO_3 from reference 21 is in

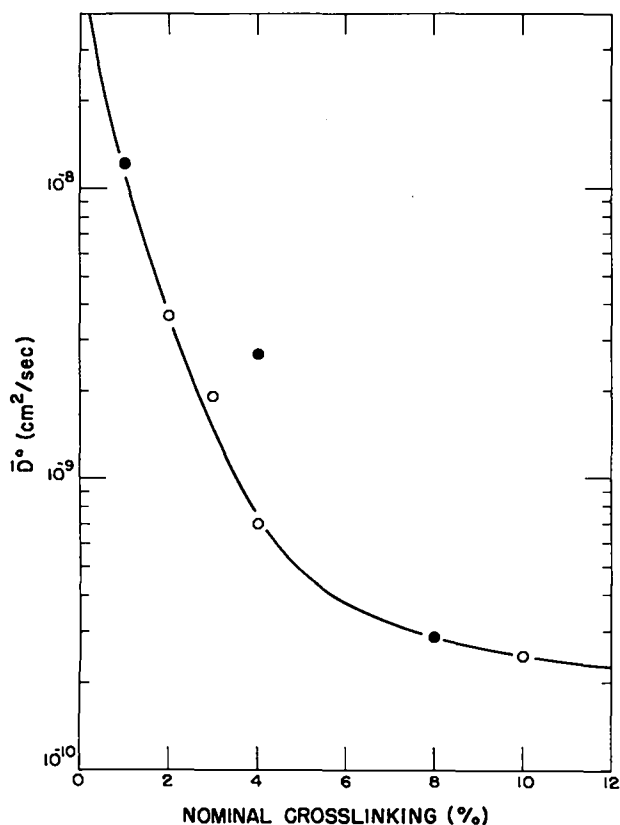


Figure IV-7. Effect of crosslinking on the trace-loading diffusion coefficient of plutonium.

qualitative agreement with the value extrapolated from the data of Ryan and Wheelwright.⁽⁷⁾ While this is rather high compared to aqueous solutions (3 to 6 kcal/mole), it is not unexpected, since the retarding effect of the plutonium-resin interaction is probably lessened by increased temperature.

There are no data in the literature on the kinetics of sorption of plutonium(IV) from nitrate solutions on anion-exchange resin that has been previously equilibrated with plutonium.

3. *Desorption Kinetics of Plutonium.* Unfortunately, there are few quantitative data and greater disagreement in the literature concerning the kinetics of the desorption of plutonium(IV) from anion-exchange resin.

A limited study of the kinetics of desorption from equilibrated resin is described in reference 14. This is the only reference which discusses desorption into more concentrated, nitric acid solutions. This process occurs during the washing cycle of a plutonium-purification operation. In all the experiments the data seemed to fit the constant

diffusion-coefficient theory (equation 2-17) after a correction for the effect of increasing aqueous concentration on x^* . Three experiments at 23°C with different initial equilibrium loading, x^0/x_m , yielded diffusion coefficients which gave the linear relation,

$$D \times 10^{10} = 6.82 - 11.1 \frac{\bar{x}^0}{x_m} \quad (4-24)$$

One experiment conducted at 60°C with $x^0/x_m = 0.691$ indicated that at this initial loading the diffusional, activation energy is about 20 kcal/mole. This is nearly what one might expect for solid-state diffusion.

Desorption into dilute nitric acid is of great process interest, for this is an effective means of removing the purified plutonium in a concentrated solution from the resin in a reasonable time.⁽⁷⁾ Reducing the nitrate ion concentration to low values reduces \mathcal{F}_i in equation (4-10) to extremely low values. Virtually all the plutonium in the aqueous phase assumes a cationic form. Donnan exclusion prohibits these species from entering the resin phase. This causes λ^0 to be very low. As nitric acid is expelled from the resin phase by the Donnan effect, cationic, plutonium species are formed in the resin phase; and these species are also expelled.

Ryan and Wheelwright⁽⁷⁾ also studied elution rates into 1M nitric acid with the various resins mentioned previously. They showed that this process is controlled by diffusion within the resin phase. All the resins except for Dowex 1X4, Permutit SK, and the extremely rapid Dowex 1X1 showed impractically slow elution rates, even at elevated temperatures. The data for Dowex 1X1 and 1X4 were used to estimate diffusion coefficients from equation (2-16). The results are reasonably constant throughout the desorption with a value of 1.1×10^{-8} cm²/sec for Dowex 1X4 at 25°C. However, these authors give no indication of the initial fractional loading level, \bar{x}^0/\bar{x}_m , or whether the preliminary loading operation was conducted for a sufficiently long period of time to insure a uniform, initial distribution of plutonium within the beads. Comparison of the 25 and 60°C results indicated a diffusional activation energy of only 4 kcal/mole. This is about the order of magnitude expected for aqueous, diffusional processes.

With Dowex 1X4, uniformly loaded to about $\bar{x}^0/\bar{x}_m = 0.8$, the desorption diffusion coefficient increases with decreasing C_{HNO_3} in the aqueous phase;⁽¹⁴⁾ but a value of 1×10^{-9} cm²/sec for 1M nitric acid, interpolated from these data, is about one order of magnitude smaller than the value of 1.15×10^{-8} cm²/sec reported by Ryan and Wheelwright.⁽⁷⁾

The desorption data of reference 14 also seem to fit the simple theory of equation (2-16) throughout the desorption process. However, desorption with $C_{\text{HNO}_3} = 0.3$ cannot be made to fit any theoretical curve. Both reference 14 and reference 7 attribute this anomalous behavior with dilute nitric acid to the formation of "insoluble" polymer in the resin phase. As C_{HNO_3} approaches zero, the distribution coefficient seems to approach a value of about 10, as shown in Figure IV-1, rather than the expected value of zero. If this were due to the formation of a less mobile, but soluble, anionic, hydroxyl species, the kinetic data should fit the simple theory with a lower, but constant, diffusion coefficient.

Possibly cationic plutonium is expelled from the resin much more slowly than is nitric acid. Some plutonium escapes before the hydronium ion concentration in the resin reaches a level sufficient to cause the Pu^{+4} to hydrolyze within the resin.

With $C_{\text{HNO}_3} \geq 0.6M$ equilibrium invasion by the nitric acid is sufficient to prohibit polymer formation. Even after the nitric acid distribution is at equilibrium, plutonium(IV), cationic species are continuously expelled, according to simple diffusion theory.

With $C_{\text{HNO}_3} < 0.6M$ the equilibrium distribution of nitric acid within the resin phase is such that polymer will form. The cationic-plutonium concentration drops to the solubility of the polymer. However, that small fraction of the plutonium that is "soluble" in the internal fluid is continuously expelled. If the polymer "dissolution" rate is slower than the plutonium diffusion rate, the "dissolution" of the resin-phase polymer will control the rate of plutonium desorption. The data in reference 14 seem to support a first-order "dissolution rate."

Elution of plutonium from anion-exchange columns by reduction with hydroxylamine nitrate

has been used at Chalk River⁽²⁸⁾ and Los Alamos.⁽²⁹⁾ The presence of hydroxylamine has no effect on the rate of desorption of plutonium (IV) from uniformly loaded resin.⁽¹⁴⁾ The desorption rate is determined solely by \bar{x}^0/\bar{x}_m and C_{HNO_3} . Polymer will form in the resin phase if $C_{\text{HNO}_3} < 0.6M$. However, anion-exchange columns, loaded in several hours or less, do not contain uniformly loaded resin beads. When operating at room temperature hydroxylamine nitrate appears to be a more efficient eluant than dilute nitric acid.⁽²⁹⁾ This matter is discussed further in Chapter V.

With $\bar{x}^0/\bar{x}_m = 0.8$ reference 14 gives a diffusional activation energy of 9.7 kcal/mole for desorption into 0.6M nitric acid. One experimental desorption with the initial, nonuniform sorption that results from only a few hours sorption time⁽¹⁴⁾ was not described by simple theory and showed a desorption rate similar to that reported by Ryan and Wheelwright.⁽⁷⁾

4. Diffusional Mechanism of Plutonium.

As described in Section B-1 of this chapter the attainment of equal, isotopic distribution in Dowex 1X4(100-200) half loaded with plutonium would take 10^8 sec while plutonium may be sorbed, as described in Section B-2, to nearly the entire exchange capacity in 10^5 to 10^6 sec. Of course, one would not expect the two systems to exhibit the same kinetic behavior. With isotopic redistribution, absent are all the perturbations due to changes in swelling, solvent content, and ionic composition and due to changes in electrical and chemical interactions of the exchanging species that are present during sorption and desorption. Nevertheless, it is difficult to attribute three orders of magnitude to such perturbations.

The slight decrease, relative to the self-diffusion data in Figure IV-6, in the apparent sorption diffusion coefficient was attributed to the loss of imbibed solvent during sorption by Ryan and Wheelwright.⁽⁷⁾ They speculate that as the resin shrinks, the intraparticle "pore diameter" approaches the size of the diffusing species. This was extended⁽²¹⁾ to include the effect of the size of the sorbed plutonium. It was shown that by substituting

$$\bar{D}(r,x) = \bar{D}^0 \left\{ 1 - \frac{x(r)}{x_m} \right\} \quad (4-25)$$

into equation (2-15) and integrating numerically, reasonable agreement with experimental sorption data is obtained. This proportionality of the local, intraparticle, sorption diffusion coefficient to the local fraction of unoccupied exchange sites may indicate that the large sorbed $\text{Pu}(\text{NO}_3)_6^{=}$ ion blocks the diffusional paths.

Figure IV-8, taken from reference 23, gives experimentally determined values of Y versus the dimensionless time parameter τ as defined by equation (4-21). The squares are data for Dowex 1X2, the circles for 1X3, and the triangles for 1X10, all for sorption from 7M nitric acid. The shaded area represents a multitude of experiments with 1X4.⁽²¹⁾ The dotted line is the numerical integration⁽³⁰⁾ of equation (2-15) with $\bar{D}(r,x) \equiv \bar{D}^0$, and the solid line is a similar integration employing equation (4-25). The first four points of the 1X3 data were fit to the calculation for $\bar{D}(r,x) \equiv \bar{D}^0$; the dashed line is the result obtained by switching to equation (4-25) when $Y = 0.41$.

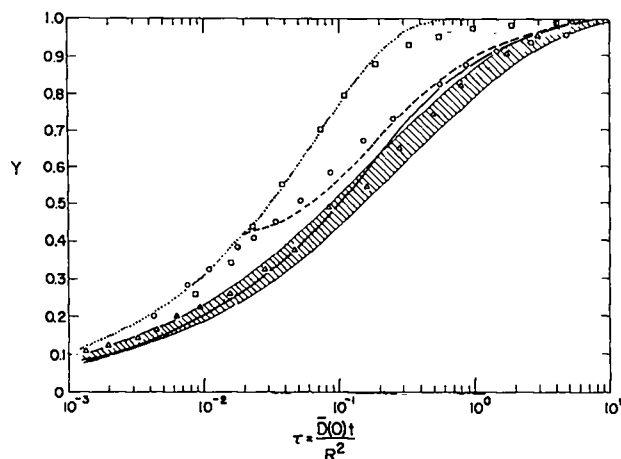


Figure IV-8. Plutonium Sorption on Dowex 1.

One might postulate that the initial data for 1X2 and 1X3 represent unrestrained diffusion. However, at about $Y = 0.8$ for 1X2 and $Y = 0.4$ for 1X3 resin, shrinkage has progressed to the point that sorbed plutonium begins to block diffusion. The data for 1X4 and 1X10 indicate initial "pore diameters" so small that the blocking mechanism is operative from the beginning. These data deviate from this model at the higher ranges of resin loading where shrinkage may have progressed to the point that the diameter of the plutonium-free pore is about equal to the diameter of the plutonium complex.

If this blocking model were the entire answer, the results of the isotopic diffusion studies as shown in Figure IV-6 should vary approximately as equation (4-25), which they obviously do not. But fractional "pore volume" at r cannot depend solely upon the concentration of sorbed plutonium at r . During sorption the plutonium-free, expanded, inner regions of the sphere certainly must inhibit the contraction of the plutonium-laden outer regions. Possibly contraction occurs near the end of the sorption process when the integral plutonium concentration is significant, allowing fast sorption rates but slow isotopic-diffusion rates in systems at chemical and swelling equilibrium. With similar elastic interaction between regions during desorption, diffusion through contracted, but plutonium free, outer regions would be rate controlling, leading to the observed,⁽¹⁴⁾ apparently constant, but reduced, desorption diffusion coefficients, which decrease with increasing initial loading. In order to simulate this strained-shell model modern theory of elasticity must be employed to numerically calculate fractional, local pore volume. Investigations at Los Alamos are proceeding toward this end.

CHAPTER IV — REFERENCES

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CHAPTER V — PERFORMANCE OF PROCESS EQUIPMENT

As described in detail in the previous chapter, plutonium(IV) in a nitrate solution of considerable strength exhibits a strong preference for anion-exchange resin. However, when this strong solution is replaced by a dilute nitrate solution, plutonium(IV) is almost completely excluded from anion-exchange resin. Because these nitrate, anion-exchange properties are nearly unique to plutonium(IV), such a sorption-desorption cycle provides an excellent means for not only the concentration but also the purification of plutonium nitrate solutions. Precautions must be taken to insure the absence of plutonium valences other than four. This can be insured by reduction in dilute acid with hydroxylamine, followed by oxidation with sodium nitrite and acidification.

This exchange of plutonium(IV) from strong nitrate solution is controlled by the mass-action law of chemical equilibrium. If the sorption is carried out in a batch process, this equilibrium is attained before the plutonium is completely removed from the solution. To remove all the plutonium from the strong nitrate solution would require either an infinite amount of resin or a series of equilibrations, using virgin exchanger in each.

The latter process can be realized approximately in a much simpler way by placing the anion-exchange resin in a tube or column and then percolating the strong nitrate solution, containing the plutonium, through the bed; it repeatedly contacts regions where the resin contains no plutonium. Practical considerations usually require that the plutonium solution be passed through the column at a rate that is too fast to allow the resin and solution phases to reach equilibrium in any of these regions. Nevertheless, if the bed is sufficiently long, all the plutonium may be sorbed before any appreciable plutonium appears in the effluent solution.

As the sorption process continues, the anion-exchange resin at the very beginning or top of the column is constantly exposed to fresh plutonium solution. It soon becomes loaded with plutonium; and that region, where the change from nitrate-form resin to plutonium-loaded resin occurs, moves along or down the column. When this exchange zone reaches the bottom of the column, *breakthrough* occurs; and plutonium appears in the effluent.

Just before breakthrough occurs, the flow of plutonium solution to the top of the column is usually discontinued. The exchange zone is still on the column so the *breakthrough capacity* of the column is less than the *equilibrium capacity*, as indicated by the equilibrium sorption isotherm and the feed concentration. The ratio of these capacities is called the *degree of utilization*. Because the exchange zone is usually longer than the column, the degree of utilization in plutonium processing is considerably less than unity.

A. Anion-Exchange Columns

Generally, the performance of an anion-exchange column for the processing of plutonium is affected by a complex interplay of many physical and chemical parameters. These parameters include properties of the resin, such as crosslinking, bead size, capacity for anions, ionic form, etc.; composition of the feed solution, such as plutonium and nitrate ion concentration, acidity, other perturbing anions, species emitting ionizing radiation, etc.; and the physical operating parameters, such as flow rate, temperature, resin packing density and uniformity, column cross section and length, etc.

A generally applicable and quantitatively rigorous theory for the description of the interplay

of these many parameters does not exist. The many ion-exchange theories that are described in the literature, some even labeled as being general and quantitative, are all based on either drastic simplifications or semiempirical relations, tested over a limited range of application.

The various theories can be divided into two general categories:

- 1.) Those based on the assumption that within a layer of the exchanger bed, local equilibrium between solution and solid is attained — the equilibrium theory.
- 2.) Those not containing this assumption and, therefore, containing expressions involving the rate of mass transport between the phases — the rate theory.

The equilibrium assumption is almost never realized in the anion-exchange processing of plutonium. Except for the very low crosslinked resins or possibly the new macroreticular resins, the rate of mass transport is so slow that even if the entire processing column were considered as one layer, equilibrium would not be approached in the normal process times. Even semiempirical expressions for the rate of mass transfer are usually nonlinear differential equations. Because we are considering univalent-divalent exchange, the sorption isotherm usually introduces a nonlinear boundary condition. A linear relation between \bar{x}^* and C_{Pu} exists only with very low C_{Pu} feed solutions where

$$\lambda = \frac{\bar{x}^*}{C_{Pu}} = \lambda^0. \quad (5-1)$$

All of these complications make it impossible to analytically provide a mathematical description of plutonium in an anion-exchange column.

The fundamental, partial differential equation which describes the operation of an ion-exchange column is the material balance,

$$\varepsilon \frac{\partial C_{Pu}}{\partial t} + v \frac{\partial C_{Pu}}{\partial z} = - \frac{\partial \bar{x}}{\partial t}, \quad (5-2)$$

where ε is the fractional, interstitial void space about the resin beads; z is distance along the column in centimeters; and v is the linear flow rate of the aqueous phase in centimeters per second. Equation (5-2) disregards perturbations due to diffusion of the plutonium in the aqueous phase along the column axis and flow maldistributions due to nonuniform ε or to eddy mixing as the solution flows around the beads. It also treats the solid phase as though it were continuous instead of small spheres of definite radius.

The rate of uptake of plutonium, $\partial \bar{x} / \partial t$, must be described by some type of rate law. It has the general form.

$$\frac{\partial \bar{x}}{\partial t} = f(C_{Pu}, \bar{x}, \bar{x}^*, t), \quad (5-3)$$

where C_{Pu} and \bar{x}^* are related in the equilibrium boundary condition by the isotherm,

$$\bar{x}^* = g(C_{Pu}). \quad (5-4)$$

For the sorption of plutonium in an anion-exchange column, equations (5-2), (5-3), and (5-4) yield a highly nonlinear problem for which an exact solution has not been derived. However, it is possible to obtain a numerical solution to the problem, using a computer. Such a computer code is given by Cooper and James.⁽¹⁾

1. *Loading Step.* Defining the fraction of equilibrium, $Y = \bar{x} / \bar{x}^*$, equation (5-3) becomes

$$\frac{\partial Y}{\partial t} = \frac{f}{g} \quad (5-5)$$

For Dowex 1X4 resin equation (5-5) is empirically described by equation (4-26). Equation (4-17) was shown⁽²⁾ to describe g / \bar{x}_m for feed containing 7M nitric acid.

The reliability of the computer calculations was demonstrated⁽³⁾ by allowing the loading of a plant-scale, anion-exchange column to proceed well past breakthrough. The three-in. diam column contained 634 oven-dry g of Dowex 1X4(100-200) NO_3^- . The flow rate was 2.58 ℓ /hr. Consecutive samples of the exit concentration were compared,

as shown in Figure V-1, with the numerical calculation which is represented by the solid line. A column volume is a bed void volume. The slight difference in the slopes of breakthrough curves could easily be due to contributions from the various, minor perturbations omitted from equation (5-2) or to mixing of the exit solution in the small volume between the bottom of the resin bed and the sampling port.

Using the experimentally verified computer code, the many performance-determining param-

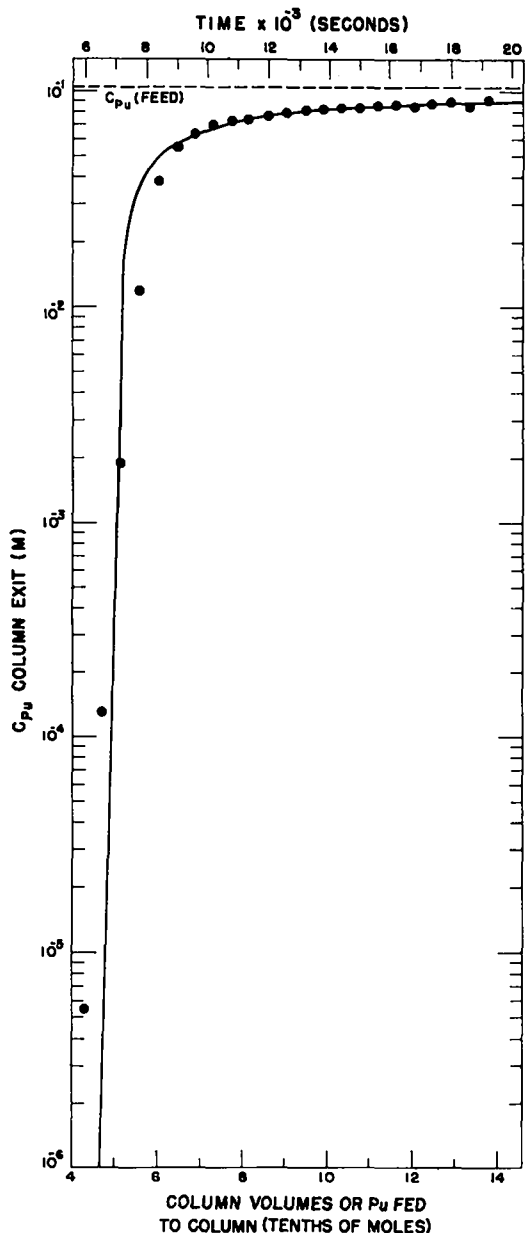


Figure V-1. Numerical duplication of plant-scale, column, breakthrough data.⁽³⁾

eters, such as temperature, flow rate, column dimensions, nitric acid concentration, etc., may be systematically varied in order to seek optimal operating conditions for a given feed solution. In operations where purification is of secondary interest, the parameter to be optimized is usually breakthrough capacity. Beyer and James⁽⁴⁾ have recently shown that if the mass flow rate, volume of the exchanger bed, and criteria for breakthrough are fixed and if the initial conditions are independent of z , then breakthrough capacity is independent of the geometry of the column. That is, the capacity of a short, fat column will be the same as that for a long, thin column of the same volume. Furthermore, nothing is gained or lost by using shapes other than cylinders. Assuming no mixing between columns, a series of short columns of the same total volume as one long one will have the same capacity.

The behavior of columns of Dowex 1X4 has received the greatest attention. Ryan and Wheelwright⁽⁵⁾ recognized that at reasonable process flow rates kinetic parameters play a far more important role in the determination of capacity than do equilibrium parameters. It is not how much plutonium may be sorbed, but how fast it is sorbed, that is important. Increasing \bar{D} by a factor of two is about equivalent to increasing λ^0 by a factor of ten. Ryan and Wheelwright chose 7.2M nitric acid as an optimum solvent because λ^0 is at a maximum at this concentration. However, it was recently demonstrated numerically⁽³⁾ for at least one set of process parameters that 3 or 4M nitric acid will yield a higher column capacity. While λ^0 is reduced from 3500 to 350, \bar{D} is increased from 7×10^{-10} to 7×10^{-9} cm²/sec. The $10^{-5}M$, breakthrough capacity of a 6-in. diam, 40-cm column of Dowex 1X4(100-200)NO₃⁻, fed at 10 L/hr with $C_{Pu} = 0.1$, is increased from 650 to 900 g of plutonium.

Ryan and Wheelwright⁽⁵⁾ also recognized the value of operating at elevated temperatures. Even though an increase from 25 to 60°C in operating temperature decreases λ^0 by a factor of two,^(3,5) it raises \bar{D} by a factor of five.^(3,5) This results in an increase of 250 g in the $10^{-5}M$, breakthrough capacity with a 7M nitric acid feed and the column described above.⁽³⁾ Even at constant mass flow rate, C_{HNO_3} , and temperature, breakthrough capacity is roughly proportional to C_{Pu} .

It is to be expected that the slower the mass flow rate, the larger the breakthrough capacity, for the column residence time for the plutonium is higher, lessening the effect of the unfavorable kinetics. Unfortunately, plant throughput requirements usually set a lower limit on the mass flow rate.

Based on a limited number of small-column experiments with Permutit SK resin, Calleri, et al.⁽⁶⁾ have concluded that for $C_{Pu} \leq 0.4 \text{ g/l}$ sorption is controlled by film diffusion. This is apparently based upon the false conclusion that the constant, equilibrium distribution coefficient in this concentration region indicates film-diffusion control. These authors give kinetic and equilibrium parameters for the sorption of plutonium(IV) on columns containing Permutit SK resin. Their calculations and conclusions are based upon a limited number of experiments, using columns instead of batch sorptions; they employ a large number of assumptions and generalizations. This attaches considerable doubt to their conclusions. Ryan and Wheelwright⁽⁵⁾ demonstrated that Permutit SK has more favorable kinetic properties than Dowex 1X4, but a less favorable equilibrium capacity. The field might greatly benefit from a quantitative consideration of the kinetics and isotherm for this resin in the manner of references 3 and 5.

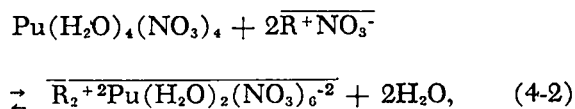
The demonstrated,^(3,5) complex character of the kinetics of plutonium sorption on Dowex 1X4 indicates that any assumptions concerning the kinetics of sorption on any other resin will be suspect until adequately proven by experiment. However, the computer methods⁽¹⁾ that were developed for processing with Dowex 1X4 could be applied to any other resin, once the isotherm, equation (5-4), and the rate law, equation (5-3), have been established experimentally for this resin over the entire range of application.

2. *Washing Step.* The quantitative description of this operation is far less well founded than is the description of the loading step. When washing is commenced, the resin beads in the column vary in average loading \bar{x} for different z . But the prohibitive complication is that the concentration of plutonium within the spheres, $x(r)$ is a different function of r for the different z . Indeed, a semiquantitative theory which attempts

to describe the intraparticle concentration profiles, $x(r)$, during sorption and which is based on a reasonable physical model for diffusion has only very recently been presented⁽⁷⁾ (see the last section of Chapter IV). To attempt to establish an empirical rate law for desorption and prove its applicability for such a complex set of initial conditions, as those which exist in the column at the start of the washing and elution steps, would be a very formidable, experimental problem.

The wash solution usually has the same composition as the feed solution but without any plutonium. It serves to advance the last of the feed solution through the column and, if purification is desired, to elute weakly sorbed impurities. The sorption-desorption of plutonium(IV) on anion-exchange resin is a reversible process. During the washing operation the aqueous phase contains no plutonium, so mass action forces plutonium into the aqueous phase. The driving force for this transfer is the concentration difference between the two phases. As \bar{x} decreases with increasing z , the desorption driving force is lessened. Near the end of the column $\bar{x} = 0$. Any significant concentration of plutonium in the aqueous stream that resulted from desorption nearer the top of the column is resorbed, for now the mass-action, driving force is reversed. If there is insufficient plutonium-free resin at the bottom of the column, the effluent from the wash step will contain plutonium. Because of the very poor desorption kinetics⁽⁸⁾ and the very high affinity of the resin for plutonium, the amount that the region which contains sorbed plutonium is lengthened by the washing step may be barely noticeable. However, if conditions are altered so as to improve desorption kinetics or lessen the affinity, the lengthening can be very significant. In this case the loading step must be stopped long before the wave of sorbing plutonium approaches the bottom of the column in order to save room for plutonium advancement during the washing step.

3. *Elution Step.* To remove sorbed plutonium from the resin phase we must alter the chemical composition of the aqueous phase in order to shift the sorption equilibrium,



to the left. This can be done by increasing $[H_2O]$, that is, by using a dilute eluant, or by decreasing $[Pu(H_2O)_4(NO_3)_4]$. We must use a plutonium-free eluant and also adjust its chemical composition so that any plutonium that is eluted is immediately converted to a nonsorbable form. This may be accomplished by keeping $[NO_3^-]$ at a minimum or by adding an oxidizing or reducing agent to the eluant to convert plutonium(IV) to plutonium(VI) or plutonium(III). Oxidants of sufficient strength to effect the (IV) to (VI) conversion would also attack the resin so this scheme is unattractive. The most common eluant for plutonium processing by anion exchange is dilute nitric acid. Reducing agents, such as hydroxylamine nitrate, ascorbic acid, hydrazine, etc., are sometimes added.

Just as with the loading step we must have not only favorable equilibria for elution but also favorable kinetics. In any practical processing operation elution must be accomplished in a reasonable time with a concentrated product. The same complications that make a quantitative description of the washing step a difficult problem are also present during the elution step. Therefore, as with the washing step our description of elution will be based more on qualitative speculation and experience than on rigorous theory.

It is apparent that plutonium(IV) can hydrolyze within the resin phase^(5,8) when the acidity of the aqueous phase is sufficient to make hydrolysis unlikely there. This has established a lower limit of about $0.6M$ ^(5,8) to C_{HNO_3} in the eluant. The addition of hydroxylamine to the eluant cannot lower this value for it does not penetrate the resin phase. Desorption of nitric acid that was sorbed during the feed and wash steps may contribute to C_{HNO_3} in the eluant reducing the resin-phase hydrolysis problem.

As the boundary between the $7M$ nitric acid wash and the $0.6M$ nitric acid eluant passes over the loaded resin, plutonium is expelled into the resin phase. The trace-loading distribution coefficient, λ^0 , drops from 3500 to about 10.⁽⁸⁾ The concentration of plutonium in the aqueous phase rises until it reaches a concentration that is in equilibrium with the resin composition, according to the isotherm. It is doubtful that the isotherm,

$$\lambda = \lambda^0 \left(1 - \frac{\bar{x}^*}{x_m} \right)^2, \quad (4-16)$$

proven for $C_{HNO_3} = 7M$, applies for $C_{HNO_3} = 0.6M$. Elution with dilute nitric acid should produce a square elution wave, as schematically shown in Figure V-2, whatever the isotherm. Because the plutonium loading was not uniform with z , the top of the wave may not be exactly horizontal. Whether it is slightly sloping to the right or left depends upon whether elution is concurrent or countercurrent to the loading direction.

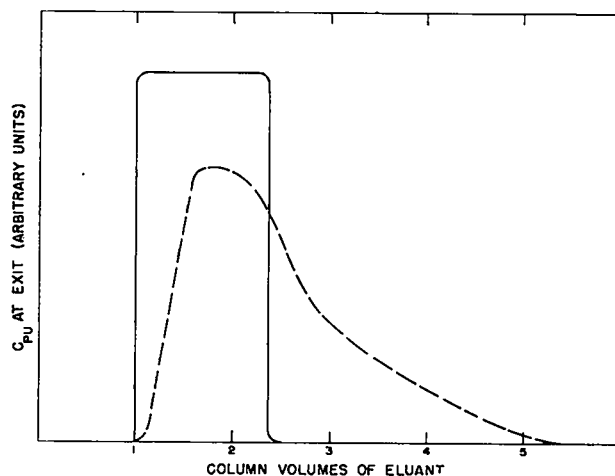


Figure V-2 Schematic elution history.

Only if equilibrium between solution and resin were reached instantaneously upon the arrival of eluant will the elution wave be square, as shown by the solid line in Figure V-2. If the kinetics of desorption are significant, the sides of the wave will have a slope less than infinite. Probably, the rate of desorption decreases as \bar{x} decreases. This will cause the trailing edge of the wave, the edge to the right in Figure V-2, to have an even smaller slope. As the kinetics of desorption become more unfavorable, this "tail" becomes longer; and the volume of eluant necessary to remove all the plutonium becomes greater and greater. The dashed line in Figure V-2 schematically shows such an elution curve. It is the more favorable elution kinetics of Permutit SK resin that led Ryan and Wheelwright⁽⁵⁾ to choose it as the best for plutonium processing. The elution step will take four times longer, and the product will be one-fourth as concentrated if the elution history is described by the dashed line rather than the solid line in Figure V-2.

B. Other Process Equipment

The engineering problems associated with the operation of fixed-bed, ion-exchange columns are inherently simple. But the price of simplicity is the use of both resin and reagents with less than highest efficiency. As was described in Chapter IV, both the relative equilibrium and rate of sorption of plutonium decrease with the degree of loading of the resin. This means that at the later stages of the loading step the top of a fixed-bed exchanger is sorbing very little plutonium while the lower portion is being loaded. This inefficiency can be reduced by segmenting the single column into a series of short columns. As the front of sorbing plutonium progresses along the sequence of columns, additional columns are connected ahead of and in series with the others. Simultaneously, columns are disconnected from the rear of the series and washed and eluted in parallel. Thereby, as regions of the resin bed become inefficient for plutonium sorption, they are regenerated while the efficient regions are still operating. Once they are regenerated, they are reconnected into the sequence at the front. The region where plutonium sorption is occurring, followed by the region being washed, and then, by the region where elution is occurring, is moved around and around the system of columns. The batch character of a single column is eliminated. Considering the entire system of columns as a single unit, it is continuous in the sense that feed solution flows in continuously and product and waste flow out continuously.

The time during which resin is highly loaded and is an inefficient sorber can be reduced still further by increasing the number of columns in the system while holding constant the total volume of resin in the system. However, subdivision is practicably limited by the increased valving and piping problem that results from many, short, column segments. There are numerous, proposed systems in the literature⁽⁹⁻¹⁷⁾ which attempt to eliminate this mechanical problem by moving the resin bed rather than the input and exit streams. Only one column is used, and the resin bed is moved countercurrently to the aqueous stream.

Resin movement may be accomplished by simply allowing it to fall through the upward-moving aqueous stream. The performance of such a

dense, falling bed⁽⁹⁻¹⁴⁾ is limited by the settling rate of the solid and by the necessity of using a sufficiently slow, aqueous flow rate so the resin particles maintain their positions relative to one another. If mixing of the particles occurs, the resin bed is said to be fluidized or agitated; the efficiencies of countercurrent flow are largely eliminated. In order to overcome these performance limitations of a falling bed, the resin may be confined and forced to move mechanically, but this seems to introduce as much mechanical complexity as resin movement sought to eliminate.

1. *Higgins' Contactor*. It was discovered by I. R. Higgins⁽¹⁵⁾ that a packed resin bed in a cylindrical column could be moved undisturbed by hydraulically introducing a sudden pressure drop across the bed. The mass of resin is moved like a piston in a cylinder. However, the aqueous phase must be stationary during the resin movement. Continuous, countercurrent contact is approached by moving the bed a short distance during a short time, relative to the operating time when the solution is moving and the resin is stationary.

The application of the principle of the Higgins' contactor to plutonium processing by anion-exchange at Hanford is described by Oberg and Swift.^(16,17) A similar unit is in operation in France.⁽¹⁸⁾ Permutit SK is used because it is commercially available in the 20-to-50-mesh size. For mechanical reasons a large particle size is desirable in the continuous contactor. The Hanford unit is slightly different than the original Higgins' design⁽¹⁵⁾ in that it uses two columns, one for sorption (XA) and one for elution (XC). The flow diagram is reproduced in Figure V-3. Feed (XAF) enters the middle of the extraction column; wash (XAS) enters at the top. Eluant (XCX) enters the top of the elution column. Waste is removed from the bottom of both columns and product from the bottom of the elution column. The resin-movement time is about 25 sec at 5-min intervals. In-line monitors⁽¹⁹⁻²¹⁾ maintain process control. Plutonium losses to waste range from 0.3 to 0.5 percent. A small volume of plutonium-containing, nitric acid solution at the wash concentration is carried over into the elution column with each resin push. This adds 2 to 5 percent to the total fraction of plutonium that is lost to waste and must be recycled.

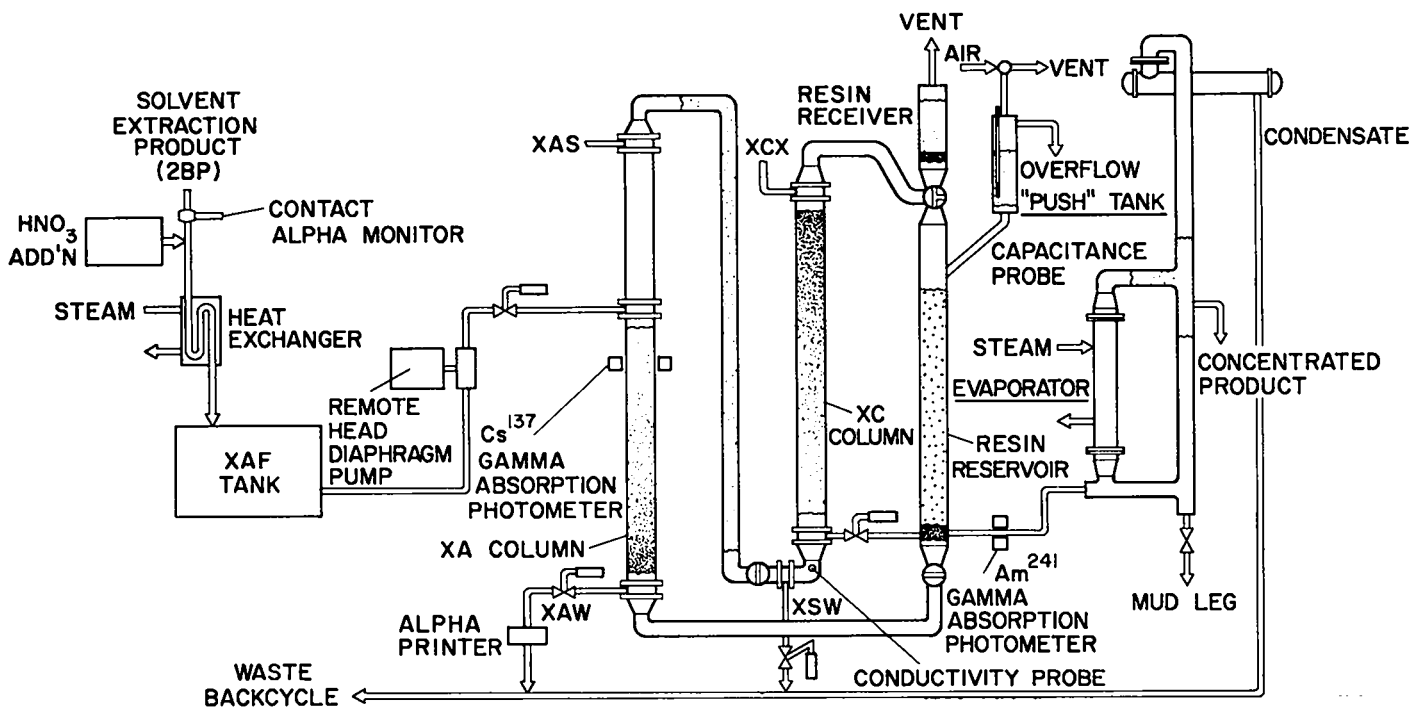


Figure V-3. Flow diagram for continuous anion exchange of plutonium (taken from reference 16).

The practical advantages of the countercurrent contactor over a multi-column, fixed-bed contactor are the lower resin inventory, provided by the much smaller segmentation of the process, and the questionable claim of greater mechanical simplicity. An appropriate, multi-direction, remotely operated valve at the top of each of the fixed-bed columns in a multi-column system could reduce the latter advantage. The capital investment and product value of plutonium processing render the fiscal gain from a lower resin inventory almost insignificant.

With an appropriate term in equation (5-2) to account for the countercurrent transfer of resin, equations (5-2), (4-17), and (4-23) could be combined so as to allow for the numerical duplication of the performance of the countercurrent contactor. Comparison of these calculations with similar calculations of the performance of a multi-column, fixed-bed contactor would establish the more favorable design for a given feed or set of feeds. Such a numerical treatment could also allow optimization of the contactor design parameters.

2. *Agitated Beds.* Frequently one encounters plutonium "solutions" containing solid matter in a very finely divided state. These "solutions" are difficult, and often uneconomical, to

filter. However, a packed bed of anion-exchange resin is a quite efficient filter. Also, the surface of the beads offers a charged double-layer which may tend to agglomerate electrically dispersed colloids. A fixed bed will become plugged by the solids, but these "solutions" can be processed by anion exchange by using agitated beds.

A series of well-stirred, batch contactors are used so that the effluent from one becomes the feed to the next. The stirring increases the mechanical attrition of the resin, but the increase over fixed beds is usually not prohibitive.

If it is assumed that the resin and solution in each contactor is so well stirred that no heterogeneities exist in the solution phase within one contactor, the material balance, analogous to equation (5-2), across the n^{th} contactor is

$$\begin{aligned} \epsilon_n \frac{d(C_{Pu})_n}{dt} + v \frac{(C_{Pu})_{n-1} - (C_{Pu})_n}{Z_n} = \\ = - \frac{dx}{dt}, \quad (5-6) \end{aligned}$$

where $(C_{Pu})_n$ is the concentration of plutonium in the effluent from contactor n , $(C_{Pu})_{n-1}$ is the con-

centration of plutonium in the feed to contactor n , and Z_n is the length of contactor n in the direction of fluid flow.

Chen, Belter, and French⁽²²⁾ discuss the numerical solution of equation (5-6) for the nitric acid, anion exchange of thorium; but they use an empirical rate law and an empirical isotherm, rather than the more theoretical forms established by Carroll.⁽²³⁾ Prout and Fernandez discuss the agitated-bed, anion-exchange processing of plutonium,⁽²⁴⁾ thorium,⁽²⁴⁾ and neptunium;⁽²⁵⁾ but they worked with very dilute solutions of the actinides so that the isotherm was nearly linear; and they used smoothed curves through experimental, sorption-time data instead of a specific rate law. Using proven computer techniques⁽²²⁾ and established kinetic and equilibrium relations,^(8,23) a numerical analysis of a given process could yield optimal values for ϵ_n and Z_n for each contactor and optimal values for v and the number of contactors for the process.

Pratt⁽¹⁴⁾ gives preliminary, engineering experience concerning two moving, fluidized-bed contactors: a single-stage Weiss contactor, and the multi-stage "MABIE" contactor. In both units the major gain over the Higgins' contactor seems to be the ability to process feed streams which contain particulate matter; this advantage is compensated by the inherently lower sorption efficiency of the fluidized beds.

C. Plutonium Purification

This section will deal with the use of anion exchange for the purification of plutonium. The subject may be conveniently divided by considering various classes of impurities to be separated from plutonium:

- 1.) those elements not sorbed by anion-exchange resin, which require no discussion from process standpoint,
- 2.) those elements which are weakly sorbed by anion-exchange resin, which behave independently of one another, and
- 3.) those few elements strongly sorbed by anion-exchange resin will require individual discussion.

Fission products generally belong in either class 1 or 2. However, a discussion of the decontamination of irradiated plutonium will be deferred, along with the specific problem of uranium-plutonium separation, to Chapter VI, which deals with the important problem of the reprocessing of plutonium-laden, reactor fuels.

The most desirable feature of plutonium processing by anion exchange is the high specificity of the process. A limited number of other elements are sorbed by anion-exchange resin from concentrated nitrate solutions, and all but a very few are only slightly sorbed. The trace-sorption, distribution coefficients of most elements with Dowex 1X4 from 7M nitric acid are given in Figure V-4.⁽²⁾ Qualitative general data⁽²⁶⁾ and specific data on various elements,⁽²⁷⁻³²⁾ given as a function of C_{HNO_3} , may be found in the literature. However, these studies were made on various types of resin and often without regard to the degree of resin loading. The trivalent, transplutonium actinides exhibit weak sorption from strong nitric acid solutions.

In the aqueous phase with its very high ionic strength all the sorbable constituents may be treated as trace components. That is, their behavior depends only upon the properties of the solution and is entirely independent of one another. However, in the resin phase any component which occupies a significant fraction of the exchange sites will affect the behavior of the other sorbable components. Significant loading can result from a high affinity of the component for the resin or from a high aqueous-phase concentration. As a general rule we shall consider as being weakly sorbed impurities, those elements having a λ° in the range $0.1 < \lambda^\circ < 10$. Unless their aqueous concentration is many times that of plutonium, their anion-exchange behavior will be independent of one another; and they will not perturb the behavior of plutonium. Elements with $\lambda^\circ > 10$ will be considered as strongly sorbed impurities. Their presence will perturb the anion-exchange behavior of all sorbable constituents. Of course, elements with $\lambda^\circ < 0.1$ remain essentially in the aqueous phase and pass directly through the anion-exchange column.

It will be considered beyond the scope of this monograph to discuss the use of anion exchange in the analytical chemistry of plutonium. The

$$\lambda' = \frac{\text{AMOUNT OF SPECIES / ml. OF RESIN BED}}{\text{AMOUNT OF SPECIES / ml. OF SOLUTION}}$$

ROOM TEMPERATURE, 7M HNO₃, DOWEX I-X4(50-100) NO₃⁻, LOW-LEVEL LOADING

													13 Al III-0.0 CC				15 P V-0.18 CI
21 Sc III-0.23 CI	22 Ti IV-0.0 CC	23 V IV-0.0 CV	24 Cr III-0.0 CV VI-8.6 CV	25 Mn II-0.0 CC	26 Fe III-0.0 CI	27 Co II-0.0 CV	28 Ni II-0.0 CV	29 Cu II-0.0 CV	30 Zn II-0.0 CI	31 Ga III-0.0 CI	32 Ge IV-0.0 CC	33 As III-0.34 CI V-0.27	34 Se IV-0.16 CI				
39 Y III-0.0 CI	40 Zr IV-0.38 CC	41 Nb V-0.19 CI	42 Mo VI-0.25 CI				44 Ru IV-0.15 CV	45 Rh III-0.94 BE	46 Pd II-5.2 CV	47 Ag I-0.23 CI	48 Cd II-0.09 CI	49 In III-0.0 CI	50 Sn IV-0.0 CC	51 Sb III-0.0 CI V-0.0 CI			
57 La III-1.4 CI	72 Hf IV-0.24 CI	73 Ta V-0.0 CI	74 W VI-1.6 CI	75 Re VII-1.6 CI	76 Os IV-1.7 CI	77 Ir IV-74 CV	78 Pt IV-47 CV	79 Au III-116 BE	80 Hg II-1.3 CI	81 Tl I-0.0 CI	82 Pb II-0.29 CC	83 Bi III-38 CI					
58 Ce III-1.2 CI			59 Pr III-0.67 CV			60 Nd III-0.59 CV			62 Sm III-0.24 CI			63 Eu III-0.18 CI		68 Er III-0.09 CV		69 Tm III-0.10 CI	
90 Th IV-102 BE			92 U VI-3.9 CV			94 Pu IV-978 BE											

ATOMIC SYMBOL
NUMBER

VALENCE - λ'

METHODS

CI - COLUMN - ISOTOPE
CC - COLUMN - CHEMICAL
CV - COLUMN - VISUAL
BE - BATCH EQUILIBRATION

ERROR:
APPROXIMATE % AVERAGE
DEVIATION FROM MEAN

$\lambda' = 0.0 \rightarrow 0.5; 50 \rightarrow 15\%$
 $\lambda' = 0.5 \rightarrow ; \sim 10\%$

Figure V-4. Distribution coefficients of the elements with 7M nitric acid.⁽²⁾

reader is referred to several recent reviews of this subject⁽³³⁻³⁶⁾ and to two specific papers.^(37,38)

1. *Separation from Weakly Sorbed Impurities.* The anion-exchange separation of plutonium from weakly sorbed impurities was quantitatively discussed by Cooper and James.⁽³⁹⁾ They treat various levels of approximation for the theoretical description of impurity behavior.

With the assumptions that the impurities behave independently from the plutonium and that impurity equilibrium between the phases is instantaneously achieved, impurity *i* will appear in the effluent when

$$V_i = aZ(\lambda'_i + \epsilon) \quad (5-7)$$

liters of feed (and wash) have been fed to the column. The column is of cross-sectional area *a* and of height *Z*. The fractional void volume is ϵ , and λ'_i is the volume, trace-loading, distribution coefficient of impurity *i*,

$$\lambda'_i = \rho \lambda^0_i, \quad (5-8)$$

where ρ , the packing density of the resin (oven-dry grams per milliliter of bed), is usually about 0.4. The volume of wash solution necessary to remove *i* from the column is also V_i . Since the diffusion coefficients of weakly sorbed species in anion-exchange resin⁽³⁹⁾ are generally relatively large, the instantaneous-equilibrium assumption is a good rough approximation; the behavior of impurities is roughly described by equation (5-7).

With the inclusion of finite, impurity diffusion rates, but the exclusion of any effect due to the presence of plutonium, the volume of wash solution necessary to remove impurity *i* is

$$V_i = aZ(\lambda'_i + \epsilon) (1 + 2\sqrt{H_i/Z}), \quad (5-9)$$

where H_i , the theoretical-plate height, is given by

$$H_i = \frac{0.14 R^2 v \lambda'_i}{D_i(\lambda'_i + \epsilon)} \quad (5-10)$$

Here \bar{D}_i is the resin-phase, diffusion coefficient of i , and v is the linear flow rate in the column.

Cooper and James⁽³⁹⁾ also considered the model where both \bar{D}_i and λ'_i are functions of \bar{x} , the concentration of plutonium in the resin phase. Of course, the calculation of \bar{x} , as a function of t and z , is a separate problem, which is described in the first section of this chapter. By the definition of a weakly sorbed impurity the presence of impurities does not complicate the behavior of the plutonium. Given the functional relations $D_i(x)$ and $\lambda'_i(\bar{x})$, Cooper and James⁽¹⁾ describe a computer code for the calculation of the behavior of several impurities and plutonium in an anion-exchange column.

A mass-action treatment⁽⁴⁰⁾ of equilibrium yields

$$\frac{\lambda'_i(\bar{x}^*)}{\lambda'_i(0)} = \left(1 - \frac{\bar{x}^*}{\bar{x}_m}\right)^2 \quad (5-11)$$

However, equation (5-11) was found not to hold for several weakly sorbed impurities when thorium was used in place of plutonium.⁽⁴⁰⁾ Thorium is also sorbed as the hexanitrate anion from concentrated nitrate solutions⁽²⁷⁾ but with a slightly lower distribution coefficient than that of plutonium. In fact, $\lambda'_i(\bar{x}_{Th}^*)/\lambda'_i(0)$ was found to be greater than unity⁽⁴⁰⁾ for several elements for $0 < \bar{x}_{Th}^*/\bar{x}_m < 0.5$. This synergistic effect of thorium has not been quantitatively explained. Possibly partial occupation of the exchange sites by the hexanitrate, thorium anion renders the remaining sites more reactive to the impurity elements.

No data are available in the literature for $D_i(\bar{x})$. Cooper and James⁽³⁹⁾ assumed \bar{D}_i shows the same exponential dependence upon \bar{x}/\bar{x}_m as does \bar{D} :

$$\bar{D}_i(\bar{x}) = \bar{D}_i(0)e^{-k\bar{x}/\bar{x}_m} \quad (5-12)$$

The impurities move down an anion-exchange column much faster than the wave of sorbing plutonium, since λ^0 is much larger than λ'_i . As plutonium is sorbed on top of the previously sorbed impurities, if equation (5-11) applies, the impurity distribution coefficients should be reduced. The impurities would be forced out of the resin by the advancing, plutonium wave. The

concentrations of the impurities in the aqueous phase in that region just ahead of the wave of sorbing plutonium should rise above their feed concentrations. Inclusion of the effect described by equation (5-12) would trap previously sorbed impurities in the region where plutonium is sorbed. They would be released slowly, and the impurity wave would develop a long "tail" as it separates from the plutonium wave during the washing step.

One pilot-plant, column purification with impurities of silver, mercury, uranium, and bismuth is reported by Cooper and James.⁽³⁹⁾ They compare numerically calculated, impurity breakthrough curves with experiment. Reasonable agreement was obtained by the inclusion of equation (5-12). That is, the experimental data showed a trailing effect. However, the maxima in the experimentally determined, elution waves showed no effect due to (5-11). Agreement between experiment and calculation was obtained by using $\lambda'_i(\bar{x}) \equiv \lambda'_i(0)$.

These results can be regarded as only a hint to the possible behavior of weakly sorbed impurities in the anion-exchange process for the purification of plutonium. However, given specific impurities, a few independent measurements of $D_i(\bar{x})$ and $\lambda'_i(\bar{x})$ would allow the numerical prediction, according to the computer methods of Cooper and James,⁽¹⁾ of process performance.

2. *Separation from Thorium.* From Figure V-4 the trace sorption distribution coefficient for thorium with Dowex 1X4 from 7M nitric acid is 10^2 . This indicates that thorium has a high affinity for anion-exchange resin. The separation from plutonium is so poor as to be impracticable from a process standpoint.

There is very little of a quantitative nature in the literature regarding the nitrate, anion-exchange behavior of thorium-plutonium(IV) mixtures. Carroll⁽²³⁾ describes the anion-exchange behavior from nitrate solutions of thorium alone. Any quantitative calculations for strongly sorbed impurities, such as described in the previous section for weakly sorbed impurities, are complicated by the fact that not only are \bar{D}_{Th} and λ_{Th} functions of \bar{x} and \bar{x}_{Th} ; but also \bar{D} and λ are functions of \bar{x} and \bar{x}_{Th} . A few qualitative measurements in our laboratory indicate that the mass-action description,

$$\frac{\lambda(\bar{x}, \bar{x}_{Th})}{\lambda(O, O)} = \frac{\lambda_{Th}(\bar{x}, \bar{x}_{Th})}{\lambda_{Th}(O, O)} =$$

$$= \left(1 - \frac{\bar{x} + \bar{x}_{Th}}{\bar{x}_m} \right)^2, \quad (5-13)$$

is not valid. To measure $\bar{D}_{Th}(\bar{x}, \bar{x}_{Th})$ and $\bar{D}(\bar{x}, \bar{x}_{Th})$ in mixed systems for sufficient \bar{x} and \bar{x}_{Th} to establish an empirical relation between these four parameters appears to be a hopeless task. Quantitative, numerical calculations of the performance of the anion-exchange processes for the separation of plutonium from strongly sorbed impurities will have to await theoretical descriptions of the resin-phase phenomena so that quantitative mass-transfer and equilibrium relations can be based on this theory.

A process for the separation of plutonium and thorium by anion exchange from hydrochloric acid was described by James and Christensen.⁽⁴¹⁾ The distribution coefficient of thorium with anion-exchange resin from chloride solutions is zero while the coefficient for plutonium(IV) is similar to that for the nitrate system. This provides an excellent separation process, especially for high-thorium, low-plutonium mixtures. However, the chloride, anion-exchange system has a much poorer specificity than the nitrate system. Many elements form chloride complexes and are sorbed by anion resin from chloride solutions⁽²⁸⁾ (e.g. iron, gallium, chromium, manganese, etc.). Therefore, both anion-exchange processes must be employed for complex, thorium-containing mixtures. The corrosive problem of handling hydrochloric acid-containing, waste and product solutions in the conventional, stainless-steel, plutonium-processing equipment can be overcome by adding aluminum nitrate to these solutions.⁽⁴¹⁾

It is interesting to postulate a universal, plutonium-purification scheme, using anion exchange from hydrochloric acid. Plutonium(IV) is easily reduced and held as plutonium(III) in the non-oxidizing atmosphere of strong, hydrochloric acid solutions. A two-cycle process could first separate plutonium(IV) from all nonsorbable impurities and then, after reduction, separate plutonium(III) from all sorbable impurities. A similar two-cycle process with universal application might be postulated by employing nitrate anion exchange from

high-salt, low-acid solutions. Such solutions are considerably less oxidizing than nitric acid solutions which provide the same anion-exchange performance characteristics (see Chapter IV). Hydroxylamine nitrate will effect and hold the reduction of plutonium(IV) to plutonium(III) in solutions containing 1M aluminum nitrate and 0.5M nitric acid. The anion-exchange behavior of plutonium(IV) in this solvent is very similar to its behavior in 7M nitric acid.

3. *Separation from Neptunium.* The recent interest in plutonium-238 as a heat source has stimulated an interest in the separation of neptunium from plutonium. Plutonium-238 is produced by neutron irradiation of neptunium-237, which is produced in small quantities as a by-product in the formation of plutonium-239 in nuclear reactors, using uranium-238-235 mixtures as fuel. The neptunium-237 follows the fission products into the waste stream with most fuel-reprocessing schemes.

Ryan⁽⁴²⁾ discusses a fixed-bed, anion-exchange process for the recovery of neptunium from waste solutions containing plutonium, uranium, fission products, thorium, and common metallic impurities. Many of the conclusions regarding the performance of this process are based upon the similarity of neptunium(IV) and plutonium(IV). Data reported by Ryan⁽²⁷⁾ for λ_{Np} versus C_{HNO_3} , are similar, but slightly lower at the same C_{HNO_3} , than the data for plutonium(IV).

The oxidation-reduction chemistry of neptunium is similar to that of plutonium, except that the higher oxidation states are more stable. Neptunium(IV) is unstable toward oxidation to the weakly sorbed neptunium(V) in strong, nitric acid solutions. However, the strong, nitrate complexing and fourth-power dependence of the oxidation on the hydrogen ion concentration tend to help stabilize the four-valent state.

The anion-exchange separation of neptunium and plutonium is based upon the reduction of plutonium(IV) to the very weakly sorbed plutonium(III). With the strong, nitric acid solutions necessary to provide a sufficiently high affinity of the resin for neptunium(IV), a more powerful reducing system is necessary to hold plutonium(III) than is necessary to hold neptunium(IV). With 6M nitric acid and an operating temperature of 25°C, hydrazine is sufficiently stable if used in conjunction with ferrous sulfamate.

The ferrous ion provides a single-electron, exchange mechanism for the rapid reduction of plutonium(IV).

Ryan⁽⁴²⁾ suggested a single-cycle process, but only fair separations were achieved. Burney⁽⁴³⁾ has more recently described a three-cycle process. In the first cycle no attempt is made at any separation of plutonium and neptunium; but separations from uranium, fission products, and other metallic impurities are achieved in the same manner as with plutonium alone. No reduction to plutonium(III) is effected, and the two elements behave as one. In the second cycle the plutonium-neptunium separation is achieved. No reason is given for the sorption of both elements in the four-valent state, and then the desorption of plutonium by its reduction to the three-valent state with a 5.5M nitric acid wash, containing ferrous sulfamate and hydrazine. This desorption process is certainly limited by diffusion of plutonium(IV) within the resin, for probably very little of the reductant penetrates into the solid. Since the diffusion rates of the two elements are probably similar, as much neptunium(IV) would be desorbed as plutonium(IV), the unreduced neptunium(IV) being resorbed further down the column. It would seem much more feasible to elute the first cycle with dilute nitric acid, containing ferrous sulfamate and hydrazine. Addition of concentrated nitric acid to this product could form the second-cycle feed. That Burney's process is limited by resin-phase diffusion of plutonium(IV) is confirmed by the reported strong dependence of the separation upon resin particle size and cross-linking. The third cycle in the process is a final purification of plutonium. The engineering and performance of the process are described by Tetzlaff⁽⁴⁴⁾ and by Caracciolo.⁽⁴⁵⁾

The higher alpha activity of plutonium-238 causes several radiolytic effects. The radiolytic oxidation of plutonium(III) to (IV) and (IV) to (VI) is more rapid than with plutonium-239, causing greater losses to the decontamination-wash and feed effluents. Furthermore, radiolytic attack of the resin is greater than with plutonium-239 (see Section E of this chapter).

The neptunium oxide targets contain aluminum oxide. It is interesting to speculate that the plutonium-neptunium separation could be effected more easily using a low, nitric acid feed, containing about 1M aluminum nitrate. As described in

Chapter IV, the anion-exchange behavior of plutonium(IV) in this solvent is similar to its behavior in 7M nitric acid. If the anion-exchange behavior of neptunium(IV) is also favorable in the salt solution, it might be possible to effect and hold the plutonium reduction with a weaker, less dangerous and less expensive reducing agent, such as hydroxylamine.

D. Common Specific Recovery Problems

There are a few specific compositions of feed solution which are generated by operations common to nearly all plutonium-processing facilities. Metallurgical scrap is generated by the investigation of specific metallic fuels; oxalate filtrate results from the precipitation of plutonium oxalate; and reduction residues from the reduction of plutonium to metal produces solutions containing calcium, magnesium and aluminum nitrates, and fluoride.

1. *Metallurgical Scrap.* Anion exchange offers a general recovery method of sufficient specificity for the recovery of plutonium, metallurgical scrap.^(46,47) Elements which are of current interest for alloying with plutonium include magnesium aluminum, iron, cobalt, copper, gallium, zirconium, tantalum, mercury, bismuth, uranium, thorium, the rare earths, and the platinum metals. Systems using stainless steel add chromium, manganese, nickel, and molybdenum to this list. From the trace loading, distribution coefficients (see Figure V-4) these elements may be divided into three groups: those showing no sorption, magnesium, aluminum, iron, cobalt, copper, tantalum, gallium, chromium, nickel, and manganese; those showing weak sorption, molybdenum, zirconium, mercury, bismuth, uranium, rare earths, osmium, ruthenium and rhodium; and those showing strong sorption, thorium, neptunium, platinum, palladium, and iridium. Of course, the elements in the first group offer no problem, and the general behavior of those in the second group was discussed in Section C-1 of this chapter. The separations of thorium and neptunium from plutonium were discussed in Sections C-2 and C-3 of this chapter.

Although the three platinum metals, platinum, palladium, and iridium, are strongly sorbed by the resin and cannot be efficiently removed during the washing step, they can be separated from plutonium because they are not removed

from the resin by the elution step. The decomposition of the nitrate complexes of the platinum metals is kinetically inert; the sorbable, anionic complexes remain for some time, even in the presence of the dilute eluant. As successive cycles are made with the same column, platinum metals in the feed will accumulate in and poison the resin, lowering its capacity for plutonium. The same argument applies to osmium, ruthenium, and rhodium if they are insufficiently removed during the washing step. Also, molybdenum forms a highly sorbed oxyanion in dilute nitric acid so any that remains on the column after washing will not be removed with the plutonium product.

2. *Oxalate Filtrate.* Many plutonium-processing operations include the precipitation of plutonium as the oxalate from dilute-acid solutions by the addition of oxalic acid. Plutonium losses to the filtrate range from 0.05 to 1 g/L.^(48,49) Direct recovery by anion exchange of the plutonium from this oxalate filtrate has been demonstrated.^(48,49) Wheelwright⁽⁴⁸⁾ proposes direct acidification of the feed with nitric acid to a final concentration of 9M. The higher concentration is necessary to reduce the complexing effect of the oxalate. Plant experience⁽⁴⁹⁾ indicates that this also may be accomplished by adding 0.2M aluminum nitrate to the conventional 7M-nitric acid feed. This reduces column capacity, due to less favorable kinetics;⁽³⁾ column capacity can be restored by using decreased flow rates or by using elevated-temperature operation⁽⁴⁸⁾ if a high throughput is necessary. Filtrates which contain fluoride will show no adverse, processing performance if 1 mole of aluminum nitrate per mole of fluoride is added.⁽⁴⁸⁾ A 24-hr digestion with hydroxylamine, before oxidation with sodium nitrite and acidification, may be necessary to insure the removal of any plutonium(VI).⁽⁴⁹⁾ Wheelwright⁽⁴⁸⁾ suggests, and sites a plant process for, the use of a three-column, "merry-go-round" flow sheet, as discussed at the beginning of this chapter, for the anion-exchange processing of oxalate filtrate.

3. *Reduction Residues.* Plutonium tetrafluoride is reduced to the metal by reaction with calcium. Unreduced plutonium and small bits of metal remain with the slag, crucible, and other reduction residues in sufficient quantity that the plutonium must be recovered. The dissolution of these residues in nitric acid is discussed by Christensen, Maraman, and Baker.⁽⁴⁹⁾ The filtered, nitric acid solution, containing corrosion

products from stainless-steel equipment, magnesium from the crucible, calcium from the slag, aluminum which has been added to reduce corrosion by fluoride, and plutonium at about a gram per liter,⁽⁵⁰⁾ may be processed by nitrate anion exchange.⁽⁴⁹⁻⁵¹⁾

Russell⁽⁵⁰⁾ measured distribution coefficients λ with synthetic, dissolver solution under different conditions. Varying C_{HNO_3} , from 5.5 to 6.5M had little effect, but increasing fluoride ion molarity above that of aluminum decreased the coefficient. Apparently aluminum should be added to the feed to approximately the molar concentration of the fluoride. Breakthrough curves,⁽⁵⁰⁾ as a function of volume flow rate and C_{Pu} , are qualitatively consistent with the behavior that is to be expected from the results of fundamental studies,⁽³⁾ which indicates that with these high salt concentrations lower acidities may give better process performance. Operation at 65°C caused considerable resin attack, but Russell⁽⁵⁰⁾ demonstrated satisfactory operation at 45°C. It would appear that established, computer techniques⁽¹⁾ and fundamental, kinetic, and equilibrium relations⁽³⁾ could be used to determine optimal, process parameters for this specific feed and for whatever plant performance may be required.

A few column volumes of 8M-nitric acid wash⁽⁵⁰⁾ will reduce the impurities, none of which is sorbed by the resin, to a few hundred parts per million of plutonium. All of the conventional, elution techniques, as discussed in Section A-3 of this chapter, may be applied to the anion-exchange recovery of plutonium from reduction residues.^(50,51)

E. Resin Stability

In addition to the economic consideration, the life expectancy of anion-exchange resin is of interest because resin degradation is gradual and its effects can alter process performance. This degradation is manifested by physical fracture; swelling, due to loss of crosslinking; decreased exchange capacity; and decreased basicity.

Fracture can be due to mechanical handling of the resin, which is especially important in continuous-contactor and agitated-bed applications, or to the internal, transient strains that occur during the shrinking or swelling of the beads

in a plutonium cycle. Unfortunately, there are no quantitative data in the literature regarding mechanical attrition, and cycling effects are always coupled with the more serious, chemical and radiation effects.

Decreased crosslinking, capacity, and basicity are caused by both chemical and radiolytic attack. There is considerable discussion of both of these problems in the literature.

1. *Chemical Stability.* In recent years a few instances of pressurization and fire have occurred in plutonium-processing facilities employing anion-exchange columns. Two incidents, one involving a fixed-bed column at the Rocky Flats plant,⁽⁵²⁾ and the other involving a continuous contactor at Hanford,⁽⁵³⁾ have been described in the literature. These incidents have prompted detailed investigations of the thermochemical stability of the process.^(54,55) The Hanford work⁽⁵⁵⁾ describes externally-heated, pipe-pressurization tests and calorimeter experiments with Permutit SK resin. Measured thermal and kinetic parameters are applied to operating conditions with the aid of computer techniques, which are also described. These numerical techniques could be applied to any process design in order to evaluate its thermochemical safety. The Rocky Flats work⁽⁵⁴⁾ describes studies of the stability of Dowex 1X4, which was degraded by prolonged contact with hot, strong, nitric acid solutions.

It is difficult to draw quantitative conclusions from these investigations, but a few qualitative facts are apparent.

- 1.) Instability reactions are exponentially dependent upon temperature, so designs which favor the rapid dissemination of heat and lower operating temperatures are desirable.
- 2.) Instability reactions in a system containing water are quenched by evaporative cooling upon venting; so degraded resin, equilibrated with nitric acid, should not be allowed to go dry.
- 3.) Idle columns should always remain in a vented condition, and operating columns should be equipped with pressure release devices.

- 4.) Strong oxidizing agents should be avoided (e.g. dichromate or permanganate).
- 5.) System temperatures $> 100^{\circ}\text{C}$ are necessary to initiate rapid reactions.

In the absence of pressures > 200 psi, external heat sources, strongly exothermic exchange reactions or radiolytic heating, nitric acid, anion-exchange, plutonium processing offers no explosive hazard. However, the normally very slow oxidative attack by strong nitric acid on anion-exchange resin may be rapidly accelerated under conditions of temperature and pressure that are above normal.

Little is known about the actual mechanism of chemical attack. Molen⁽⁵⁴⁾ postulates carbon-carbon bond cleavage, based upon excess carbon dioxide in the reaction products. Swelling and softening indicate that crosslinks are broken. The initial, slight increase in capacity of used resin may be due to oxidative formation of weak-base, exchange groups at the ends of broken chains.

It should be mentioned that anion-exchange resins can be very effective catalysts for chemical reactions in the aqueous phase, especially with a large, solid-to-liquid, volume ratio. Operations involving reagents such as hydrogen peroxide, hydrazine, or hydroxylamine should be conducted in vented equipment. Plutonium(III)-plutonium(IV) mixtures and plutonium(IV) polymer can also provide catalytic, decomposition mechanisms.

The chemical degradation of several anion-exchange resins by 7M nitric acid under normal operating conditions was discussed by Ryan and Wheelwright.⁽⁵⁾ Resin in static solution at 60°C for two weeks showed severe damage; the authors attribute this to autocatalytic buildup of nitrite. Dowex 1X4 in moving 7.2M nitric acid at 60°C for five weeks showed a 20-percent, plutonium-capacity loss, but little physical damage. Permutit SK from the Hanford continuous contactor after 140 days of elevated-temperature, plutonium processing showed about a 10-percent capacity loss per unit volume of loaded resin. Shrinking with plutonium loading was four times that of new resin, indicating the degradation also included loss of crosslinkage. Life expectancies for Permutit SK of four months of continuous processing are suggested by Ryan and Wheelwright,⁽⁵⁾ but Swift⁽¹⁶⁾ indicates it may be only half this long.

2. *Radiolytic Stability.* The radiolytic degradation of anion-exchange resin by its exposure to gamma radiation has been extensively studied.⁽⁵⁶⁻⁶²⁾ The capacity of Dowex 1X4 shows a slight increase for gamma doses between 10^7 and 10^8 rad.⁽⁶¹⁾ Exposures above 10^8 rad cause a nearly linear loss in capacity.⁽⁵⁴⁾ With a 10^9 -rad exposure the resin is almost completely degraded. Odor indicates the release of amines; the resin beads retain their shape, but turn from pale yellow to dark brown. Loading the resin with thorium nitrate had little effect on radiolytic stability.⁽⁶¹⁾ Ryan and Wheelwright⁽⁵⁾ measured relative changes in the plutonium sorption capacities of various resins exposed to various levels of radiation. Radiation resistance decreased in the order, Permutit SK > Amberlite IRA-401 > Dowex 21K and Dowex 1X4. With all resins studied, loss of capacity was accompanied by a volume increase, indicating solvent sorption due to crosslink rupture. With the most radiation-resistant resin, Permutit SK, exposures to 3×10^8 rad can be tolerated before process performance is prohibitively poor.⁽⁵⁾

Using plutonium-238, Ahrens⁽⁶³⁾ studied the alpha radiolysis of Dowex 1X3 and 1X4 and Permutit SK and S-1. The energy sorption was numerically calculated from the determined, bead-radius distribution and with the assumption that the plutonium was uniformly distributed in the spheres. Sorption times were not given, but this assumption was probably invalid in view of the kinetic data of Ryan and Wheelwright⁽⁵⁾ and James⁽³⁾ This may be the reason that it appeared that the resins were slightly more stable to alpha radiolysis than to gamma radiolysis. A nonuniform, plutonium distribution would cause greater energy losses than calculated by Ahrens.⁽⁶³⁾ As with gamma radiolysis, the capacity loss was nearly linear with dose. Bulk-volume changes indicated that loss of capacity is accompanied by loss of crosslinkage. As with gamma radiolysis, Permutit SK showed greater stability to radiation damage at the highest doses.

It appears that chemical degradation from 7M acid at 60°C and alpha degradation from plutonium-239 will occur at about the same rate during the processing of plutonium by anion exchange. It is difficult to compare the data concerning radiolytic attack in the literature because various sources with different intensities were

used for often unstated, total doses of energy. However, the following qualitative conclusions might be drawn:

- 1.) Permutit SK is the most radiation resistant of the strongly basic, anion-exchange resins.
- 2.) Doses below 200 W-hr/kg of dry resin serve only to increase the capacity of the resin for plutonium.
- 3.) Above this level the capacity loss varies somewhat linearly with increasing dose, up to greater than 50 percent above doses of 2000 W-hr/kg.
- 4.) The physical effects of radiation damage are large volume changes, softened beads, and increased pressure drop.

Therefore, if one assumes that a batch of contaminated plutonium would contain no more than 1000 curies of 1-MeV $\beta\gamma$, which would be 100 percent adsorbed (6 W-hr/hr), and that an insignificant amount of fission products remains on the resin between cycles, the resin would suffer a 10 percent capacity loss only about every 100 cycles.

F. Criticality Considerations

Six critical accidents with process equipment have occurred in the United States. All have involved aqueous solutions; all can be attributed to equipment malperformance or maloperation, not to misinterpreted or faulty criticality information; all were the result of a chain of events, no one of which would have been harmful by itself; and only two have involved plutonium.

Fissile material is just critical when the number of new fissions per fission is unity, but this involves a balance between those neutrons inducing fissions and those undergoing capture or leakage from the system. The most probable interaction a neutron from fission can experience is deflection, the amount of energy transfer varying inversely with the mass of the particle with which it collides. This energy transfer or moderation is important in criticality considerations because, in general, fission probability increases greatly with decreasing neutron energy.

Because of its high hydrogen content, water is a very effective moderator. If a mass of plutonium-239 is immersed in water, neutrons that would normally escape may be scattered (reflected) back into the material, and at a lower energy. If plutonium and water are homogeneously mixed, the effect can be different for different mixtures. As the percentage of water increases from zero, the same amount of plutonium becomes less critical because the moderating effect is less than the effect of decreasing density (fissile material per unit volume). With further increase in water content, at very roughly 50-percent water, moderating effects become important; and the same amount of plutonium moves closer to the criticality limit. This trend is finally reversed in very dilute solutions when neutron capture by the very abundant hydrogen offsets the moderation effects. The limiting, critical concentration of plutonium is $8.0 \pm 0.3 \text{ g/l.}$ ⁽⁶⁴⁾ This value is for a water solution. The presence of nitric acid raises the critical concentration, since water is displaced, changing the hydrogen-to-plutonium ratio; nitrogen is a more effective poison than hydrogen.

Critical dimensions of homogeneous, water-moderated, plutonium shapes (spheres, infinite cylinders, infinite slabs), both bare and water-reflected, were compiled by Paxton.⁽⁶⁵⁾ Plutonium-240 captures neutrons, so its presence will modify these dimensions slightly.⁽⁶⁶⁾ Discussions of the relations for converting critical data from one geometric shape to another appear in the literature.^(66,67) These homogeneous critical dimensions are inversely proportional to uniformly changing

density. Heterogeneities with at least one dimension smaller than the distance a neutron travels before inducing a fission may be considered as homogeneous. This distance usually is of the order of a centimeter.

Very little appears in the literature regarding the critical dimensions of ion-exchange columns for the processing of fissile material. Ketzlach⁽⁶⁸⁾ gives limits for the Hanford continuous contactor. In a proposed revision the single-parameter limits of the American Standards Association⁽⁶⁹⁾ include the "ever-safe," cylinder diameter of 11.2 cm for plutonium-239, aqueous solutions. To consider ion-exchange columns as aqueous solutions is reasonable, since the solid resin is 70 to 80 percent water. Carbon must be present in large proportions in order to moderate neutrons significantly.⁽⁶⁵⁾

Multiparameter control may allow the use of more convenient and economically favorable dimensions. Rigid, mass controls at Los Alamos⁽⁴⁹⁾ allow the use of 6-in., anion-exchange columns, which are "geometrically favorable" to a kilogram per liter, for the processing of plutonium-239.

A series of columns may constitute an array of fissile cylinders. Arrays are discussed by Paxton.⁽⁶⁷⁾ This work is a comprehensive discussion of criticality control in the processing of fissile materials. While admittedly qualitative, it is developed without recourse to theoretical, reactor physics and provides an excellent introduction to the field for the process chemist or engineer.

CHAPTER V — REFERENCES

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CHAPTER VI — REPROCESSING OF PLUTONIUM-LADEN FUELS

Fission-product atoms can act as neutron absorbers in the fuel of a nuclear reactor by competing with the fertile material for neutrons. Fission products and the high radiation environment may cause chemical and physical changes in fuel, which may prohibitively affect its performance. By adjusting the placement of control rods and fuel in the reactor, burn-up of fissionable material during reactor operation can be compensated, but eventually loss of reactivity requires the fuel to be removed and reprocessed.

The use of ion exchange for the reprocessing of reactor fuel was briefly summarized by Wells and Pepper.⁽¹⁾

A process⁽²⁾ has been described for the final purification of the plutonium product (1BP) from a one-cycle Purex process. A single cycle of anion exchange can replace three plutonium-purification, solvent-extraction columns, as well as reduce the evaporative-concentration problem of the product. This anion-exchange modification is in use at nearly all fuel reprocessing plants which employ the Purex process.⁽²⁻⁵⁾

Ryan and Wheelwright⁽²⁾ and Aiken^(6,7) describe similar two-cycle processes, based entirely upon anion exchange, for the reprocessing of plutonium-uranium reactor fuels. The process is especially attractive for moderate-capacity plants. The applicability of the process to the treatment of irradiated, plutonium-aluminum-alloy fuels has been demonstrated with the facilities at Chalk River,⁽⁷⁾ Savannah River,⁽⁸⁾ and Oak Ridge.⁽⁹⁾ Zebroski, Alter, and Collins^(10,11) support the use of anion exchange for the reprocessing of ceramic fuels from fast-neutron, breeding power reactors.

A. Separation from Uranium

A discussion of the plutonium-uranium separation by nitrate, anion exchange was deferred from Chapter V because this separation problem is common to the reprocessing of nearly all reactor fuels. Uranium, less than about 1 mM in feed solutions, will behave as a weakly sorbed impurity, as described in Chapter V, Section C-1. Unfortunately, most fuel-reprocessing feeds contain uranium concentrations much greater than this; the sorbed uranium occupies a significant number of exchange sites, and its presence perturbs the anion-exchange behavior of plutonium.

Plant-scale, nitrate, anion-exchange separations of uranium and plutonium are also reported in the literature.^(6,7,12,13) Process feasibility is adequately demonstrated; anion exchange is especially attractive to low, throughput requirements. However, the kinetic and equilibrium parameters of the system have not been sufficiently studied to permit process optimization.

The anion exchange of uranium(VI) from nitrate solutions has been investigated by a number of authors.⁽¹⁴⁻¹⁹⁾ The resin predominantly sorbs the tetranitrato anion, $\text{UO}_2(\text{NO}_3)_4^{-2}$, along with lesser amounts of the trinitrato complex, $\text{UO}_2(\text{NO}_3)_3^-$. The relative amount of each is independent of the composition of the aqueous phase but is dependent upon resin-phase properties, such as fractional, uranium loading and equivalent, exchange capacity.⁽¹⁹⁾

Foreman et al.⁽¹⁵⁾ compared λ_U° for nitrate solutions of various metal nitrates and nitric acid with a constant, total-nitrate concentration of 6M. They concluded that uranium complexing power is

the same order as hydration, $\text{Al}^{+3} > \text{Ca}^{+2} > \text{Li}^{+} > \text{NH}_4^{+}$. As discussed by Ryan,⁽¹⁹⁾ this interpretation is complicated by the presence of nitric acid, which is appreciably associated and which promotes the protonation of the anionic complexes. If the data of Foreman et al.⁽¹⁵⁾ are compared at constant, nitrate ion concentration, $\text{Li}^{+} \cong \text{Al}^{+3} \gg \text{Ca}^{+2} > \text{NH}_4^{+}$.

The strong dependence of the affinity of uranium(VI) for anion-exchange resin upon the nature of the electrolyte cation was also demonstrated by Googin et al.⁽¹⁸⁾ These authors give the equilibrium, sorption isotherms for the various nitrate solutions. The distribution coefficient λ_U on Dowex 21K from 6M nitric acid is about ten and is independent of C_U up to the highest concentration studied, about 0.05M. This work also gives some qualitative, kinetic information. The kinetics are similar to the behavior of plutonium.

Unfortunately, there are no quantitative, anion-exchange, kinetic or equilibrium data in the literature that describe the behavior of uranium and plutonium in the presence of one another. Several workers,^(2,20-22) using laboratory-scale columns, have investigated the separation. These results can only give qualitative information concerning the optimal performance of plant-scale equipment. Studies⁽²⁾ with Dowex 1X4 (50-100) demonstrate a significant gain in process performance by operating at 60°C with a feed containing 7M nitric acid, uranium-to-plutonium ratios from 60 to 1440, and plutonium at about 1 to 10 g/l. At 25°C with 200 g uranium/l and a uranium-to-plutonium ratio of 1500, an optimal value for C_{HNO_3} is about 7.2M.⁽²²⁾ With very low plutonium concentrations (30 to 160 mg plutonium/l) and very high uranium concentrations in the feed to laboratory-scale columns, capacity for plutonium decreases linearly with increasing, total-uranium concentration and exponentially with increasing uranium-to-plutonium ratio.⁽²¹⁾

As plutonium begins to load on the top of the column, the entire column becomes rapidly loaded with uranium to a degree dictated by uranium isotherm in the absence of plutonium. Hence, plutonium is sorbed upon resin previously loaded with a uranium solution of the same composition as the feed. Certainly both λ and \bar{D} for plutonium are adversely affected by the presence of uranium in

the resin. Computer techniques⁽²³⁾ could be used to study process variables and design parameters if functional relations between $\lambda_{\text{Pu}}(\text{U})$, $\lambda_{\text{U}}(\text{Pu})$, $\bar{D}_{\text{Pu}}(\text{U})$, and $\bar{D}_{\text{U}}(\text{Pu})$ were established experimentally.

B. Decontamination from Fission Products

The decontamination of plutonium by nitrate anion exchange is extensively reported in the literature.^(2,3,6-9,12, 21,22,24) With an 8M-nitric acid feed, containing 2×10^8 $\beta\gamma$ cpm/mg plutonium, using laboratory-scale columns and ten column volumes of wash, Allam et al.^(21,24) obtained a gross decontamination factor of 7×10^2 with one anion-exchange cycle and 1×10^4 with two cycles. Zirconium and niobium were the limiting fission products, decontamination factors of 1×10^2 and 2×10^3 , respectively, were realized for these elements. Using plant-scale columns and ten-times more active feed, overall factors of 5×10^2 and 2×10^4 were obtained with one and two cycles, respectively.

Ryan and Wheelwright⁽²⁾ made detailed, laboratory studies of this process and demonstrated improved decontamination factors. They found niobium to be the limiting fission product. Using 7.2M nitric-acid-feed solutions, containing 10^9 cpm/mg plutonium and 40 to 60 column volumes of wash, they obtained gross decontamination factors of 5×10^4 for one cycle and 4×10^7 for two cycles with zirconium-niobium decontamination factors of 4×10^4 and 3×10^7 , respectively. These authors speculate that the difficulty with zirconium and niobium may be due to physical entrapment by the resin as it shrinks, due to plutonium loading. This theory is strengthened by recent studies of diffusional mechanisms in plutonium-loaded resin⁽²⁵⁾ (see Chapter IV, Section B-4).

It was demonstrated⁽²⁾ that decontamination from zirconium and niobium can be improved by adding small amounts of hydrofluoric acid to feed and wash solutions. The hydrofluoric acid complexes these elements, reducing their sorbability. However, it also complexes plutonium. Hydrofluoric acid in the feed halved 50-percent-break-through capacity, and its presence in the wash displaced the plutonium front 5 to 10 times faster than the displacement with an all-nitric acid wash. Addition of aluminum nitrate to the feed

and wash restored some of the loss in plutonium performance, but total nitrate concentration was maintained at $7.2M$. Under these conditions the presence of aluminum nitrate decreases the effective diffusion coefficient of plutonium in the resin phase, causing a reduction in effective capacity.^(2,26) Recent studies^(26,27) indicate that with mixed, aluminum nitrate-nitric acid feeds, less than $7M$ total nitrate in the feed can produce the same process performance as obtained with $7M$ nitric acid. Raising the total nitrate concentration to $7M$ may lessen the effective capacity for plutonium. With hydrofluoric acid in both the feed and a portion of a 38-column-volume wash, Ryan and Wheelwright⁽²⁾ obtained a single-cycle, zirconium-niobium, decontamination factor of 4.64×10^5 ; but the plutonium resin performance was significantly reduced. Possibly, a computer-optimized⁽²³⁾ choice of the concentrations of aluminum nitrate and nitric acid in the process solutions could restore much of this loss, while maintaining the high decontamination.

The problem of the waste volume that is generated by 38 column volumes of wash can be reduced with very little lessening of wash efficiency by using the final portions of the wash effluent from one run as the initial portions of wash for the next run.⁽⁷⁾ The first half of the wash effluent contains about 99 percent of the total activity in the entire wash effluent.⁽²⁾

C. Anion Exchange Versus Other Reprocessing Methods

Generally, the relative costs of the recovery of valuable fissionable material, the relative costs of the possible reprocessing schemes, and the relative costs of the fuel inventory necessitated by cooling and reprocessing times are all complexly interdependent factors in the complicated economics of fuel reprocessing. In view of this it would be extremely difficult to argue quantitatively for or against a specific process, even given a specific application. In the absence of a specific application all arguments must be qualitative.

It is becoming increasingly apparent that fast-neutron, ceramic-fueled, power reactors will be important, civilian, power sources in the future. It has been critically argued that nitrate anion exchange could provide the best reprocessing method for these reactors.^(10,11)

All of the modern nonaqueous processes (e.g., oxide slagging, fluoride volatilization, etc.) apparently will provide insufficient decontamination factors to permit anything but remote, fuel fabrication, and may allow overall plutonium losses of more than 1 percent to economically unrecoverable wastes. Losses less than 1 percent may be required to sustain the breeding ratio upon which the economic life of the fast reactor depends. The ability of two cycles of anion exchange to provide decontamination factors of 10^6 to 10^8 and maintain losses below 1 percent has been clearly demonstrated.

There is presently little economic incentive to recover the depleted uranium from the spent, long-lived, fast-reactor fuel. This makes the separation of uranium and fission products, as in a typical Purex cycle and most other proposed processing schemes, an economic waste. Presence of uranium-237 in a purified, uranium product may render it too radioactive to handle directly, even in the absence of fission products.

With anion exchange the entire organic-solvent treatment of the Purex process is not necessary. There are only three simple plant solutions with anion exchange, as compared with five or six for Purex. No pulsers, plates, disengaging, sections, etc., are required for anion exchange; flow control, while necessary within wide limits, is much less critical than with solvent extraction.

Radiation damage to anion-exchange resin may create even less of a problem than radiation damage to tributylphosphate. Because of a lower yield of short-lived, fission isotopes with long fuel lifetimes, the slight gain from lower radiation levels for fuels which are cooled longer than a few months would be lost in the cost of the increased inventory. Therefore, the reprocessing chemistry must be able to tolerate high radiation levels. As described in Chapter V, Section E-2, the threshold for radiolytic degradation of the processing performance of anion-exchange resin may be about 100 W-hr/l , as compared to about 10 W-hr/l for tributylphosphate.⁽²⁸⁾ The resin contact time per cycle is about ten-times longer with the resin process, indicating approximately equal lifetimes. Waste-handling costs are usually proportional to volume, so much more frequent resin replacements can be tolerated.

The reprocessing requirements for the long-lived fuels will be small, possibly 100 g of fuel per day per megawatt electrical; but it will be many years before there will be sufficient fast reactors to supply a high capacity plant. As throughput decreases, the unit costs for solvent extraction increase more rapidly than for anion exchange because the simpler process requires less capital which is not directly proportional to throughput.

In view of the demonstrated reliability and versatility of aqueous methods for the reprocessing of uranium-plutonium fuels, it seems doubtful that any of the nonaqueous schemes will be attractive for a commercial fuel-processing plant. Even if a Purex-type flow sheet provides the major separation, purification of the plutonium stream by anion exchange is a proven advantage. One might conclude from the qualitative arguments above that anion exchange could economically provide the entire separation, especially if the separation of uranium and fission products is not an economic necessity.

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