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E U R O C H E M I C
T E C H N I C A L R E P O R T N O . 120

Study of the Kinetics of Loading Pu(IV) on Permutit SK
Resin from 7.2 M Nitric Acid

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SUMMARY

The Final Purification Group of the Applied Chemistry Section studied the possibility of using ion exchange resins for the final purification of plutonium separated from irradiated fuel.

This report gives the results obtained for plutonium loaded on 40-70 mesh Permutit SK resin at 60°C from a solution 7.2 *M* in nitric acid and with initial plutonium concentrations of 0.8-5 g/liter.

1. INTRODUCTION

The properties of anion exchange resins were studied by Ryan and Wheelwright (1); their publication, "The Recovery, Purification and Concentration of Plutonium by Anion Exchange in Nitric Acid," was the basis for our work.

2. SELECTION OF CONDITIONS

2.1 Resin

A series of comparative studies with different types of resin was made by Ryan and Wheelwright; their conclusions were that two types of resin are the most suitable: Dowex 1-4X and Permutit SK. After exchange of a series of private communications (2) with Ryan and Wheelwright and the Permutit Company, it was decided that Permutit SK was better for the initial studies because of (a) its greater resistance to radiation (1, 2) and (b) its lower loss of load to liquids (2).

The choice was between 20-50 mesh and 40-70 mesh. The 40-70 mesh was selected because the smaller size of the granules gives a higher decontamination factor (1). Permutit SK is a polystyrene base anion resin with the addition of divinylbenzene; its cross-linkage is about 4%. Its equilibrium capacity at 25°C is 3.5 meq/g.

2.2 Operating Temperature

A temperature of 60°C was selected, based on studies made at different temperatures (1), which showed that this temperature is the best for highest loading on the resin.

2.3 Solutions

2.3.1 Nitric Acid

A nitric acid concentration of 7.2 *M* was selected, based on the conclusions of Ryan and Wheelwright (1).

2.3.2 Plutonium Concentration

The plutonium concentration of the initial solution was selected from the results given in ETR-78 (8).

3. OPERATING METHOD

3.1 Preparation of Reagents

3.1.1 Plutonium Nitrate Solutions

Solutions with a plutonium concentration of 0.8 to 11 g/liter and a nitric acid concentration of 7.2 *M* were prepared from (a) a nitric acid solution of plutonium nitrate, 130 g/liter, from CEA, which was diluted with nitric acid (Merck p.a.*) of known strength and with distilled water; or (b) various recovered solutions (elution, etc.) to which were added, if necessary, concentrated p.a.* nitric acid to the desired acidity. To the solution thus prepared was added several drops of sodium nitrite to stabilize the plutonium to a valence of IV; this stabilization was made the day before the test. The plutonium concentration was determined by counting and the valence state by extraction with thenoyl trifluoroacetone (TTA).

3.1.2 Resin Preparation

By decantation, 5 g of resin was washed with 0.6 *M* HNO₃ until the chloride ion disappeared; washing was continued with 7 *M* HNO₃ (10 times the volume of the resin). No tests were made on controlling resin degradation, but in order to keep the resin properties constant during the runs, the resin bed was changed every three or four tests.

3.2 Apparatus

3.2.1 Column

Figure 1 is a schematic drawing of the apparatus used. The column was made of Pyrex and had the dimensions

31 cm height	0.125 cm ² cross-section	3.88 cc useful vol
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The connections were made from PVC to prevent rigidity of the assembly, and therefore, breaking. The valves were manual, and therefore, flexible. The dead volume of the piping upstream of the column was 5.5 cc; that of the piping downstream (flowmeter, etc.) was 4.5 cc (3).

*Translator's note: presumably, "pour analyses" = analytical grade.

3.2.2 Liquid Movement

Experience showed that the only way to obtain constant feeding, and thus a constant flow, was to place the feed vessel under a constant pressure. The pumping system was not used because of the very low flows. The apparatus is shown schematically in Fig. 2.

3.2.3 Flow Measurement

The flowmeter used was a Greiner, Model 9142 B. This meter covers the range of flows used in the tests made with solutions of initial plutonium concentration < 2 g/liter. The flowmeter was first scaled for the different solutions used, and at operating temperature. The precision of flow measurement was less than 1%.

3.2.4 Thermostats

The thermostat for maintaining the column at 60°C was placed, for safety reasons, in the glove box; the apparatus used was a Haake brand, Model F. The error was less than 0.1°C .

3.3 Resin Loading

The column temperature was maintained at operating temperature (60°C) for 30 min, and the plutonium solution in Vessel A (Fig. 1) was passed through the resin column at a fixed rate; this rate was regulated by the pressure in "1" and by the needle valve in B or C (Fig. 1); it was monitored during the run by indirect reading (no. of ml passed and time measured for this passage) from Flowmeter 9.

3.4 Sampling

After passing the resin, the solution entered the capillary at B (Fig. 1) when the initial plutonium concentration was from 0.8 to 2 g/liter. For solutions of initially higher plutonium concentration, the original volumes were small. Since the dead volume in the piping after the column (4.5 cc) was not negligible, the solution went directly to the capillary at C after passing the column. Samples for analysis were taken at regular intervals, which were determined by the nature of the initial feed solution and the flow rate.

3.5 Analyses

3.5.1 Original Plutonium Solution

The plutonium concentration and valence were determined.

Note. Since spectrometric examination of the original solution did not indicate the presence of other α emitters than plutonium, the α determination on the solution was made again after passage through the resin; these solutions should contain all the americium and curium in the original solution, since they are not sorbed by the resin; further, since most of the plutonium is sorbed by the resin, the (Am + Cm)/Pu ratio should be higher.

Under these new conditions, the presence of a maximum of 2-3% americium and curium was noted; no account was taken of this amount in our calculations, and our solution was considered as containing pure plutonium.

3.5.2 Sampling during Loading

The samples taken at regular intervals during loading were analyzed to determine the plutonium concentration. A sample was taken at the beginning of the loading (after passage of 5-6 cc, for example) for extraction with TTA to determine the stabilization of the plutonium valence at IV and titration to determine the nitric acid molarity of the initial loading solution.

3.6 Analytical Method

3.6.1 Nitric Acid Concentration

The nitric acid concentration was determined by titration with sodium hydroxide of known concentration, with a pH meter or a colored indicator (phenolphthalein) to show the end of the reaction. The precision was better than 2%.

3.6.2 Plutonium Concentration

3.6.2.1 Preparation of Samples

The plutonium concentration of the various solutions was determined by counting a stainless steel coupon. A known amount of solution was placed on a 1-in.-diam stainless steel plate and evaporated with an infrared lamp. The amount of solution deposited was such that the count rate was between 5000 and 30,000 c/100 sec. If the plutonium concentration of the solution was such that direct pipetting would give too high a count rate (e.g., initial solution), part of the solution was diluted to a known volume and aliquots were taken.

3.6.2.2 Apparatus

The α -counting assembly was made from a scintillation detector without window, developed at CEN. It was Model 7C20. This detector was connected to a counting scale Model AS1, also developed at CEN. The efficiency of this assembly is about 45%.

3.6.2.3 Control

To eliminate error in the measurements, the following rules were applied:

For direct pipetting, two coupons were prepared; when dilution was necessary, two dilutions and two coupons were prepared for each dilution, four coupons in all for the measurement; each coupon was counted three times, and the average of the three measurements was taken; then, the over-all average was determined from two coupons (direct pipetting) or from four coupons (pipetting with dilution). A determination was considered exact only when the difference between the general average and the average of the three measurements made on each coupon was less than 5%. In cases where the difference was more than 5%, two more coupons were made or a new dilution.

The background and the efficiency of the counting assembly were determined before and after each series of measurements, as well as at regular intervals during the counting to prevent any irregularity in the measurements.

3.6.3 Control of the IV Valence of Plutonium

An aliquot of the original solution was diluted to give 1000 c/100 sec/ λ and to be 1 M in nitric acid. One cubic centimeter of this solution was contacted with an equal volume of a solution of thenoyl trifluoroacetone, 0.15 M in benzene. After decantation, the activities of the organic and aqueous phases were counted. If the plutonium is in the IV valence state, all the activity should be found in the organic phase, as Pu(III) and Pu(VI) are not extracted by TTA solution. We considered stabilization good when 99.5% of the plutonium was found in the organic phase.

4. EXPERIMENTAL RESULTS

4.1 Objective of Tests

The tests were made with the objective of determining the experimental relations from which could be calculated the loading conditions for a resin column as a function of its dimensions and of the plutonium concentration in the loading solution.

The study was carried out as follows:

a. A series of tests was made at different loading rates with a loading solution of constant plutonium concentration, 7.2 M in nitric acid, and a temperature of 60°C.

b. A series of tests was made with a constant loading rate (expressed as mg of Pu/min/cc of resin) for plutonium concentrations in the loading solution of 0.8 to 11 g/liter, 7.2 M in nitric acid, and a temperature of 60°C.

c. The experimental results were interpreted to show the relations between the plutonium loading rate, the time of contact of the solution with the resin, the initial plutonium concentration of the solution, the plutonium concentration of the column effluent solution, column exit, the size of the resin particles, and the resin loading.

4.2 Tests at Different Loading Rates for a Constant Plutonium Concentration

Table 1 gives the original solution conditions and the loading rates used.

TABLE 1

Test No.	Pu Conc., g/liter	HNO ₃ Conc., M	Pu Loading Rate, mg/min/cm ³	Temp., °C
1	0.805	7.2	0.416	60
2	0.729	7.2	0.1886	60
3	0.784	7.2	0.7825	60
5	0.835	7.05	0.626	60
6	0.7662	7.15	0.3058	60
7	0.7185	7.3	0.186	60
9*	1.9038	7.2	1.48	60

*Test 9 was made with a higher concentration, because of the high rate, we were limited by the capacities of the apparatus at our disposal. The results are included here since they were in agreement with the preceding.

Figure 3 gives the results of the tests reported in Table 1. On the abscissa is shown the milligrams of plutonium that entered the column and on the ordinate, the milligrams of plutonium leaving the column. For some points the possible error is given, assuming that the counting error of the original solution is $\pm 5\%$.

Preliminary Observations. A negative effect of the loading rate is noted, the higher the loading rate, the more the resin capacity decreases, resulting in a more rapid appearance of the breakthrough point. The curves of Tests 3 and 5 and of 1 and 6 were interchanged with respect to the general behavior of the other curves; but as may be seen from Fig. 3, this change is within the limits of experimental error. It may also be noted that for all loading rates, before saturation of the resin, a plateau was present near a concentration of 1.5 mg Pu/liter in the column effluent. The average plutonium value calculated for the tests is 1.7 mg/liter.

4.3 Tests at Constant Loading Rates for Variable Plutonium Concentrations

These tests were made to determine the plutonium concentration in the original solution that could give the same loading characteristics as were obtained

in tests with an original solution having a plutonium concentration of 0.8 g/liter, so that the most general formula possible could be determined for loading.

Table 2 gives the original conditions of these tests.

TABLE 2

Test No.	Pu Conc., g/liter	HNO ₃ Conc., M	Pu Loading Rate, mg/min/cm ³	Temp., °C
15	11.88	7.2	0.366	60
16	5.48	7.16	0.354	60
18	7.74	7.25	0.366	60

The results led to the following conclusions:

1. For plutonium concentrations in the original solution of 0.8-5.4 g/liter and for the same loading rate expressed as mg Pu/min/cc, the behavior of the resin does not change significantly. These results confirm and complete those of Ryan and Wheelwright (1). Figure 4 gives the curve for resin loading with a solution containing 5.48 g of plutonium per liter (Test 16) compared with one for an 0.8-g/liter solution (Test 6) at very nearly the same loading rate expressed as mg Pu/min/cc.

2. For plutonium concentrations higher than 5.48 g/liter, the resin loading changes significantly. The results are not reported since they are not complete and require confirmation. It may be preliminarily stated that these tests indicate: (a) for plutonium concentrations higher than 5.48 g/liter, the plateau is at a higher concentration, i.e., at 6-7 mg/liter for a solution containing 7.74 g/liter (Test 18) and at 5-6 mg/liter for a solution containing 11.8 g/liter (Test 15); and (b) the resin loading is higher than for concentrations between 0.8 and 5 g/liter; it does not follow the same formula.

The results of the completed tests together with the supplementary results obtained will be reported later with considerations on the possible use of more concentrated plutonium solutions in the application of resins to final plutonium processing.

5. INTERPRETATION OF EXPERIMENTAL DATA

5.1 Introduction

Based on the data given in Sects. 4.2 and 4.3, it may be concluded that (a) the resin loading is inversely proportional to the flow rate of the solution

through the column, and (b) the plutonium concentration is not important in the range 0.8-5.5 g/liter.

From the report of Ryan and Wheelwright (1), it may be concluded that (a) the chemical species of plutonium sorbed by the resin, from the work of Durham and Mills (4, 5) and of Ryan and Wheelwright (1), from nitric acid solution is the Pu(IV) ion in the form $\text{Pu}(\text{NO}_3)_6^{=}$. This was determined by measuring the plutonium capacity of a resin of known capacity in milli-equivalents per gram. For all measurements made, the resin capacity was determined to be very close to but never higher than the capacity that it has for a divalent ion. The following reactions may be written:

and (b) three different reactions may be considered responsible for the ion exchange between an aqueous solution and a resin (1):

- I. Chemical exchange reaction at the resin surface.
- II. Gradient of laminar diffusion at the surface of the resin bed.
- III. Diffusion of particles across the bed cross-linkage.

Each of these reactions has its own rate; the slowest controls the kinetics of the exchange.

1. If the chemical exchange reaction at the surface of the resin controls the extraction mechanism, the exchange rate should be independent of the resin particle size. It has never been shown that a resin sorption reaction is controlled by this reaction.

2. If the gradient of laminar diffusion at the surface of the resin bed controls the extraction mechanism, the exchange rate would be directly proportional to the solution concentration. Further, the resin loading at equilibrium Q_∞ expressed as g Pu/g resin would be proportional to the original concentration. It has been shown (1, 4) that with 1% cross-linked resin at 60°C for plutonium concentrations < 0.4 g/liter, the loading at equilibrium is proportional to the plutonium concentration. Based on the above, these authors thought that the same phenomenon operated in different types of resins, especially the Permutit SK used in our tests. From these considerations, it may be concluded that for plutonium concentrations < 0.4 g/liter, sorption by Permutit SK, 4% cross-linked, is controlled by the mechanism of laminar diffusion.

3. If the extraction is controlled by the diffusion rate of the particles in the bed cross-linkage, the following relation, as demonstrated by Boyd and Adamson (6) holds:

$$F = \frac{Q_t}{Q_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{e^{-n^2 Bt}}{n^2} \quad (2)$$

where Q_t = amount of ion loaded on resin in time t
(seconds) (g ion/g resin)

Q_∞ = amount of ion loaded on resin at equilibrium
at infinite time (g ion/g resin)

$$B = \pi^2 D_i / r^2 \quad \text{or} \quad (3)$$

where D_i = interdiffusion coefficient, cm^2/sec

r = radius of the resin particle, cm

From this formula the following preliminary conclusions may be drawn:

1. F is independent of the ion concentration for given values of t
2. Q_∞ is a fixed value, independent of the ion concentration

It has been shown (1, 4) that under our operating conditions (60°C , 7.2 M HNO_3), the diffusion mechanism of the particles across the resin cross-linkage governs the extraction according to the law of Boyd and Adamson (Formula 2) for plutonium concentrations in the solution $> 0.4 \text{ g/liter}$.

General Conclusions. It may be concluded that under our operating conditions (60°C , 7.2 M HNO_3) and for plutonium concentrations less than 0.4 g/liter , the reaction is controlled by the mechanism of gradient of laminar diffusion while for higher concentrations, the reaction is controlled by the mechanism of diffusion of particles across the resin bed cross-linkage.

5.2 Tests at Different Loading Rates and Constant Plutonium Concentration

5.2.1 Plutonium Concentration $\leq 0.4 \text{ g/liter}$

5.2.1.1 Preliminary

During resin loading, the concentration of the column effluent is around 1.7 mg/liter for part of the loading (see observations in 4.2). When the resin is saturated, the concentration increases progressively (Fig. 3) to reach a limit approaching the concentration of the initial loading solution. On this basis, if all the experimental points for which the plutonium concentration of the solution leaving the resin is higher than 0.4 g/liter are plotted with an abscissa showing the operating time and the ordinate the plutonium loading on the resin, a curve should be obtained which has the same shape as the equation of Boyd

and Adamson (see Sect. 5.1). In operating in this way, one forgets that during the first part of the loading, only a part of the column operates according to the theory of Boyd and Adamson while another part operates according to the rule of laminar diffusion of particles. This hypothesis in all cases is approximately valid if the actual time of contact of the solution with the resin is negligible with respect to the total operating time.

Figure 5 gives the experimental points obtained for concentrations of ≥ 0.4 g/liter. As may be seen, this experimental curve has the form of an asymptotic negative exponential curve. The value of the asymptote is the resin loading at infinite time, i.e., at resin saturation.

5.2.1.2 Calculation of Saturation Loading of the Resin, Q_{∞} and Diffusion Coefficient D_i

If Relation 2 in Sect. 5.1 is taken, we may write:

$$F = \frac{Q_t}{Q_{\infty}} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{e^{-n^2 B t}}{n^2} \quad (4)$$

Q_t = amount of Pu loaded on resin at time t
expressed as g Pu/liter resin

Q_{∞} = amount of Pu loaded on resin at infinite
time expressed as g Pu/liter resin*

*In Sect. 5.1 this amount is given as g Pu/g resin; in our case it is given as g Pu/liter of resin, the volume of the resin being measured in a 7.2 M HNO₃ medium. To go from one expression to the other, the density of the resin in 7.2 M HNO₃ must be inserted. The value of the ratio Q_t/Q_{∞} does not change, regardless of the dimension used to express the plutonium resin loading.

B = a function of the diffusion coefficient D_i (see Sect. 5.1, Relation 3)

As may be noted, Expression 4 relates Q_t and t (Fig. 5) and assumes that the values of Q_{∞} and B are unknown.

This expression is of the form

$$D(K_j) = \frac{D_i}{(1 - e^{-K_j \cdot t_i})} \quad (5)$$

an expression for which a very elaborate solution was given by Erben (7). We solved this equation by the method given in Ref. 7. To solve it by this method, it must be assumed that K_j , in our case B , is constant as a function of time t .

It is assumed, then, in summary:

- a. Although during loading part of the column operates with a plutonium concentration < 0.4 g/liter, the law of Boyd and Adamson is followed by all points for a Pu concentration in the column effluent > 0.4 g/liter.
- b. The coefficient B, and consequently, the diffusion coefficient D_i , remain constant as a function of time for the tests made. On this basis Eq. 5 may be solved by the method given in Ref. 7.

Development of the Procedure.

1. An arbitrary value for B is taken, and from relation 4 the values of Q_{∞} are calculated by substituting the experimental values for t sec and Q_t (g Pu/g resin) (Fig. 5).
2. The average $\bar{Q}_{\infty}$ is calculated.
3. The sum of the differences of the squares between the Q_{∞} corresponding to the experimental points and the $\bar{Q}_{\infty}$ (avg) calculated in 2 ($\sum \Delta Q_{\infty}^2$) is calculated.
4. Other arbitrary values for B are taken, and the calculations are repeated.
5. A diagram is constructed in which the values of $\sum \Delta Q_{\infty}^2$ are reported as a function of $\bar{Q}_{\infty}$ (Fig. 6). The minimum of this curve gives the most probable value of $\bar{Q}_{\infty}$.
6. A diagram is constructed in which the values arbitrarily selected for B are given as a function of the corresponding $\bar{Q}_{\infty}$ (Fig. 7). The most probable value of B is the value corresponding (Fig. 7) to the value of $\bar{Q}_{\infty}$ determined in Sect. 5.
7. The values found in this case are

$$Q_{\infty} = 100.5 \text{ g/liter (Fig. 6)}$$

$$B = 14.5 \times 10^{-5} \text{ liter/sec (Fig. 7)}$$

But B is related to the diffusion coefficient, D_i , by Eq. 3:

$$B = \pi^2 D_i / r^2 \quad (3)$$

where $B = 14.5 \times 10^{-5}$ liter/sec and r = radius of resin particles or the average r for 40-70 mesh resin = 0.146×10^{-1} cm. Substituting these values in Expression 3 gives $Di = 3.125 \times 10^{-9}$ cm²/sec.

5.2.1.3 Determination of the Validity of the Hypotheses Advanced

Hypothesis a (Sect. 5.2.1.2). To study this hypothesis, the curve of Boyd and Adamson (Formula 4) was calculated by substituting the corresponding values found for Q_{∞} and B . The following expression was obtained:

$$F = \frac{Qt}{100.5} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{e^{-n^2 14.5 \times 10^{-5} t}}{n^2} \quad (6)$$

The curve calculated from this expression is shown in Fig. 5; its shape is in reasonable agreement with the experimental points.

Hypotheses b (Sect. 5.2.1.2). Figure 8 gives the values of the product Bt as a function of t for the experimental points as well as the average value of Bt as a function of t calculated with $B = 14.5 \times 10^{-5}$ (straight line).

The variation of the experimental points around this line does not change regularly as a function of time, and thus the second hypothesis may be said to be valid.

5.2.2 Plutonium Concentration < 0.4 g/liter

5.2.2.1 Preliminary

As said above, during loading, the plutonium concentration of the column effluent is constant during the first part of the loading but increases with saturation of the resin (Fig. 3).

5.2.2.2 Relation between Loading Rate and Load on Resin

The fact that the loading on the resin is inversely proportional to the loading rate suggested plotting the experimental points with the abscissa as the operating time and the ordinate, the resin loading.

Figure 9 shows the curves thus obtained; for each rate used, all the experimental points are on a straight line with its origin at zero. The slope of the line is equal to the loading rate expressed in mg/min/cc of resin.

It may be concluded that during loading of a column and for a concentration in the column effluent of plutonium 0.4 g/liter, the relation between the loading and the operating time is linear. The line representing the loading as a function of operating time starts at the origin, and its slope is the rate

expressed in mg/min/cc, i.e., a specific rate based on the volume of resin in the column, and thus independent of the column dimensions. The loading on the resin as a function of the loading rate may thus be expressed as

$$Q_t = Vt \quad (7)$$

where Q_t is the load, g/liter; V is the loading rate, mg/min/cc or g/min/liter; and t is the time, min.

5.2.2.3 Relation between Column Load and Plutonium Concentration of Column Effluent

If the curves in Fig. 3 are cut by lines at different ordinate values (e.g., 3, 6, 10, 20, 50, 100 mg/liter) and the corresponding loadings for the different tests are plotted as a function of the operating time, Figs. 10-15 are obtained. The points are distributed according to a curve whose shape is similar to that obtained with the points for a plutonium concentration of ≤ 0.4 g/liter (Fig. 5).

Let us assume that plutonium has been loaded on the resin from a solution of original plutonium concentration 0.8 g/liter, a rate of 0.416 mg Pu/min/cc (Test 1), and the loading stopped when the effluent plutonium concentration is 3 mg/liter.

The column may be represented as follows:

The upper part operates under conditions for which the rule of Boyd and Adamson is valid. The lower part operates under conditions controlled by the mechanism of the gradient of laminar diffusion of particles, giving a loading rate proportional to the plutonium concentration (Sect. 5.1). The load may thus be expressed as

$$Q_t = f(c)Q_\infty \left(1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{e^{-n^2 Bt}}{n^2}\right) \quad (8)$$

where $f(c)$ is a function of the column effluent concentration (breakthrough)

Q_∞ (1...) is a function of the law of Boyd and Adamson

If this formula can be reduced to a simple expression and the value of $f(c)$ determined, we may arrive at a final formula from which the load on the resin and the operating time could be determined for any loading rate and for any concentration in the column effluent (Fig. 10).

In other terms, the load on the resin may be represented by the product of two functions:

$f(c)$ = function of the column effluent concentration

$Q_{\infty}(1\dots)$ = function of time t , the values Q_{∞} and B determined above remaining unchanged

Let us examine the function $f(c)$ more closely. For values of $c \geq 0.4$ g/liter, its value should be 1; in this case Expression 8 is reduced to the formula of Boyd and Adamson.

On the other hand, there is a significance only at the beginning of the point of saturation of the resin, i.e., at the end of the plateau (Fig. 3). Thus we may write

$$f(c) = f(c/C_0) \quad (9)$$

where c is the plutonium concentration between 1.7 and 400 mg/liter and $C_0 = 400$ mg/liter. Relation 8 may thus be written as

$$Q_t^c = f\left(\frac{c}{C_0}\right) Q_{\infty} \left(1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{e^{-n^2 Bt}}{n^2}\right) \quad (10)$$

where Q_t is the load on the resin at time t for a loss in the column effluent of c mg/liter, c being between 1.7 and 400 mg/liter.

$$f\left(\frac{c}{C_0}\right) Q_{\infty} = Q_{\infty}^c \quad (11)$$

= load on the column at infinite contact time
for a column effluent loss of c

Summarizing, we may make the following hypotheses:

- a. For column effluent values between 1.7 (plateau) and 400 mg/liter, the loading phenomenon may be expressed as the product of two expressions (Relation 8) in which the first, $f(c)$, is a function of the plutonium concentration of the column effluent and the second, a function of the law of Boyd and Adamson.

- b. The function $f(c)$ may also be written in the form of Expression 9, an expression independent of the diffusion coefficient D_i .
- c. The values of B , and therefore, of D_i as well as of Q_{∞} of the formula of Boyd and Adamson (Relation 8) remain constant.

Their values are: $B = 14.5 \times 10^{-5}$ liter/sec; $Q_{\infty} = 100.5$ g Pu/liter

5.2.2.4 Calculation of Q_{∞}^c and $f(c/C_0)$

Calculation of Q_{∞}^c . Based on the above hypotheses, the average values of Q_{∞}^c ($\bar{Q}_{\infty}^c$), corresponding to the average of the different Q_{∞}^c for each experimental point, and those for different values of c were calculated. Table 3 gives these values

TABLE 3

c , mg/liter	$\bar{Q}_{\infty}^c$
3	77.3
6	83.3
10	85.6
20	89.1
50	91.3
100	94.6

Calculation of $f(c/C_0)$. A series of tentative graphical solutions of Eq. 11 led to the diagram in Fig. 16 on a double logarithmic scale. It may be seen that there is a linear relation between

$$\log \frac{Q_{\infty}^c}{Q_{\infty}} \quad \text{and} \quad \log \frac{c}{C_0}$$

Thus we may write

$$\log \frac{Q_{\infty}^c}{Q_{\infty}} = K \log \frac{c}{C_0} \quad (12)$$

If we now determine the value of K graphically, we obtain

$$\frac{Q_{\infty}^c}{Q_{\infty}} = \left(\frac{c}{C_0} \right)^{0.0463} \quad (13)$$

where $Q_{\infty} = 100.5$ g/liter and $C_0 = 400$ mg/liter

Expression 13 is not valid for $c < 1.7$ mg/liter, becoming equal to 1 for $c = 400$ mg/liter, as shown in Sect. 5.2.2.3.

5.2.2.5 Confirmation of the Hypotheses

Hypotheses b. Since the term D_i is not found in Expression 13, it may be concluded that this expression is independent of D_i .

Hypotheses c. Based on the experimental points obtained for a value of the effluent concentration and with the mathematical method proposed in Ref. 7, the optimum value of B for each concentration of column effluent was calculated.

Development of the Procedure.

1. For a determined value of c , an arbitrary value of B was taken, and with Relation 10 the values of Q_{∞}^c were calculated by substituting for t sec and Q_f^c the experimental values.
2. The average Q_{∞}^c ($\bar{Q}_{\infty}^c$) was calculated.
3. The sum of the differences of the squares ($\sum |Q_{\infty}^c - \bar{Q}_{\infty}^c|^2$) between the Q_{∞}^c corresponding to different experimental points and the $\bar{Q}_{\infty}^c$ calculated in 2 was calculated.
4. Other arbitrary values for B were taken and the calculations repeated.
5. A diagram was constructed in which the values of $\sum |Q_{\infty}^c - \bar{Q}_{\infty}^c|^2$ were given as a function of B .
6. The calculation was repeated for another value of c . Figure 17 gives the curves thus obtained (on this figure different scales were taken on the ordinate to show the minimum of each curve). Table 4 gives the optimum B obtained for each c considered.

TABLE 4

c , mg Pu/liter	$\bar{B} \times 10^{-5}$
3	11.30
6	15.125
10	15.0
20	14.40
50	12.50
100	15.0

As may be noted, the variation of $\bar{B}$ is not regular with the variation of c ; further, B calculated with these values gives $\bar{B} = 13.9 \times 10^{-5}$. In hypothesis c it is assumed that B is equal to 14.5×10^{-5} , the difference between these two values being less than 5%. It may be concluded that hypothesis c is equally valid.

Hypothesis a. Confirmation of the validity of hypotheses b and c implies automatically the validity of hypothesis a.

5.2.2.6 Conclusions. The semi-experimental relation between the resin loading, the effluent solution concentration in mg/liter, and the operating time is

$$Q_t^c = \left(\frac{c}{400}\right)^{0.0463} \cdot 100.5 \left(1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{e^{-n^2 \cdot 14.5 \cdot 10^{-5} \cdot t}}{n^2}\right) \quad (14)$$

From this formula the curves given in Figs. 10-15 were calculated, with the respective experimental points.

As may be seen, there is good agreement between the curves thus calculated and the points found experimentally.

Figure 18 gives all the curves together.

5.2.3 General Conclusions on Tests with Variable Loading Rate and Constant Concentration

a. During column loading, the concentration in the column effluent is constant up to a certain value during the first part of the loading.

b. At the beginning of saturation, the concentration of the effluent increases according to a law; there is a linearity between the load on the resin and the operating time for plutonium concentrations < 0.4 g/liter (Fig. 9).

The slope of the line that shows resin loading as a function of operating time is equal to the loading rate expressed as mg Pu/min/cc, represented by Formula 7.

c. The relation between the load on the resin, Q_t^c , the effluent concentration c , and the operating time t for plutonium concentrations of 1.7-400 mg/liter is represented by Formula 14. For plutonium concentrations of ≥ 400 or higher, Formula 6 applies.

d. These relations should be independent of the column dimensions.

5.3 Tests with Constant Loading Rate and Variable Plutonium Concentrations

As said in the introduction (Sect. 4.3), tests made with plutonium concentrations > 5.4 g/liter are not considered here because they must be confirmed.

From the test with 5.4 g/liter (Test 16), it may be seen that:

1. The curve of the effluent concentration as a function of the milligrams of plutonium passed through the column is very close to that obtained for the test with 0.8 g/liter made at a rate expressed in mg Pu/min/cc (Test 6). These two curves are shown in Fig. 4.
2. The curve for column load as a function of operating time is very close to the identical curves obtained for tests made with a plutonium concentration of 0.8 g/liter.

This may be seen in Fig. 19, in which are shown the parts of the curves from Figs. 10-15 as well as the experimental points obtained for Test 16 at 5.4 g/liter for different effluent concentrations.

3. For effluent plutonium concentrations of 0-400 mg/liter, the loading curve as a function of operating time is a straight line whose slope is equal to the loading rate expressed in mg Pu/min/cc (Fig. 20), as for the case of the tests with 0.8 g/liter (Fig. 9).

5.4 Conclusions

For concentrations between 0.8 and 5.4 g/liter plutonium, the law that controls the resin loading is practically the same and the phenomenon may be expressed by the mathematical expressions in Sect. 5.2.3.

6. EXTENSIONS OF CRITERIA GIVEN IN SECTION 5.2.3 TO LOADING OF PERMUTIT SK OF DIFFERENT SIZE THAN USED FOR THE TESTS

6.1 Introduction

Based on studies of Boyd and Adamson (6) on the theory of the exchange in the region controlled by the mechanism of diffusion of particles across the resin, it may be said that if the resin particle size is changed, the diffusion coefficient does not change; it depends solely on the chemical nature of the resin in question. On this basis, Expressions 6 and 14 were recalculated for Permutit SK of 20-50 mesh.

6.2 Expression of Resin Load on 20-50 Mesh Permutit SK

The diffusion coefficient, D_i , calculated for Permutit SK is:

$$D_i = 3.125 \times 10^{-9} \text{ cm}^2/\text{sec} \text{ (Sect. 5.2.1.2)}$$

But D_i is related to the factor B in the formula of Boyd and Adamson by

$$B = \pi^2 D_i / r^2 \quad (3)$$

where r is the average radius of the resin particles in centimeters. For Permutit SK, 20-50 mesh, $r_m = 2.845 \times 10^{-2}$ cm.

If the values are substituted in Eq. 3, we obtain

$$B = (3.14)^2 \times 3.125 \times 10^{-9} / (2.845)^2 \times 10^{-4} = 3.81 \times 10^{-5} \text{ sec}^{-1}$$

But Q_{∞}^{20-50} mg Pu/liter for the 20-50 mesh resin is related to Q_{∞}^{40-70} mg Pu/liter for the 40-70 mesh resin by

$$Q_{\infty}^{20-50} = Q_{\infty}^{40-70} \cdot \frac{D^{20-50}}{D^{40-70}} \quad (15)$$

where D^{20-50} is the density of Permutit SK of 20-50 mesh in g/liter of resin and D^{40-70} is the corresponding value for 40-70 mesh resin.

The density of the two resins was determined experimentally in the following way: a known amount of 20-50 mesh resin and of 40-70 mesh resin in the nitrate form in a 7.2 M HNO_3 medium was dried at 60°C to constant weight.

The results were

$$D^{20-50} = 386 \text{ g/liter and } D^{40-70} = 375 \text{ g/liter}$$

From Relation 15 we obtain

$$Q_{\infty}^{20-50} = 100.5 \times 386/375 = 103.5$$

Relation 14 may then be written

$$Q_t^c = \left(\frac{c}{400}\right)^{0.0463} \times 103.5 \left(1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{e^{-n^2 3.81 \times 10^{-5} t}}{n^2}\right) \quad (16)$$

This formula should be applicable to 20-50 mesh Permutit SK.

6.3 Partial Confirmation of the Validity of Formula 16

No tests were made with 20-50 mesh Permutit SK. However, Ryan and Wheelwright made a series of tests at 60°C with this resin.

Table 5 shows the operating conditions of their tests and of ours, from which we calculated Expression 16.

TABLE 5

Conditions	Ryan and Wheelwright	Eurochemic
Permutit SK mesh	20-50	40-70
Column ht, cm	45	30
Column section, cm ²	0.28	0.125
Temperature, °C	60	60
Pu Conc., Pu g/liter	0.55	0.8
Pu HNO ₃ Conc., M	7.2	7.2

It may be seen that the essential differences between the two tests were (a) resin particle size and (b) column dimensions.

Some experimental results of Ryan and Wheelwright are shown in Fig. 21, the resin load as a function of operating time for different effluent concentrations (55, 110, 165, 220, and 275 mg/liter); these data were taken from Fig. 10 of Ref. 1.

But from Formula 16, the curve thus calculated was also drawn in Fig. 21; the two curves are practically identical.

Table 6 gives the results of a more exact method.

TABLE 6

Effluent Pu Conc., mg/liter	Time, min	Ryan and Wheelwright Experimental	Eurochemic Calculated	Difference, %
55	166	49.6	52.00	+ 4.62
110	193	56.0	56.75	+ 1.34
165	207	59.4	59.4	0
220	218	61.3	61.4	+ 0.16
275	233	63.6	63.6	0

6.4 Conclusions

6.4.1

The semi-empirical Formula 16 obtained with 40-70 mesh resin is valid for 20-50 mesh resin and for an original concentration of 0.55 g/liter.

6.4.2

This formula is applicable to a column 45 cm high and 0.28 cm² cross section (rather than 30 cm and 0.125 cm² in our case); this indicates that the formula is independent of the column dimensions, but since the differences between the dimensions of the two columns are not great, this cannot be stated conclusively. Tests should be made with larger columns; an apparatus for tests with 60- and 120-cm-high columns is being prepared.

From the tests that will be made with these large columns, one of the two following conclusions may be expected:

- There is no effect of column dimensions on Formula 16; and, therefore, this formula is valid for any column.
- There is an effect of column dimensions on Formula 16, and the relation between this formula and the column dimensions would have to be found. This formula could be expressed by

$$Q_t^c = \left(\frac{c}{400}\right)^{0.0463} Q_\infty \left(1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{e^{-n^2 Bt}}{n^2}\right) f(h,s) \quad (17)$$

where $f(h,s)$ is a function of the column dimensions. The function $f(h,s) = 1$, based on data at our disposal.

7. EXAMPLE OF CALCULATION OF A PLUTONIUM ABSORPTION COLUMN

7.1 Introduction

The following assumptions are made:

- The column is not used for decontamination but only for plutonium concentration; it is thus not washed.
- Plutonium losses in the column effluent should be decreased to a minimum (maximum plutonium concentration, 3 mg/liter).
- In Eq. 17 the value of $f(h,s) = 1$.
- Permutit SK, 40-70 mesh, is used.

7.2 Calculation of the Column and Operating Conditions

7.2.1 Properties of Original Solution

Plutonium, 4 g/liter; HNO_3 , 7.2 M; amount to be processed per cycle, 1000 g of Pu (case a of ETR 78, Ref. 8)

7.2.2 Selection of Optimum Operating Conditions

Section 5.2.3 indicates that with the loss visualized in the aqueous raffinate (3 mg Pu/liter), we are in the region of linearity between the resin load and the loading rate. Relation 7 thus applies:

$$Q_t = Vt \quad (7)$$

But the load on the resin is related to time by Relation 14, in which known values have been substituted:

$$Q_t^3 = \left(\frac{3}{400}\right) \times 100.5 \times \left(1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{e^{-n^2 14.5 \times 10^{-5} t}}{n^2}\right) \quad (18)$$

shown in Fig. 10. Thus we must solve a system of two equations in three unknowns: Q_t , V , and t .

The easiest unknown to determine is V ; from Fig. 22 we may determine:

Region I: if a loading rate in Region I is selected ($V \times$ very large), the saving in time is counterbalanced by incomplete utilization of the resin (very small loading).

Region III: in this region the opposite phenomenon takes place, the maximum column capacity being used but the operating time being too long.

Region II: this region is a compromise between the two above solutions; the loading rate should thus be in this region; it is between 0.29 and 0.43 mg Pu/min/cc, which corresponds to the slope of the two lines that limit the region: in our case, the value of 0.35 mg Pu/min/cc is taken for V . Thus there remains to be solved a system of equations, 7 and 18, in two unknowns, Q_t and t .

The graphic solution of these two equations is given in Fig. 23.

In summary, we obtain $V = 0.35$ mg Pu/min/cc, $Q_t = 70$ g/liter, and $t = 200$ min.

Since these formulas may lead to an error of $\pm 10\%$, we will have $V = 0.35$ mg Pu/min/cc, $Q_t = 63$ g/liter, and $t = 180$ min.

7.2.3 Column Calculation

Given the amounts of plutonium to be processed, criticality considerations indicate that a column of diameter greater than 11.7 cm cannot be used.

The surface of such a column is thus

$$S = \pi 11.7^2/4 = 107.5 \text{ cm}^2 = 1.075 \text{ dm}^2$$

One could then load 1000 g from a solution of plutonium on a 1.075-dm² column from a solution of 63 g/liter. One would then have: $\text{vol} = 1.075 \times h = 1000/63$ liters, from which we calculate $h = 148$ cm. The column would thus have the dimensions $S = 107.5 \text{ cm}^2$ and $h = 148$ cm. The plutonium solution flow rate would be $V \times \text{vol}/c = D$, where V is the rate in mg/min/cc, vol is the column volume in cc, c is the loading solution concentration in mg/cc, and D is the flow rate in cc/min.

Substituting the known values gives $0.35 \times 15,900/4 = D = 1,390$ cc/min.

7.2.4

Table 7 gives all the operating parameters obtained above.

TABLE 7

h, cm	148
S, cm ²	107.5
Flow rate, liters/min	1.39
Loading, g/liter	63
Operating time, min	180
Effluent conc. Pu, mg/liter	< 3

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APPARATUS FOR PROCESSING

- ① Compressed air
 - ② Entrance for air bubbles
 - ③ Loading
 - ④ Discharge
 - ⑤ Heating jacket (H_2O at $60^\circ C$)
 - ⑥ Resin
 - ⑦ Filter
 - ⑧ Needle Valve
 - ⑨ Flowmeter
-
- (A) Solutions Receiver
 - (X) 2-Way Valve
 - (T) 3-Way Valve
 - (B) Exit for Low-Concentration Material
(0.8 to 2 g/liter Pu)
 - (C) Exit for High Concentration Material
and Elution

Fig 1

D. 767

FIG. 5

FIG. 6. DETERMINATION OF Q_{∞} FOR 40-70 MESH PERMUTIT SK RESIN BY THE METHOD OF LEAST SQUARES.

FIG. 7. VARIATION IN B AS A FUNCTION OF $\bar{Q}_\infty$.

D.769

0.776

D. 777

Nr. 369 $\frac{1}{2}$:2 P

Beide Achsen logar. geteilt, 1 bis 1000 u. 1 bis 100, Einheit 83.33 mm.

$$\sum \frac{P_c - P_c}{P_c - P_c} = 2$$

P.F. = Point de Fuite = Breakthrough Point

Ordinate Scale

P.F.	Origin	Unit / cm
3	200	5
6	200	5
10	190	1
20	100	5
50	0	5
100	10	1

FIG. 17

5×10^{-5}

FIG. 19

D.782

FIG: 21

FIG 22

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G. Vandeveldre

D.785

FIG. 23

Eurochemic 27-3-61

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