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CONCENTRATION AND PURIFICATION OF URANIUM, PLUTONIUM, AND NEPTUNIUM BY ION EXCHANGE IN NUCLEARLY SAFE EQUIPMENT

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INTRODUCTION

The initial products from the processing of irradiated fuel elements are usually relatively dilute solutions of uranium, plutonium, or neptunium which must be concentrated and further purified. Ion exchange has proved to be a useful method for accomplishing these objectives. Several isotopes which are, or accidentally could be, present in the process streams are fissionable. All the equipment, therefore, must be designed to prevent the accumulation of fissionable material which could generate an excessive amount of neutrons by multiplication. Even with the limitations imposed to provide nuclear safety, the processing can be done economically by ion exchange because a large batch of product can be absorbed, purified, and eluted within a short period of time. Nuclear safety is easily obtained by using resin beds with small diameters, or by using a composite column that consists of a series of shallow beds separated sufficiently to avoid interaction of the neutrons from the individually safe beds. Rapid processing is obtained by using the maximum flowrates that are practical. The rates of processing are directly proportional to the cross-sectional area but are independent of the depth of resin in the ion exchange column.

The following survey consists of four major sections. General requirements that are common to all the processes are discussed first, followed by separate discussions of processes for uranium, plutonium, and neptunium. Typical chemical flowsheets are presented. The process data needed to develop ion exchange processes and the basic chemistry that illustrates specific problems are described.

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Including work by G. A. Burney, F. L. Livingston, E. R. Russell, et al.

GENERAL REQUIREMENTS

Processes for the concentration and purification of any element usually consist of four steps: (1) Feed Absorption, in which the product element is absorbed from a dilute solution, (2) Selective Elution, in which undesired elements are removed by an elutriant that does not significantly affect the desired element, (3) Product Elution, in which most of the desired element is removed at a high concentration, and (4) Reconditioning, in which the resin bed is prepared for repetition of the process cycle by flushing out the residual product elutriant with a solution that is compatible with the feed.

Ion exchange processes can be operated in three ways which differ principally in the procedure used to load the column during the absorption step. The three basic modes of operation and their advantages are:

(1) Complete Loading: Absorption of the product element is continued until the concentration of the element in the effluent stream approaches its concentration in the feed stream. Control is simple because the appearance of the product element in the effluent is easily detected by instruments, and delays in operations of the process are avoided. Since feed can be passed through the column until the resin has attained its equilibrium saturation, the concentration of the element in eluate is significantly higher than it would be if the resin were only partially saturated. The unabsorbed product element in the effluent can be recovered very simply in a separate operation.

(2) Partial Loading: Absorption of the product element is stopped before its concentration in the effluent is significant; consequently, the effluent can be discarded without further processing. To avoid loss of valuable material in the effluent and to obtain a uniform product, the amount of the desired element absorbed from the feed and the amount removed as product must be equal in a series of repetitive cycles.

(3) Tandem Loading: Two or more columns in series are used alternately - first to absorb the desired element until the resin is completely loaded; and second, in the next process cycle, to remove all of the desired element from the absorption effluent. Instruments can detect the appearance of the product element in the effluent from the column that is being loaded. This mode of operation has many of the desirable features of operation by complete loading, with the added advantage that the effluent can be discarded without any loss of valuable material.

The properties required for a good ion exchange resin are: (1) rapid exchange of ions, (2) low resistance to flow at high rates, and (3) small change in volume during the process cycle. Compromises are necessary to satisfy all of these requirements to an acceptable degree. Resin consisting of beads in the 50 to

100-mesh range, U. S. Standard Screens, provides rapid exchange rates and acceptably rapid flowrates. Equilibrium is attained rapidly with cation exchange resins, but only slowly with anion exchange resins. Cation exchange resins which are approximately 8 and 12% cross-linked, usually designated as 8 and 12% DVB resins, exchange ions rapidly and do not shrink excessively. The shrinkage of these resins in nitric acid is shown in Fig. 1. Anion exchange resins should be cross-linked no more than 4%; otherwise, they will not provide acceptable exchange rates. Anion exchange resins such as "Dowex" 1-4X and 21K shrink 11 and 6%, respectively, when placed in 8M nitric acid after being washed with water.

The equilibrium capacities of a typical cation exchange resin, "Dowex" 50-X12, for trivalent plutonium, uranyl, and hydroxylammonium ions in dilute nitric acid solutions, up to 1M acid, can be calculated from the data in Fig. 2. Data for the absorption of uranyl ions on 8% DVB resin also are presented. The capacities are expressed as the percentage of the total exchange capacity of the resin utilized by absorption of the indicated ion, and are referred to as partial capacities. Thus, S_u = 70% means that the composition of the solution in contact with the resin is such that at equilibrium 70% of the exchange capacity of the resin is saturated with uranyl ions. The ordinates of the curves in Fig. 2 represent the values of S_u, S_p, and S_h - the partial capacities for absorption of uranyl, plutonium, or hydroxylammonium ions, respectively. The abscissa represents the function defined by

$$K = \frac{H^v}{C}$$

where

H = concentration of H^+, equivalents per liter

C = concentration of the indicated cation, grams per liter

v = valence of the indicated cation

This correlation has been confirmed by experiments, and it can be derived from the Law of Mass Action if simplifying assumptions are made about the relative values of the activity coefficients of the ions in the resin and in the solution phases. For convenience, the absorbability of an ion from a given solution can be represented by the partial capacity of the resin in equilibrium with the solution.

In anion exchange processes the practical capacities of the resins for an element depend on the time of contact that is available. The capacities attained in these processes are discussed later.

Several methods for correlating ion exchange process data produce sets of curves which can easily be interpolated. If the concentration of the desired element in the product that is eluted from a resin bed is plotted against the amount eluted, expressed as the percentage of the total amount initially absorbed on the bed, the effects of many variables are easily shown. For example, the effects of bed depth on the concentrations obtained in the product are shown in Fig. 5 and 6. Similarly, if the concentration in the product is plotted against the volume of product eluted, expressed as the number of bed volumes, easily interpolated curves are obtained as shown in Fig. 11. A bed volume is defined to be 0.47 times the volume of the resin in the column and is equal to the volume of the liquid phase. The volume of the resin beads is measured in water; this is usually the maximum volume.

URANIUM PROCESSES

Uranium, as dilute uranyl nitrate, may be absorbed on a bed of cation exchange resin of the sulfonic acid type, and then eluted at high concentrations with either a mineral acid or a complexing solution, such as one that contains ammonium acetate and citric acid. The concentrations of uranium in the eluate from typical runs made with these types of elutriants are shown in Fig. 3. The concentration in the eluate is plotted as a function of the fraction eluted from the column.

Absorption Step. The uranium is absorbed rapidly. At a flowrate of 30 ml/(min-cm^2), about 96.5% of the equilibrium amount is absorbed if the bed is loaded until uranium almost breaks through into the effluent. Even at a flowrate as high as 80 ml/(min-cm^2), about 93% of the equilibrium amount is absorbed.

The feed to the columns is usually composited from several sources. The fresh feed to the process contains primarily uranyl nitrate and nitric acid. Minor amounts of other solutions, which contain low concentrations of uranium from preceding process cycles, as well as complexing compounds, which aid purification, can be added. If the added solutions contain only nitrate as the anion, the amount of dilute uranium that can be recycled is limited only by the maximum concentration of acid that can be tolerated in the final feed. If the solutions contain ammonium salts of the organic acids, the concentration of nitric acid in the final feed must be at least 0.15M to suppress the ionization of the acetate and the citrate ions. Many fission products and other impurities react with fluoride ions to form complexes that are not absorbed on cation exchange resins. If 0.005 mole of fluoride is added per liter of feed, the loss of uranium during the absorption step is less than 0.002% of the total uranium, and significant decontamination from fission products is attained. If 0.015 mole of fluoride per liter is added, the loss of uranium increases to more than one per cent.

Elution with Nitric Acid. Fig. 4 is a typical chemical flowsheet for the concentration and purification of uranium when the product is eluted with 4M nitric acid. More than 99.95% of the uranium fed to the process can be easily recovered as product. For this process 90% of the total uranium absorbed on the bed is eluted at a concentration of 50 g/l. Higher concentrations can be obtained if less of the uranium is eluted; i.e., if a larger "heel" is left on the column. In Fig. 3, the concentrations obtainable are shown as a function of the fraction eluted. The maximum concentration of uranium in the product is obtained with 4M nitric acid; higher and lower concentrations of acid are significantly less effective. The concentration at which uranium can be eluted increases when a greater depth of resin is loaded with uranium, as shown in Fig. 5.

Ion exchange is a useful method for separating uranium from non-ionic, organic compounds, which will pass through the column unabsorbed. If a high concentration of uranium is not needed, the time required to process large volumes of solution can be shortened by using very fast flowrates for both the absorption and the elution of the uranium. The uranium can be absorbed at 80 ml/(min-cm^2) and eluted at 6 ml/(min-cm^2). Less than 0.05% of the uranium is lost during the feed absorption step. Even at this fast elution flowrate, 90% of the absorbed uranium is eluted at 24 g/l with 3M nitric acid from a column loaded to a depth of 25 cm at a partial capacity of 70%. If the elution flowrate is only 0.50 ml/(min-cm^2), 90% of the uranium is eluted at 55 g/l.

Elution with Ammonium Salts of Organic Acids. Very high concentrations of uranium are obtained by elution with complexing compounds. Fig. 4B presents a typical chemical flowsheet for the processing of uranium when the product is eluted with a solution of 4.5M ammonium acetate and 0.75M citric acid which has a pH of 5.2. More than 99.99% of the uranium in the feed is recovered as product. The concentration of uranium in the eluate is not significantly increased if higher concentrations of either ammonium acetate or citric acid are used in the elutriant. When the elutriant contains 8M ammonium acetate and 0.75M citric acid, the concentration of uranium in the eluate is high enough to precipitate a compound of uranium and flow through the column is stopped. The pH of this elutriant is 5.9. The concentration at which uranium can be eluted increases when a greater depth of resin is loaded with uranium, as shown in Fig. 6.

The effects of the elutriant flowrate on the concentrations of uranium obtained in the product are complex. If about 98% of the uranium on the bed is eluted, the concentration of uranium decreases as the flowrate is increased. When less than 98% is eluted, however, higher concentrations are obtained at the faster rates.

Typical data are shown below:

Effect of Elutriant Flowrate
on Concentration of Uranium in Eluate

Elutriant: 4.7M Ammonium Acetate and 0.75M Citric Acid,
Resin: "Dowex" 50-X8, Temperature: 70°C,
S_u = 70%, Bed Depth: 57 cm

Flowrate, ml/(min-cm^2)	Concentration of Uranium in Eluate, g/l	
	90% Eluted	98% Eluted
0.25	275	258
0.50	273	201
0.75	353	193

The initial portion of elutriant of the complexing type that passes through the resin bed does not elute any uranium. This initial elutriant is ineffective because ammonium ions are lost by exchange for hydrogen ions and by the diffusion of equivalent amounts of ammonium and acetate ions into the resin bed. The deactivated elutriant that remains is essentially a mixture of un-ionized acetic and citric acids. For the flowsheet shown in Fig. 4B, about 25% of the elutriant fed to the column is deactivated. The acetate ions and the equivalent ammonium ions diffuse out the beads during the reconditioning step.

The uranium solution is bright, canary yellow immediately after elution; but, after a few days, the color darkens and in some solutions a canary yellow precipitate eventually forms. These changes are produced by the formation of colloidal precipitates of uranium trioxide. The product obtained with the elutriant used for the procedure in Fig. 4B, however, can be stored for 12 weeks without the formation of a visible precipitate.

PLUTONIUM PROCESSES - CATION EXCHANGE

Trivalent plutonium may be absorbed from dilute nitric acid by a bed of cation exchange resin of the sulfonic acid type and may then be eluted either with nitric acid stabilized with sulfamic acid to prevent oxidation of the Pu(III) or with a complexing solution, such as one that contains ammonium lactate and sulfamate. The plutonium in the feed should be completely in the trivalent state. Pu(IV) is absorbed more strongly than Pu(III); therefore, Pu(IV) is difficult to remove completely from the resin, particularly when nitric acid is used as the elutriant. Sulfuric acid, which is used to elute uranium selectively, readily elutes Pu(IV), but it has little effect on Pu(III). Plutonium in feed with concentration of nitric acid less than 0.75M is reduced essentially completely to the trivalent state in about four hours by hydroxylamine sulfate when, in addition to the amount required to reduce the plutonium, 0.025 mole excess reductant per liter is present. The excess of hydroxylammonium ions is absorbed on the resin bed and is eventually eluted with the plutonium in the product.

Absorption Step. Pu(III) is absorbed rapidly; a flowrate of 30 ml/(min-cm^2) can be used. The concentrations of plutonium in the effluent at flowrates of 15, 30, and 60 ml/(min-cm^2) are shown in Fig. 8. Essentially all of the plutonium is absorbed from the feed until the bed has been loaded to nearly its equilibrium capacity.

The exchange capacities of cation exchange resins of the sulfonic acid type decrease as shown in Fig. 7 upon exposure to the alpha particles emitted by plutonium. The volume of the exposed resin increases; therefore, cross-linkages are broken. The resins with the highest initial degree of cross-linkage are the most resistant to damage. After 470 days of exposure, samples of "Dowex" 50 - X16, X12, and X4 expand 40, 50, and 90%, respectively, in volume when loaded with plutonium to a partial capacity of 70%. Exposure of the resin for a corresponding period to the chemicals used in the process shows that these changes are not due to chemical attack.

Elution with Nitric Acid. Trivalent plutonium can be eluted with nitric acid only if its oxidation by the nitric acid to tetravalent plutonium is retarded by a stabilizer such as sulfamic acid. If the elutriant is not effectively stabilized, vigorous oxidation will occur during the elution, with the evolution of gases in the resin bed. This gassing can be sufficiently vigorous to disrupt the bed and permit solutions to bypass parts of the bed. The gas formed is almost pure nitrogen if the oxidation is slow, but during rapid oxidation a mixture of nitrogen and nitrous oxide is formed. Sulfamic acid stabilizes plutonium in the trivalent state by retarding the chain of reactions by which the oxidation normally proceeds. Nitrous acid, which is an important link in the chain, is destroyed by reaction with the amine group of the sulfamic acid, and the oxidation is slowed down. The typical product that is eluted with 5.7M nitric acid stabilized with 0.30M sulfamic acid contains 50 to 60 grams of plutonium per liter, 4.7M nitric acid, 0.30M sulfamic acid, and 0.35M hydroxylammonium nitrate. As soon as this solution is eluted from the resin bed, the Pu(III) is slowly oxidized, at the rate of approximately 6% per day, until about 42% of the plutonium is in the tetravalent state. Further oxidation is even slower, less than 0.5% per day.

Fig. 9A presents a typical chemical flowsheet for the concentration and purification of plutonium when the product is eluted with 5.7M nitric acid stabilized with 0.30M sulfamic acid. More than 99.99% of the plutonium fed to the process is recovered as product. About 10% of the absorbed plutonium must be left on the resin bed as a "heel" in order to obtain a concentration of

55 grams per liter or greater in the product.

Elution with nitric acid is satisfactory, but operation of the process would be easier if all the absorbed plutonium were eluted during each cycle and if retention of the plutonium in the trivalent state did not depend on an oxidation inhibitor. If the sulfamic acid were inadvertently omitted, gases would be generated rapidly. This is a potential hazard of the process.

The maximum concentration of elutriant that can be used without oxidizing the Pu(III) depends on depth of resin loaded with plutonium. All the elutriants that contain nitric acid are stabilized with 0.30M sulfamic acid. The peak concentrations of plutonium attained during the elution increase as the depth of resin is increased, and the oxidation is more difficult to control. In a bed loaded to a depth of 35 cm, the maximum concentration of the elutriant that can be used is 5M, i.e., 4.7M nitric and 0.30M sulfamic. In a bed loaded to a depth of 25 cm or less, the concentration of the elutriant can be increased to 6M without the formation of gas. The same concentrations of plutonium, however, are obtained with either 5 or 6M elutriant as shown in Fig. 10. The 7M elutriant generates gas even in a 15-cm-deep bed.

The concentration at which plutonium can be eluted increases when a greater depth of resin is loaded with plutonium; but, as shown on Fig. 11, only small gains are obtained when the depth is made greater than 15 cm. A larger volume of product, however, is eluted from the deeper beds.

The concentration of plutonium in the eluate decreases as the flowrate of the element is increased. At flowrates greater than 0.50 ml/(min-cm^2), both the peak and the average concentrations of plutonium in the eluate decrease. If a bed 25 cm deep that is loaded with plutonium at a partial capacity of 75% is eluted with 6M elutriant at 0.50 and 1.0 ml/(min-cm^2), the respective peak concentrations obtained are 145 and 122 grams of plutonium per liter. The concentrations in the eluate when 90% of the absorbed plutonium is collected are 56 and 42 g/l. For high productivity, elution flowrates less than 0.50 ml/(min-cm^2) are not used because the concentration of plutonium in the product is not significantly increased. Oxidation of Pu(III) in a resin bed can be stopped even after the reaction has started if the flowrate of the elutriant is increased severalfold.

Good separation of plutonium from uranium can be obtained. Plutonium is more strongly absorbed than uranium, and it displaces absorbed uranium from the resin bed during the feed absorption step. Most of the remaining uranium can be eluted selectively with dilute sulfuric acid. Thus, if the flowsheet described in Fig. 9A is used with a feed that contains equal concentrations of plutonium and uranium, the product eluted with 5.7M nitric acid stabilized with 0.30M sulfamic acid contains less than 0.001 gram of uranium per gram of plutonium. If during the uranium elution step, 12 bed volumes of 0.10 or 0.05M sulfuric acid are used instead of 0.25M acid, the respective products from the plutonium elution step contain 0.002 and 0.006 gram of uranium per gram of plutonium.

Significant decontamination of the plutonium from ruthenium and zirconium-niobium is achieved if the flowsheet shown in Fig. 9A is used. The results obtained are best expressed as ranges of values or average values for the decontamination factor which is defined as the ratio of the activity per gram of plutonium in the feed to the activity per gram of plutonium in the product. Normally, 50 to 65% of the ruthenium in the feed is not absorbed and appears in the effluent. Most of the absorbed ruthenium is eluted with the plutonium in the product and, therefore, the decontamination factors obtained are 2 to 3. Most of the zirconium and niobium present in the feed are absorbed. Very significant decontamination, however, is attained by selective elution of zirconium and niobium during the uranium elution step and by preferential retention on the resin bed during the plutonium elution step. The average decontamination factors are 7.5, 10, and 25 when 6, 12, and 24 bed volumes, respectively, of 0.25M sulfuric acid are used during the uranium elution step. The zirconium and niobium accumulate on the resin bed and must be removed periodically to decrease the gamma radiation from the column and to avoid a decrease in the decontamination factors obtained across the ion exchange process. This activity is eluted from the column with 5 bed volumes of 0.5M oxalic acid at a flowrate of 0.2 ml/(min-cm^2) or slower.

<u>Elution with Ammonium Lactate</u>. The use of ammonium lactate as the elutriant avoids some of the problems that arise when plutonium is eluted with nitric acid. Since almost all the plutonium is eluted during each cycle, the total amount of plutonium on the column is easy to control in repetitive operation of the process. It is very unlikely that unrecognized buildup in the amount of plutonium can continue to the point where the bed is loaded excessively and plutonium is lost in the effluent stream. Furthermore, the lactate elutriant is not an oxidizing agent and cannot generate a gas under the conditions of use.

Fig. 9B is a typical chemical flowsheet for the concentration and purification of plutonium if the product is eluted with 3.25M ammonium lactate at a pH of 5.3. More than 99.95% of the plutonium fed to the process is recovered as product. When the column is heated to 60°C, more than 99% of the absorbed plutonium can be eluted at the high concentration of 85 grams per liter.

To attain best operation of this process, hydrogen and hydroxylammonium ions should be eluted before the column is heated for the plutonium elution step. This can be accomplished by using a solution consisting of 0.085M ammonium sulfate and 0.015M ammonium sulfamate during the uranium elution step instead of 0.25M sulfuric acid. This solution does not elute significant amounts of plutonium, but it elutes hydrogen and hydroxylammonium ions as well as uranyl ions. The hydrogen ions should be removed to avoid deactivation of the initial portion of elutriant by the formation of un-ionized lactic acid. Since this deactivation of the elutriant occurs during the initial stage of the elution when the highest concentrations of plutonium are normally attained, the average concentration of plutonium in the eluate is significantly decreased. When a solution of hydroxylammonium sulfate and ammonium lactate is heated, a rapid evolution of gas occurs. Thus, if hydroxylammonium ions are still on the resin bed when the column is heated, gases are generated in the bed.

The effect of the flowrate of the elutriant on the concentrations of plutonium in the product is complex, and the behavior is similar to that shown by uranium when eluted with a complexing solution. As shown on Fig. 12 the concentration of plutonium in the product is higher when the flowrate is 0.4 ml/(min-cm^2) than at 0.2 ml/(min-cm^2). This behavior is the result of two competing chemical processes: (1) the desorption of the cation from the resin followed by the formation of the complex in the eluate, and (2) the reverse process, which consists of the re-ionization of the complex and the reabsorption of the cation. Which process dominates depends on: (a) the flowrate of the elutriant, (b) the temperature of the elutriant, and (c) the concentrations of the cation in the resin and solution phases.

PLUTONIUM PROCESSES - ANION EXCHANGE

Plutonium is conveniently separated from other elements when the anionic complex that it forms in concentrated nitrate solutions is absorbed on a strong base anion exchange resin. Very few elements form strong anionic complexes with nitrate ions, and excellent purification of the plutonium is obtained. The impurities that are removed include many fission product elements, uranium, iron, chromium, nickel, aluminum, calcium, and magnesium. A. M. Aiken of Atomic Energy of Canada Limited has described(1) the use of this process for recovery of plutonium from irradiated fuel elements.

The chemical flowsheet is presented in Fig. 13 for the recovery of plutonium from nitrate solutions of metals such as aluminum, magnesium, or calcium. Of the cations in the solution, only plutonium forms a strongly absorbed anionic complex. The other cations pass through the resin bed unabsorbed. About 97% of the plutonium absorbed on the column can be eluted with 0.30M nitric acid at a concentration of 45 grams per liter. The plutonium product contains 99.9% of the plutonium fed to the process. Concentrations of the other cations in the product do not exceed a few hundred parts per million parts of plutonium.

Absorption Step. The rate of absorption of the plutonium is low, and at practical flowrates the operating capacities of the resin in a column are about 50% of the equilibrium capacities. If a column that has been loaded to its operating capacity is left standing overnight, however, it can absorb additional plutonium on the following day. The operating capacity of a column also decreases when the concentration of plutonium in the feed is increased, probably because the diffusion rate of the anionic complex in the resin bead decreases. Thus, when plutonium is absorbed on a bed of "Dowex" 1-X4 at 23°C and at a flowrate of 12 ml/(min-cm^2), until breakthrough occurs, 38 grams of plutonium are absorbed per liter of resin from feed containing 1 gram plutonium per liter, whereas, only 18 grams per liter of resin are absorbed from feed containing 4 grams per liter. The diffusion rates are less limiting at higher temperatures. A bed of "Dowex"-21K, 36 cm deep, fed at 12 ml/(min-cm^2) with feed containing 1 gram of plutonium per liter will absorb 80 grams of plutonium per liter of resin at 23°C and 120 grams per liter at 50°C.

The capacity of the anion exchange resins for the absorption of plutonium depends on the concentrations of nitrate ions in the feed. The maximum capacities are obtained if the nitrate concentration is between 7.5 and 9M. The capacity of the resin is not changed significantly when the concentration of hydrogen ions is varied if the concentrations of the other cations and of nitrate ions in the feed remain as shown in Fig. 13. Thus, when the concentration of hydrogen ions in the feed is varied from 5 to 8M, but the total nitrate concentration remains 9M, the operating capacity of a 36-cm column of "Dowex" 1-X4 is constant at about 70 grams of plutonium per liter of resin.

NEPTUNIUM RECOVERY

Neptunium can be conveniently isolated by anion exchange from concentrated nitric acid solutions produced by solvent extraction during the processing of irradiated fuel elements. The strong anionic complex formed by Np(IV) in 8M nitric acid is easily absorbed on strong base anion exchange resins. The other oxidation states of neptunium that can exist in nitric acid, Np(V) and (VI), do not form strong anionic complexes. In the solutions from which neptunium can be recovered, the concentration of neptunium may vary from a few tenths of a milligram to a few hundred milligrams per liter. In this dilute range, the relative amounts of neptunium absorbed by the resin are independent of the concentration of the neptunium in the solution. The capacities, therefore, are most conveniently expressed in terms of the distribution coefficient, K_d, which is the ratio, at equilibrium, of the neptunium absorbed per ml of resin to the neptunium remaining in the solution per ml.

Np(IV) is most readily absorbed from 8M nitric acid. Fig. 14 shows the effect of the concentration of nitric acid on the distribution coefficient. This figure also shows the rapid decrease in the value of the distribution coefficient when sulfate ion is added to a solution containing neptunium in 8M nitric acid. Neptunium has a distribution coefficient of 625 in 8M nitric acid, whereas the coefficient for Np(V), and (VI), and for uranyl ions are only about 10. Under these same conditions, the distribution coefficients for Pu(IV) and Th(IV) are 900 and 180, respectively. At the concentrations that are usually present in the feeds, neither plutonium nor uranium affects the distribution coefficient of Np(IV). Because most other cations do not form an anionic complex in 8M nitric acid, considerable purification is obtained.

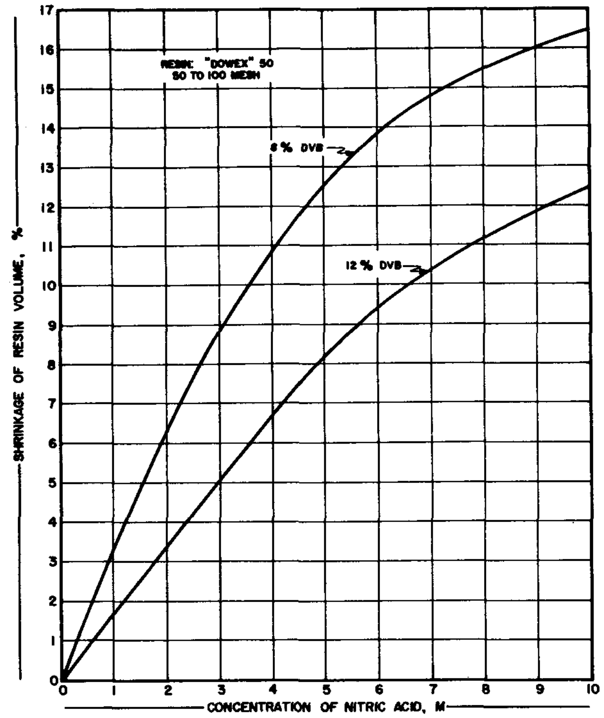
Any Np(V) and (VI) in the 8M nitric acid solution may be chemically reduced to Np(IV) in 30 minutes at 23°C by 0.02M ferrous sulfamate. Excess ferrous ion is oxidized when this feed solution contacts the resin, and small bubbles of gas completely permeate the void space between the resin beads. Neither the adsorption nor the elution of the neptunium is hindered by these small bubbles of gas. The formation of gas in the column can be avoided, however, by destroying the ferrous ions. This can be done without significant reoxidation of the neptunium by heating the reduced solution to 60°C and holding it at that temperature for 30 minutes. The feed should then be cooled rapidly to retain the neptunium in the tetravalent state. At 23°C, Np(IV) in 8M nitric acid is not oxidized at all.

The chemical flowsheet for a typical recovery process is presented in Fig. 15. Over 97% of the neptunium in the feed is recovered and concentrated 300-fold in one cycle of ion exchange. Operation of the process at room temperature is preferred. At 55°C only 60% as much neptunium is absorbed as at 23°C. The rate of removal of the neptunium from the resin bed during the elution step is the same at both 23 and 55°C. The capacity of the resin for absorption of Np(IV) decreases 28% when the feed flowrate is increased from 4 to 20 ml/(min-cm^2). For the elution step, flowrates up to 1 ml/(min-cm^2) are practical.

REFERENCE

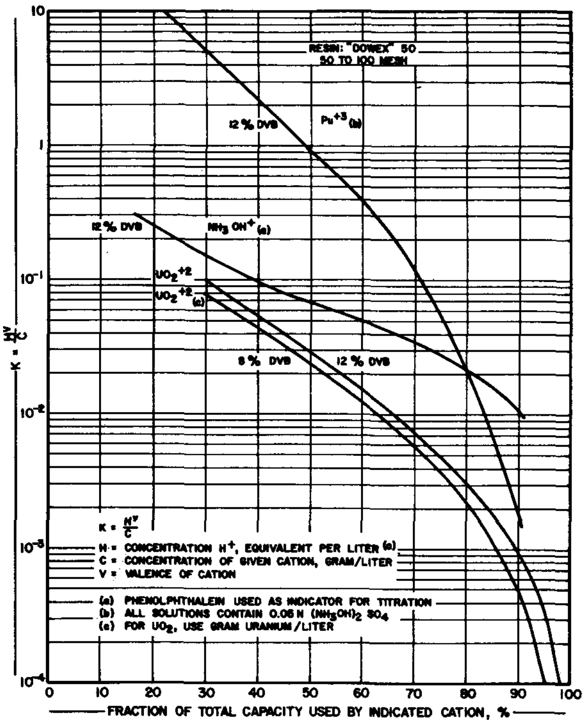
(1)Aiken, A. M., Ion Exchange Recovers Plutonium from Irradiated Fuels, Chemical Engineering Progress, 53: 82F-85F, (1957).

FIGURE 1



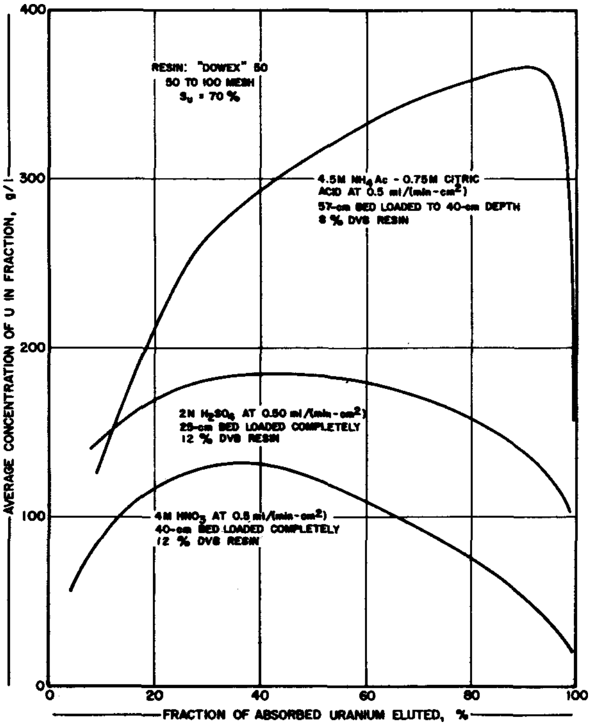
EFFECT OF HNO_3 CONCENTRATION ON RESIN SHRINKAGE

FIGURE 2



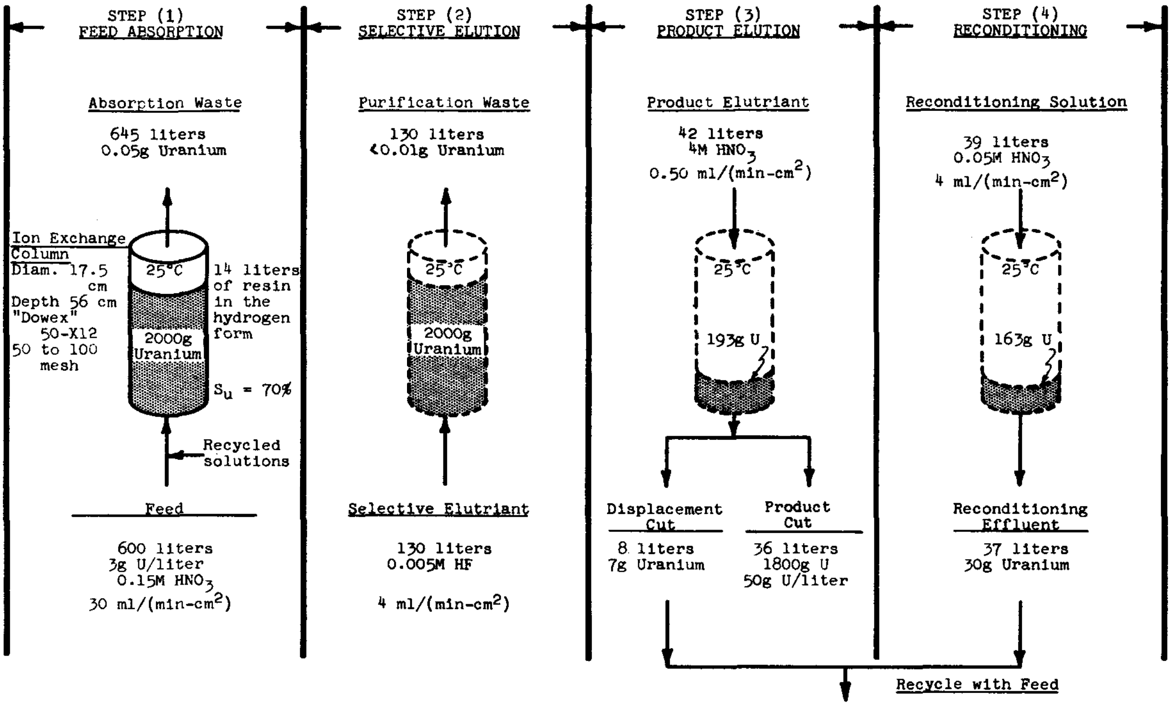
DATA FOR CALCULATION OF RESIN CAPACITIES FOR Pu^{+3}, (UO_2) AND (NH_3OH)

FIGURE 3



CONCENTRATIONS OF URANIUM OBTAINED WITH VARIOUS ELUTRIANTS

FLOWSHEET A: ELUTION WITH 4M NITRIC ACID



FLOWSHEET B: ELUTION WITH 4.5M AMMONIUM ACETATE AND 0.75M CITRIC ACID (pH = 5.2)

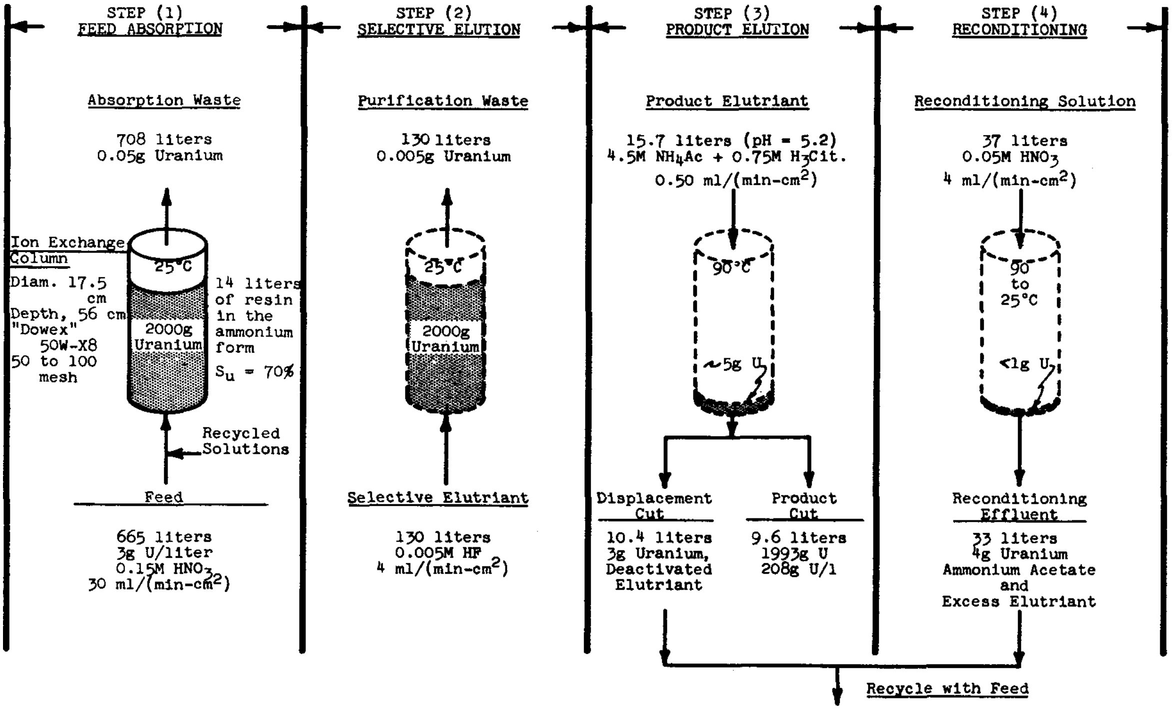
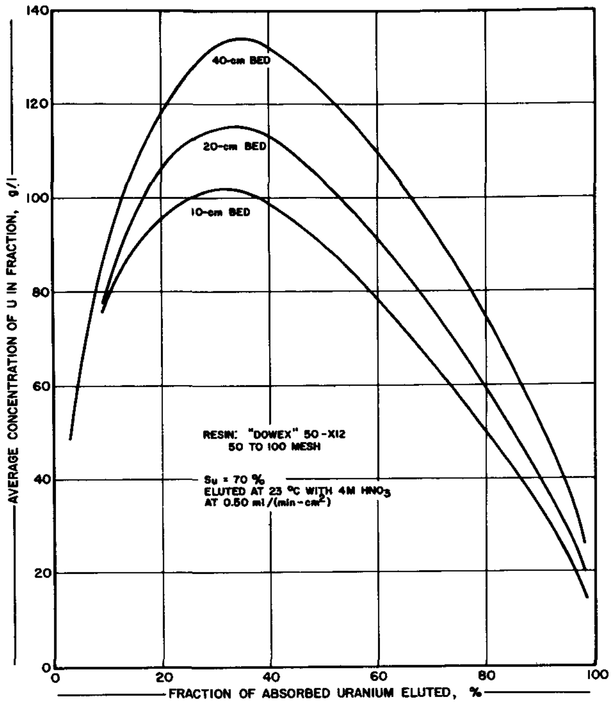


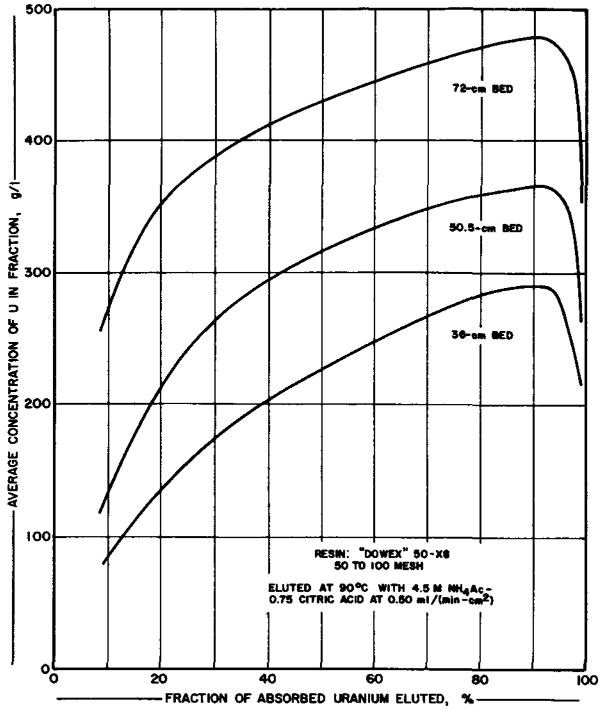
FIGURE 4 CHEMICAL FLOWSHEETS FOR PROCESSING URANIUM

FIGURE 5



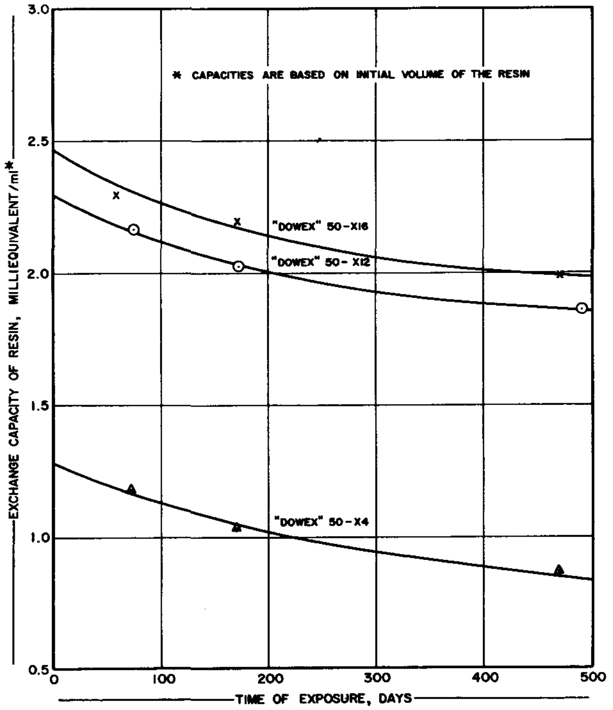
EFFECT OF BED DEPTH ON CONCENTRATION OF URANIUM IN PRODUCT

FIGURE 6



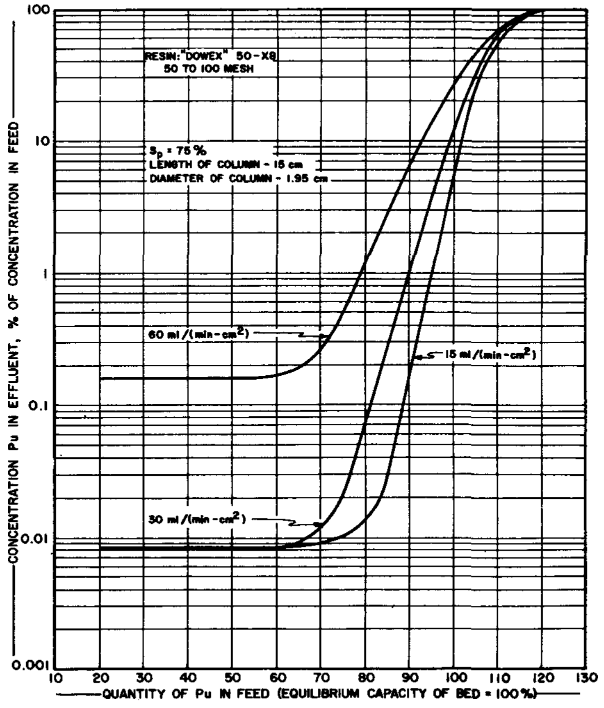
EFFECT OF BED DEPTH ON CONCENTRATION OF URANIUM IN PRODUCT

FIGURE 7



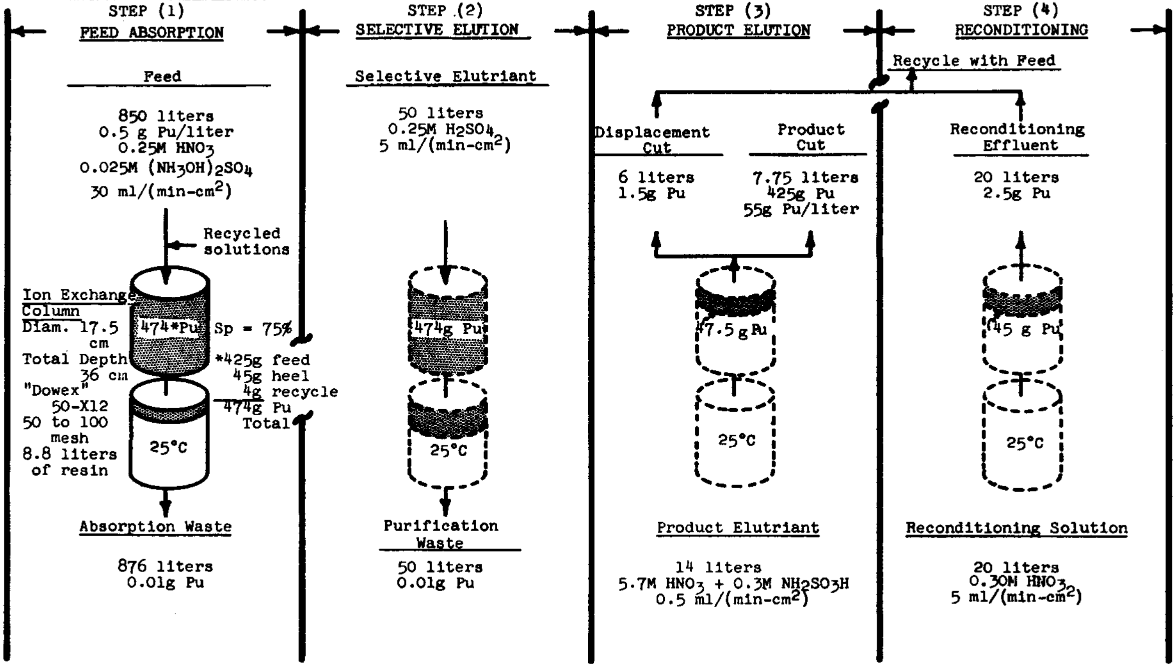
EFFECT OF ALPHA RADIATION ON EXCHANGE CAPACITY OF "DOWEX" 50 RESIN

FIGURE 8



EFFECT OF FLOW RATE ON CONCENTRATION OF Pu IN EFFLUENT

FLOWSHEET A: ELUTION WITH 5.7M NITRIC ACID STABILIZED WITH 0.3M SULFAMIC ACID



FLOWSHEET B: ELUTION WITH 3.25M AMMONIUM LACTATE (pH = 5.3)

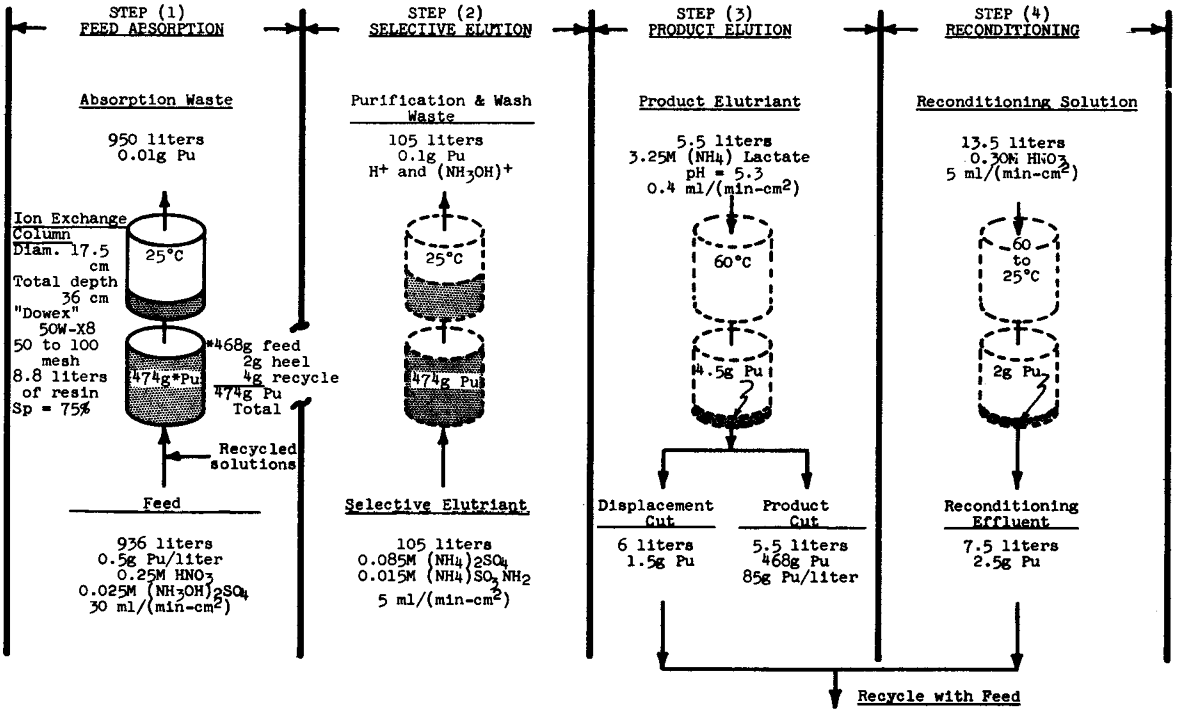
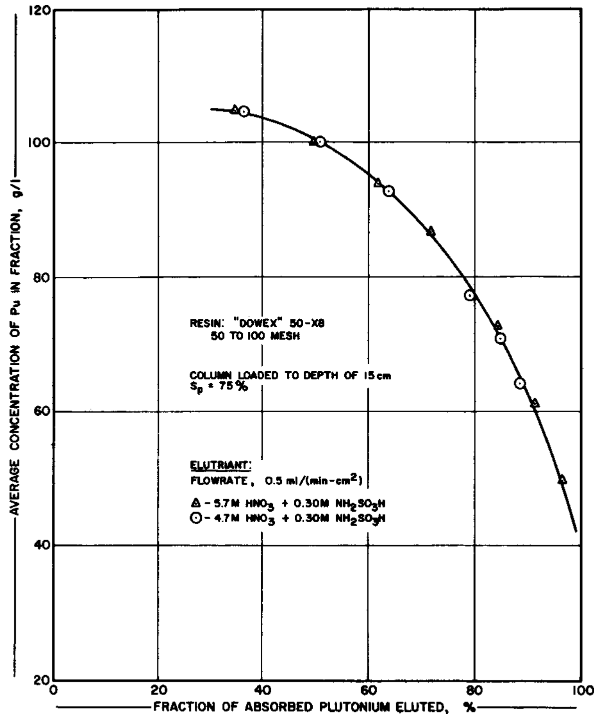


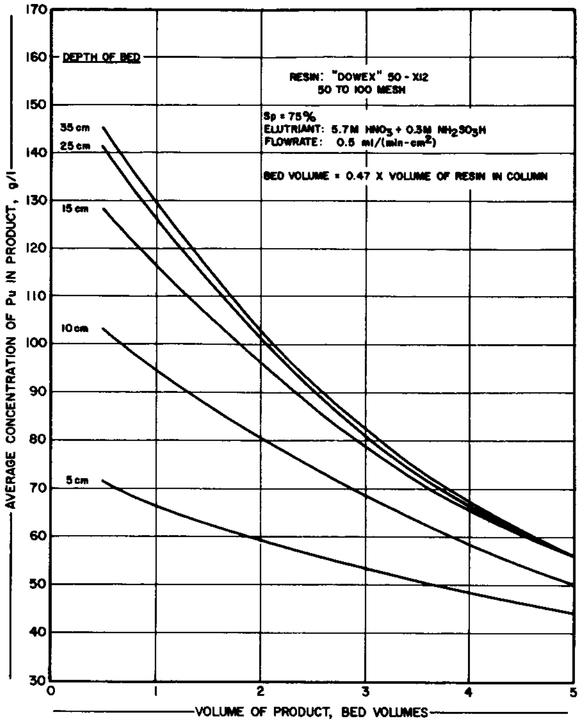
FIGURE 9 CHEMICAL FLOWSHEETS FOR PROCESSING PLUTONIUM

FIGURE 10



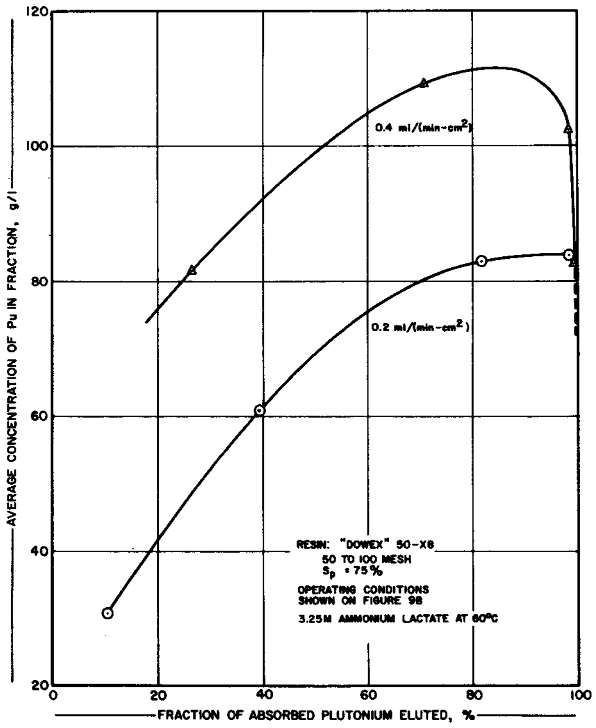
EFFECT OF ELUTRIANT COMPOSITION ON CONCENTRATION OF PLUTONIUM IN PRODUCT

FIGURE 11



EFFECT OF BED DEPTH ON CONCENTRATION OF Pu IN PRODUCT

FIGURE 12



EFFECT OF ELUTRIANT FLOWRATE ON CONCENTRATION OF PLUTONIUM IN PRODUCT

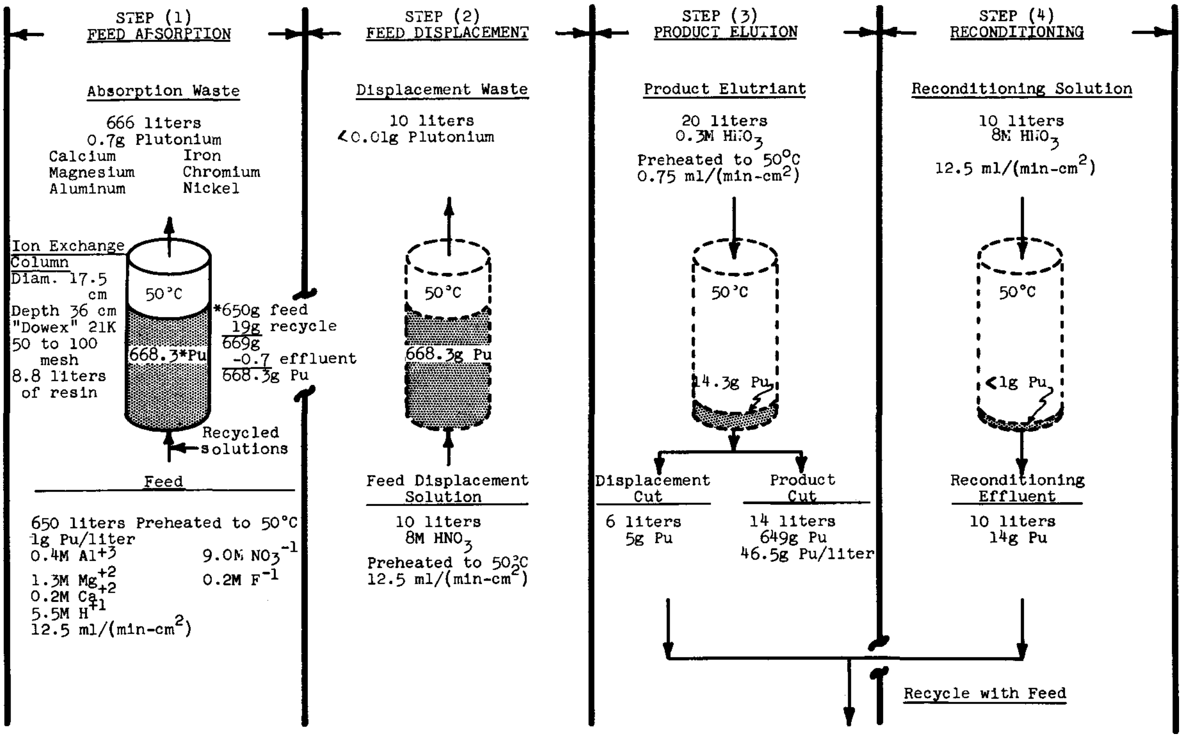
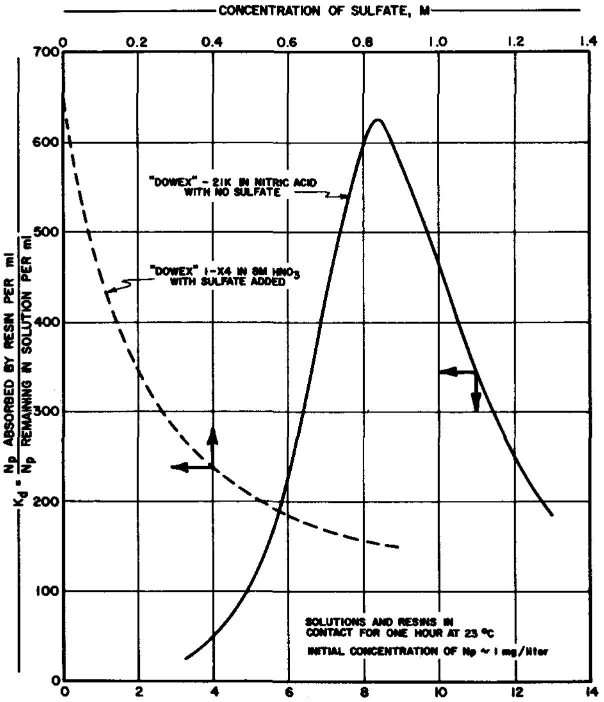
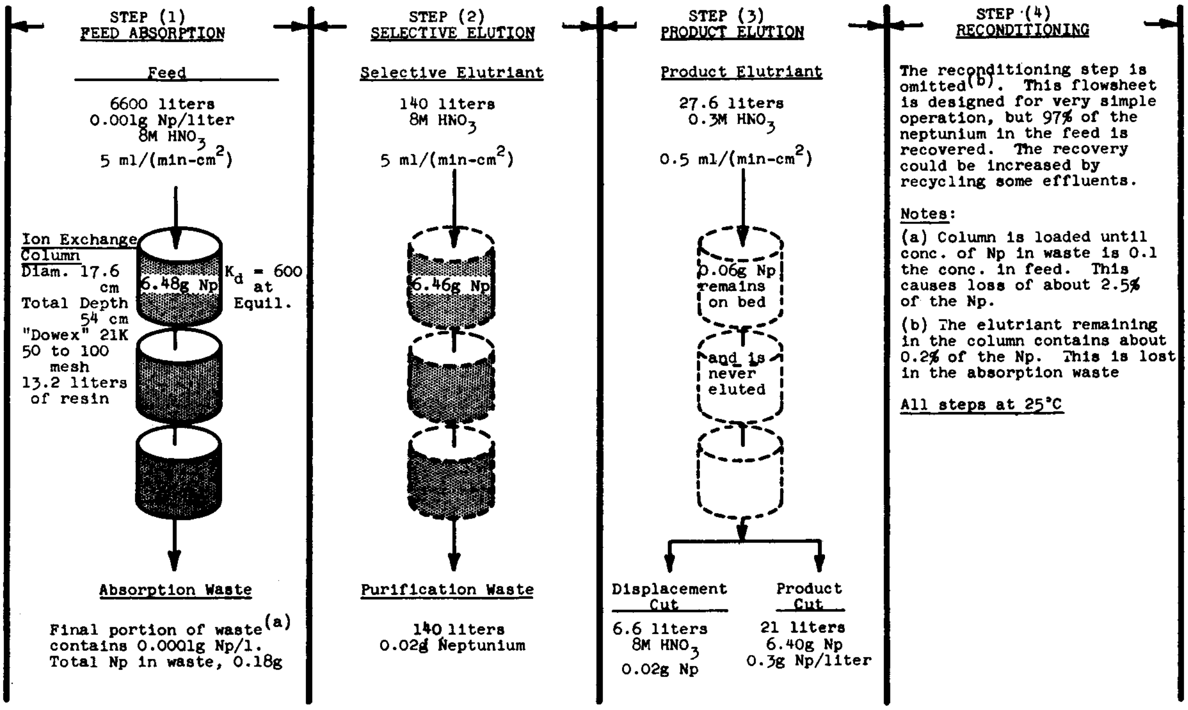


FIGURE 13 FLOWSHEET FOR RECOVERY OF PLUTONIUM BY ANION EXCHANGE

FIGURE 14



EFFECT OF NITRIC ACID AND SULFATE CONCENTRATIONS ON DISTRIBUTION COEFFICIENT FOR NEPTUNIUM



The reconditioning step is omitted(b). This flowsheet is designed for very simple operation, but 97% of the neptunium in the feed is recovered. The recovery could be increased by recycling some effluents.

Notes:

(a) Column is loaded until conc. of Np in waste is 0.1 the conc. in feed. This causes loss of about 2.5% of the Np.

(b) The elutriant remaining in the column contains about 0.2% of the Np. This is lost in the absorption waste

All steps at 25°C

FIGURE 15 FLOWSHEET FOR RECOVERY OF NEPTUNIUM BY ANION EXCHANGE

* U. S. GOVERNMENT PRINTING OFFICE : 1958 O— 469430 (J-1433)