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LABORATORY DEVELOPMENT OF A
PRESSURIZED CATION EXCHANGE PROCESS
FOR REMOVING THE DAUGHTERS
OF ^{232}U FROM ^{233}U

R. H. Rainey



OAK RIDGE NATIONAL LABORATORY
OPERATED BY UNION CARBIDE CORPORATION • FOR THE U.S. ATOMIC ENERGY COMMISSION

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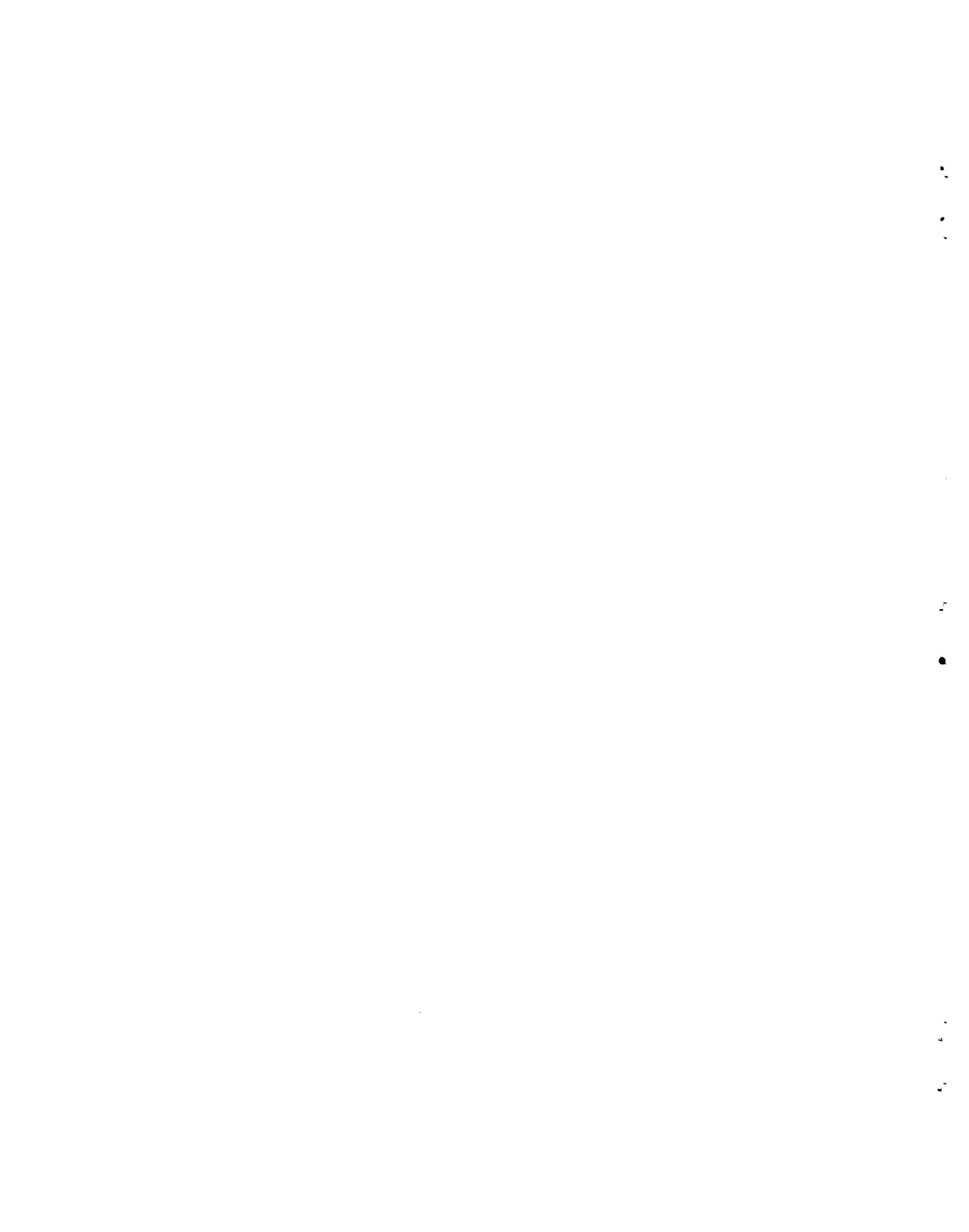
CHEMICAL TECHNOLOGY DIVISION
Chemical Development Section B

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R. H. Rainey

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ABSTRACT

A pressurized cation exchange process has been developed for decreasing the gamma activity due to the daughters of ^{232}U usually associated with ^{233}U so that the ^{233}U may be handled with minimal shielding. The process involves passing a $^{233}\text{UO}_2(\text{NO}_3)_2$ solution containing a few ppm of ^{232}U through a bed of cation exchange resin on which the long-lived daughters of ^{232}U are sorbed. The uranium-containing effluent is held for 2 days to permit decay of the short-lived daughters. The gamma activity in the resulting product solution is less than 2% of the equilibrium value and remains below this level for about 3 weeks. Chemical and physical parameters involved in the process were evaluated on a laboratory scale. Data developed in the laboratory were used in the design and construction of a plant that was a thousand times larger than the laboratory scale. Operation of this plant confirmed laboratory results.

1. INTRODUCTION

Uranium-233 is produced by the neutron irradiation of ^{232}Th . After irradiation, the thorium is dissolved in nitric acid using a fluoride catalyst. The uranium is then partially separated from thorium, fission products, and ^{232}U daughters by extraction with a 30% solution of tri-n-butyl phosphate (TBP) in a hydrocarbon diluent, using the Acid Thorex Process.¹⁻³ Further separation of uranium from thorium is obtained by using cation exchange methods.⁴ The resulting ^{233}U product is nearly free of fission products and ^{232}U daughters and contains only a few ppm of ^{232}U , about 1000 ppm of thorium, and less than 100 ppm of fluoride. Frequently, the ^{233}U from the production facilities is stored at the Oak Ridge National Laboratory, which serves as a national ^{233}U repository, either as uranyl nitrate solution or as uranium oxide

powder until needed for research or by the nuclear industry. During storage, the daughters of ^{232}U are continually produced. Previously, when it was necessary to supply ^{233}U for use in various programs, the stored ^{233}U was decontaminated from ^{232}U daughters by extraction with 30% TBP¹⁻³ or with 2.5 to 5% di-sec-butylphenyl phosphonate.^{5,6} Each of these processes yields a uranium product containing a minimum of gamma activity and about 100 ppm of thorium. However, experience with the use of ion exchange to separate uranium and thorium^{4,7,8} and data from the literature⁹ indicated that an ion exchange method for a satisfactory separation of most of the uranium from the daughters of ^{232}U might be feasible, simpler, and less expensive than the solvent extraction processes.

The purpose of this investigation was to extend and supplement the available data in order to develop an ion exchange process for use in decreasing the activity associated with ^{233}U to the level that kilogram quantities could be converted to various chemical forms in glove boxes having a minimum amount of gamma shielding. A practical application of the process should have a capacity of about 20 kg of ^{233}U per week. Conditions were sought for processing this quantity of material in one run. Other desirable features include ion exchange columns that could be loaded and eluted rapidly, which led to the use of fine resins and high pressure drops across the columns. Development of the chemical flowsheet yielded data that facilitated the approximately 1000-fold scale-up from laboratory to production-size equipment. A column suitable for reverse flow elution, which was much simpler than those previously used, was also designed and tested.

2. SUMMARY

A flowsheet was developed for removing the long-lived daughters of ^{232}U from ^{233}U by cation exchange (see Fig. 1). The circled numbers in the figure indicate the sequence of the process steps. This flowsheet was demonstrated in laboratory experiments with uranyl nitrate solutions that initially contained about 100 g of uranium and less than 0.1 g of thorium per liter, and were less than 0.3 *M* in HNO_3 . The

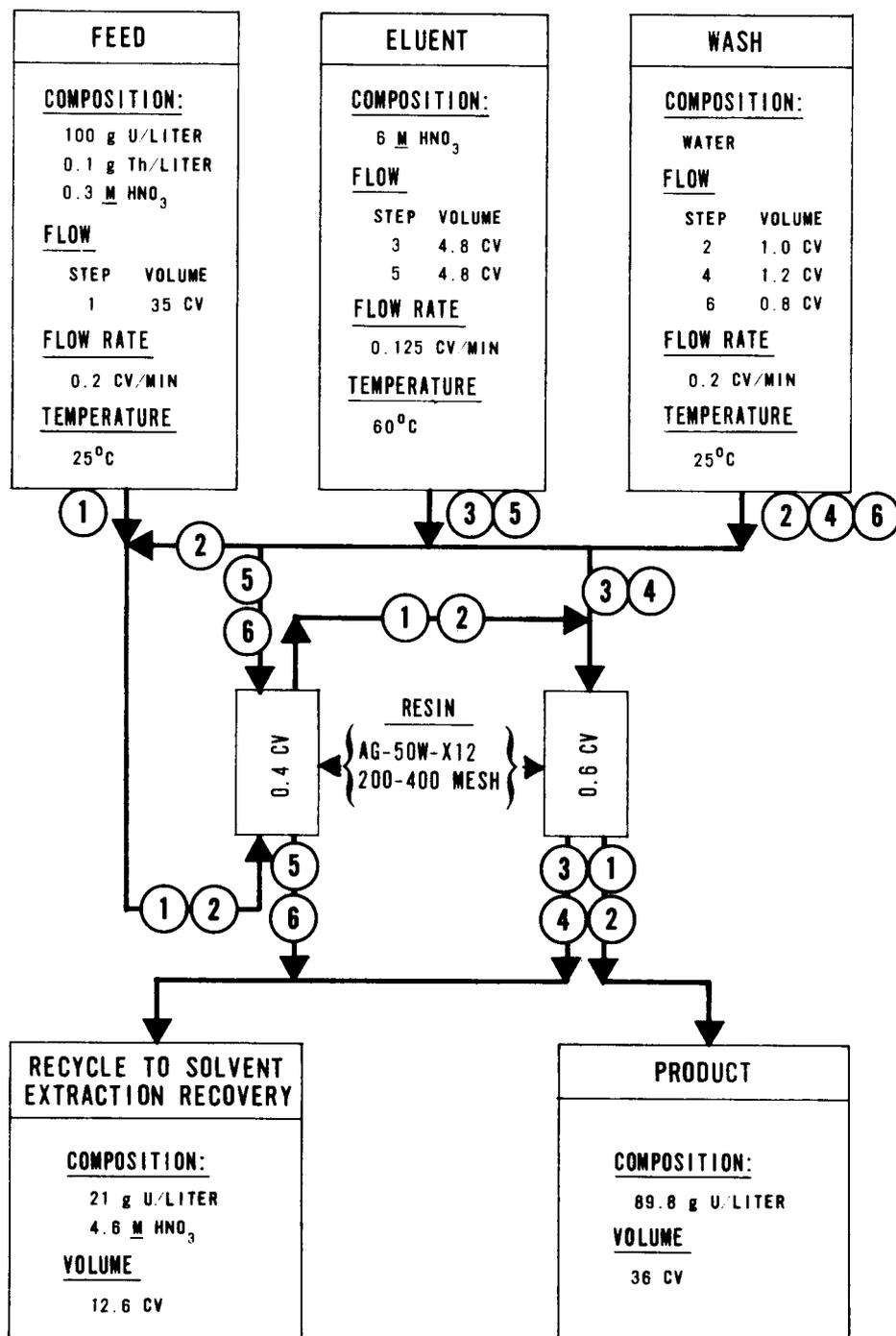


Fig. 1. Flowsheet for Removing Gamma Activity from ^{233}U by Sorbing ^{228}Th and ^{224}Ra on Cation Exchange Resin. The circled numbers denote the sequence of process steps. CV denotes column volume.

solutions were passed sequentially through two resin columns, upflow through the first and downflow through the second. The long-lived daughters of ^{232}U were retained on the resin. The uranium first saturated the resin, then broke through as a decontaminated product practically free of thorium and radium and partially decontaminated from lead. More than 99% of the thorium, about 98% of the radium, and about 50% of the lead remained on the column when 200- to 400-mesh AG-50W-X12* resin, a solution throughput equivalent to 5.3 g of uranium per milliliter of resin, and a temperature of 25°C were used. Under these conditions, the pressure drop across the two columns was about 150 psi. After the resin had been washed to displace the residual uranyl nitrate solution, the long-lived daughters of ^{232}U and the uranium that had sorbed on the resin (about 9% of the total) were eluted with 6 M HNO_3 at 60°C. The eluate, which also contained the radium, lead, and about 50% of the thorium, was recycled to solvent extraction for uranium recovery. The resin columns were then ready for reuse. Although solvent extraction is required for the recovery of the ^{233}U associated with the thorium and ^{232}U daughters eluted from the resin, purification of most of the ^{233}U by the above process is much simpler than by methods based entirely on solvent extraction.

With the long-lived ^{232}U daughters removed, the gamma activity of the ^{233}U -containing solution which passed through the resin initially decreased as the ^{212}Pb ($T_{1/2} = 10.6$ hr) decayed. The activity in the solution decreased to about 0.3% of the steady-state level in 3 days (Fig. 2), then increased at a rate approximately equal to the rate of regrowth of ^{228}Th . The activity was less than 2% of the steady-state level from the 2nd until the 24th day after separation. Experience in the Kilorod program¹⁰⁻¹³ has shown that, at 2% of the steady-state level, the operations personnel processing kilogram quantities of ^{233}U receive exposures which are low compared to current guidelines for safe occupational exposure.

The effects of the various chemical variables on flowsheet performance were evaluated in laboratory experiments. Data relating the interdependence of solution

*Analytical-grade polystyrene sulfonic acid resin prepared from Dowex 50 by a new method of sulfonation which gives a light amber to white product.

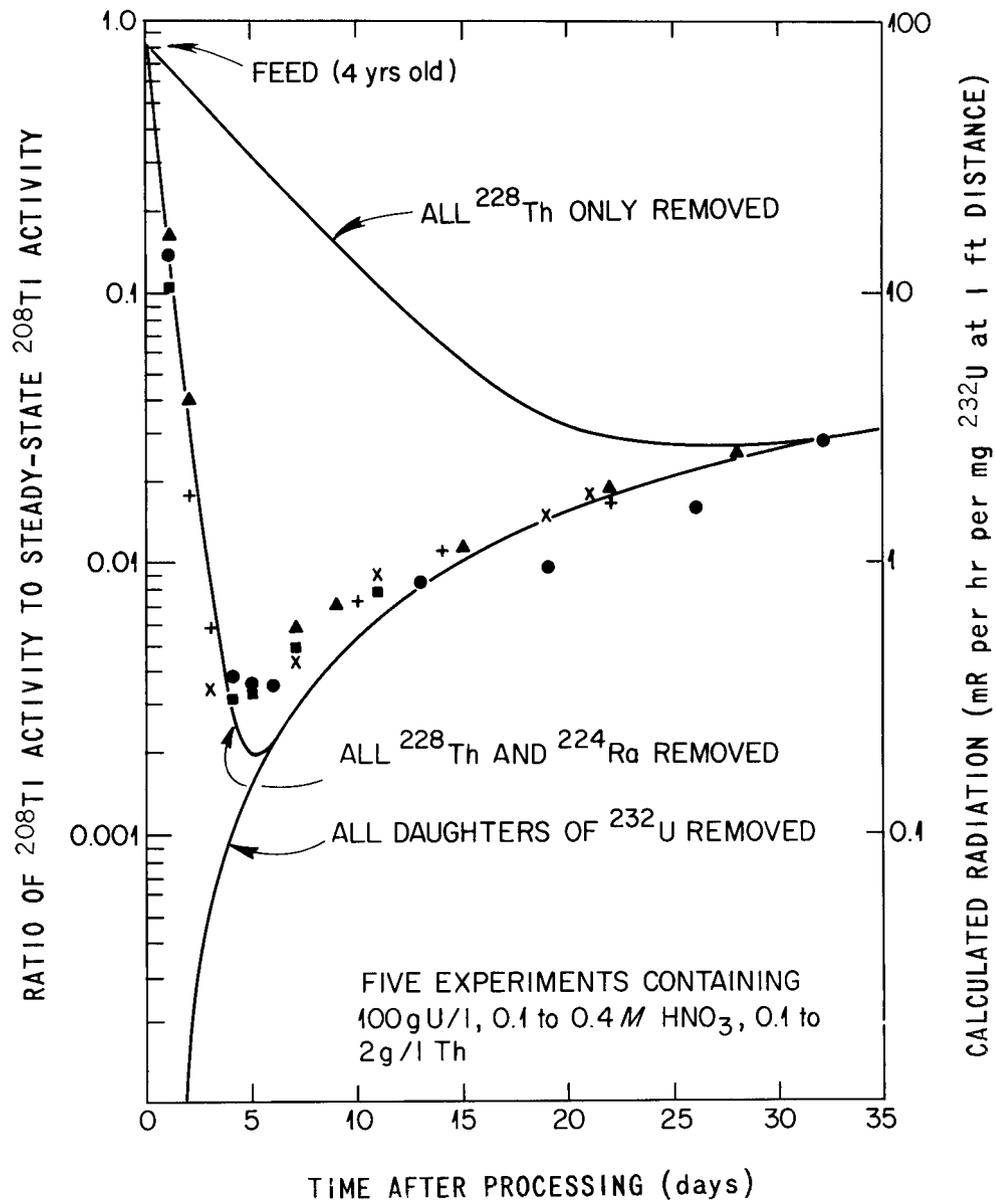


Fig. 2. Activity of ^{233}U Product Solutions. Solid curves are calculated values.

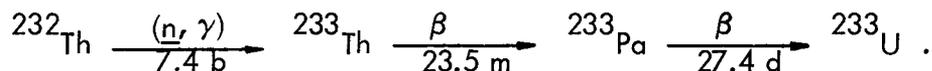
flow rate and column geometry on sorption and elution characteristics and on pressure drop across the column were obtained so that size scaling could be predicted.

The decontamination factors obtained in laboratory experiments using columns containing 1 to 5 ml of resin were confirmed in plant runs in which the columns contained 5 liters of resin.

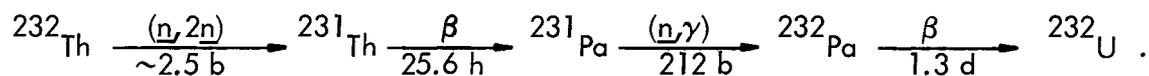
By using finely divided resin to increase sorption and enhance elution kinetics and pressurized columns to increase and maintain practical flow rates, the time required for a plant-scale run (17.5 kg of ^{233}U) was less than 18 hr.

3. BACKGROUND INFORMATION

As noted previously, ^{233}U is made by irradiating ^{232}Th with neutrons:

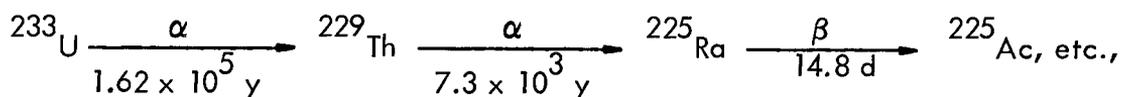


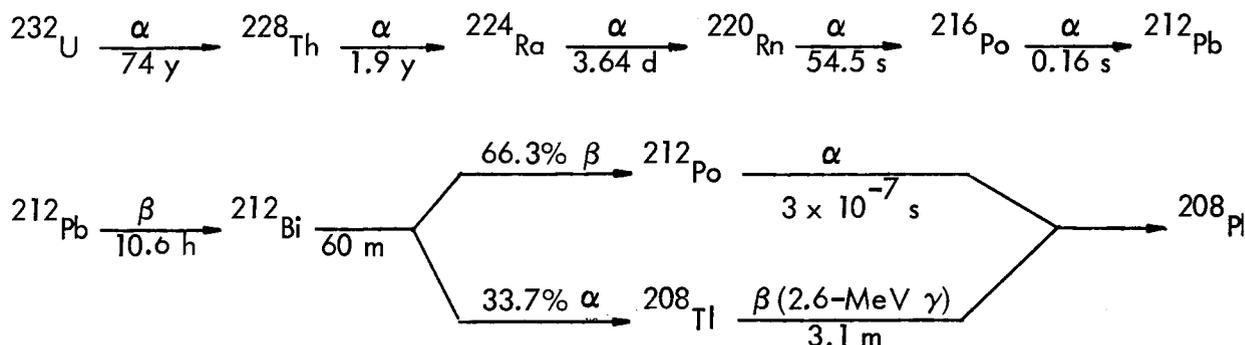
Neutrons having energies greater than 6.37 MeV promote the formation of ^{232}U as follows:



The amount of ^{232}U produced depends on the irradiation technique used; typically, the ^{233}U contains less than 100 ppm of ^{232}U .

The irradiated thorium also contains fission products as the result of ^{233}U fissioning. If the thorium, fission products, and ^{232}U daughters are separated from the uranium isotopes by the Acid Thorex solvent extraction process,¹⁻³ the uranium in the product initially is essentially free of gamma activity. The gamma activity remains low for several weeks after the separation but then increases progressively for about 10 years due to the growth of daughters of ^{233}U and ^{232}U :





The half-lives of ${}^{233}\text{U}$ and its first daughter, ${}^{229}\text{Th}$, are very long; therefore, little activity results from this decay chain. However, the growth of ${}^{232}\text{U}$ daughters causes a rapid increase in gamma activity. The principal penetrating radiation is the 2.6-MeV gamma emitted from ${}^{208}\text{Tl}$. The increase in activity of ${}^{208}\text{Tl}$ with time after Acid Thorex processing of irradiated thorium is shown in Fig. 3. Calculations and operating experience¹⁰⁻¹³ have shown that 1 mg of ${}^{232}\text{U}$ in equilibrium with its daughters has a radiation level of about 100 mR/hr at a distance of 1 ft.¹⁴ Experience also has shown that kilogram quantities of ${}^{233}\text{U}$ containing 8 ppm of ${}^{232}\text{U}$ may be processed in an alpha containment facility which does not contain gamma shielding, provided the activity is less than about 2% of that produced by the ${}^{232}\text{U}$ when it is in equilibrium with its daughters.¹⁰ Attainment of equilibrium requires 10.3 years. In order to maintain the activity at less than the 2% level for a reasonable period of time, it is necessary to remove both the ${}^{228}\text{Th}$ and ${}^{224}\text{Ra}$ (Fig. 4).

Previously, several cation exchange methods were developed for separating ${}^{234}\text{Th}$ or ${}^{232}\text{Th}$ from uranium;^{4,7,8} however, no data were obtained on the behavior of radium in those developments. The distribution coefficients* for radium have been estimated to be about twice those of barium;¹⁵ therefore, an indication of the feasibility of the uranium-radium separation may be obtained from the data of Strelow et al.⁹ A plot of their data (Fig. 5), which were obtained with hydrogen-form Dowex 50W-X8 resin, indicated that a high degree of separation of uranium from thorium and radium would be expected with low-ionic-strength solutions. In addition, the data of Bonner and Smith¹⁶ showed that, in a 0.1 M HClO_4 system, the separation

*The reported distribution coefficients are defined as the concentration of the metal ion in the resin, divided by the concentration of the metal ion in the solution (milligrams of metal ion per gram of dry resin, divided by grams of metal ion per liter of solution).

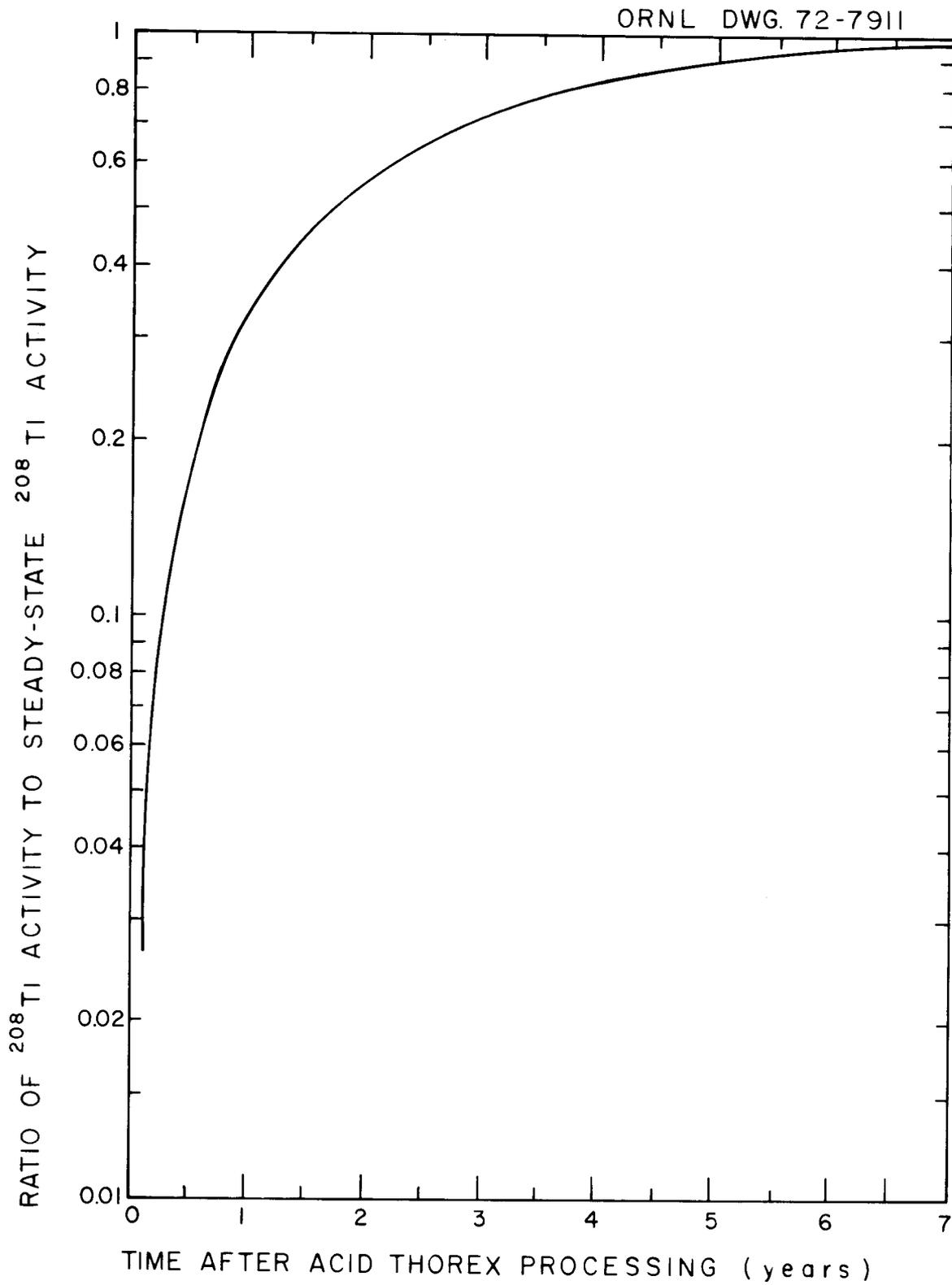


Fig. 3. Growth of ^{208}Tl due to Decay of ^{232}U . Data obtained from ref. 14.

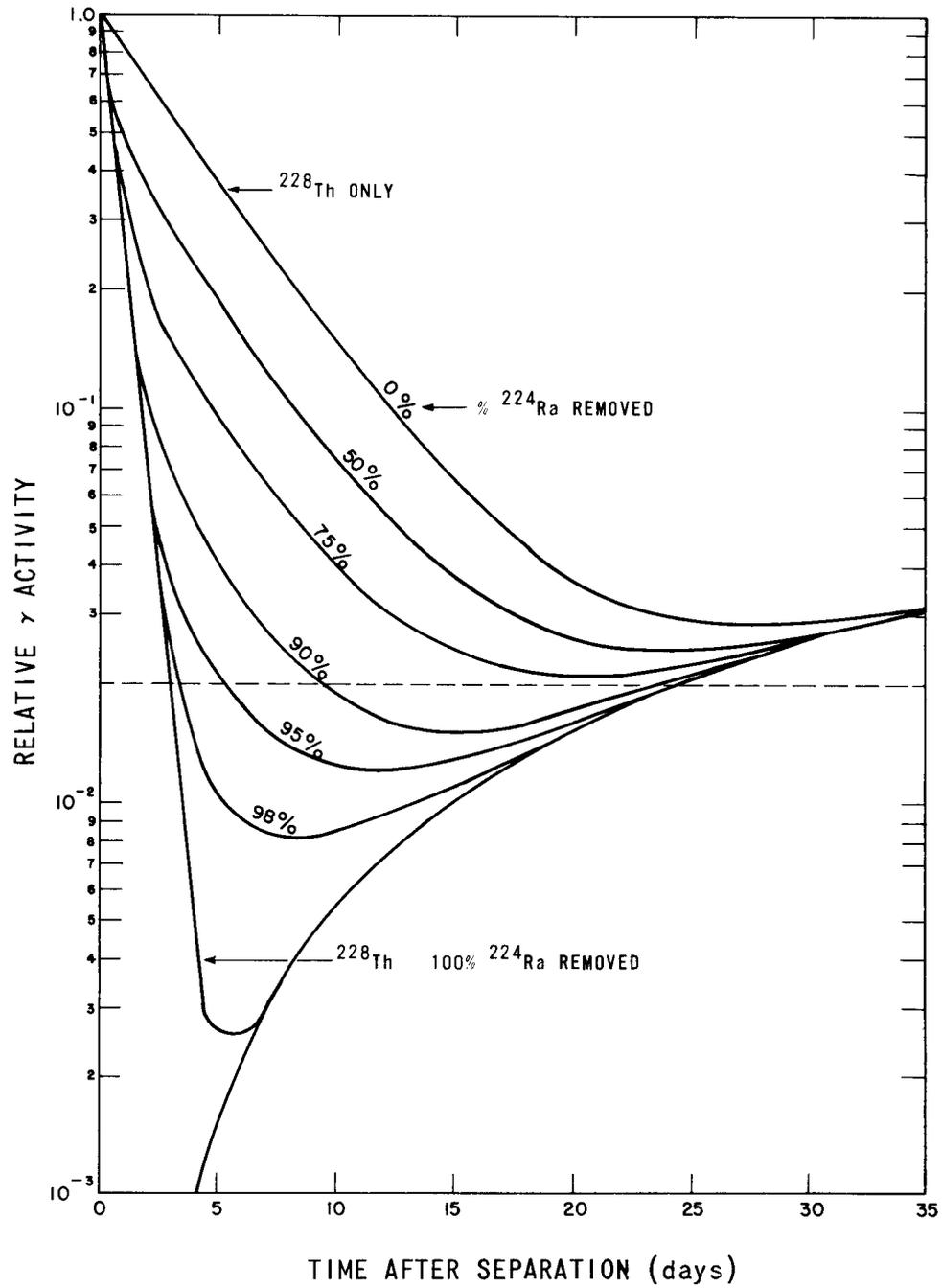


Fig. 4. Calculated ^{232}U Daughter Activity After Removal of ^{228}Th and Varying Amounts of ^{224}Ra .

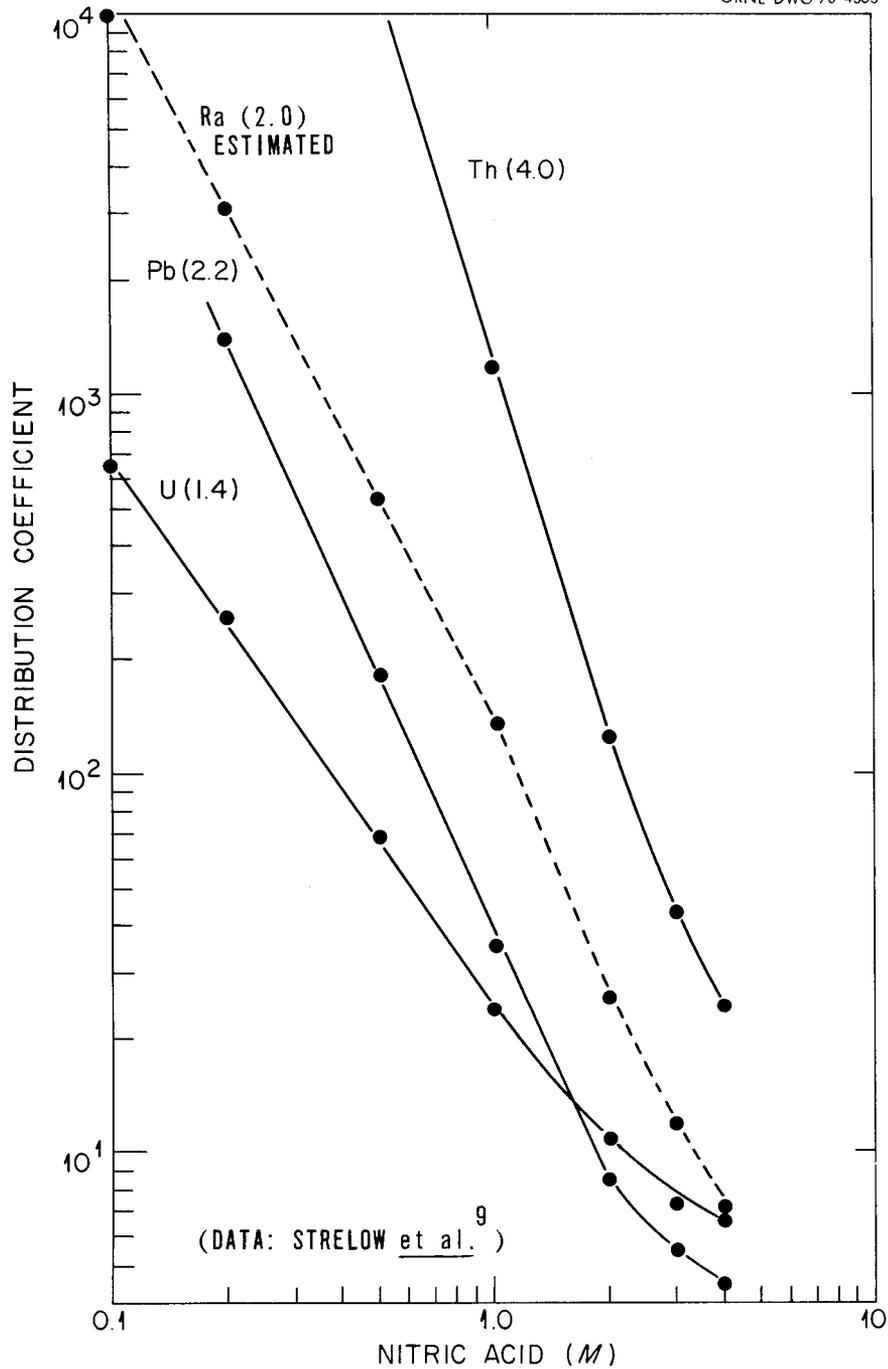


Fig. 5. Effect of Acidity on the Sorption of Thorium, Lead, and Uranium on Hydrogen-form Dowex 50W-X8 Resin. The numbers in parentheses are the slopes of the lines at low acid concentrations.

of uranyl ions from lead and barium increased with increasing cross-linkage of the resin (Table 1).

Table 1. Effect of Resin Cross-Linkage on the Distribution Coefficients of Lead, Barium, and Uranium, Using Hydrogen-form Dowex 50W Resin and 0.1 M HClO₄ Solutions^a

	Resin Cross-Linkage (%)		
	4	8	12
Relative Sorption ^b			
UO ₂ ²⁺	2.36	2.45	3.34
Pb ²⁺	6.56	9.91	18.0
Ba ²⁺	7.47	11.5	20.8
Separation Factors ^c			
Pb ²⁺ /UO ₂ ²⁺	2.78	4.04	5.39
Ba ²⁺ /UO ₂ ²⁺	3.15	4.69	6.25

^aData obtained from ref. 16.

^bRelative to value of unity for lithium.

^cSeparation factor is defined as the ratio of the relative sorption values.

4. LABORATORY EVALUATION OF CHEMICAL AND PHYSICAL PARAMETERS

4.1 Reagents and Analyses

The ion exchange resins used in preliminary investigations were Baker analyzed-grade Dowex 50W-X8 (200-400 mesh) and Dowex 50W-X12 (200-400 mesh). In later experiments, including all flowsheets demonstrations in both the laboratory and the plant, Bio-Rad analytical-grade AG-50W-X8 (200-400 mesh) and AG-50W-X12 (200-400 mesh) resins were used. These latter materials had much more narrow size

distributions than the Baker resins and, consequently, allowed operation with lower pressure drops across the resin beds. The theoretical capacity of the AG-50W-X12 resin was 5 meq per gram of dry resin, or 2.3 meq per milliliter of wet resin.

Preliminary experiments were made using natural uranium and thorium containing ^{234}Th tracer. As noted in Sects. 1 and 3, the amount of thorium associated with ^{233}U to be processed is low; consequently, all tests were made with thorium at a low concentration. Conventional chemical and counting techniques were used in the analysis of uranium and thorium. Later experiments were conducted with ^{233}U containing 8 ppm of ^{232}U . This material had been separated from daughter activity about 4 years prior to the work discussed here. Concentrations of the various radio-nuclides present in the solutions were determined by alpha-pulse-height analysis or, in the case of ^{208}Tl , by gamma spectrometry. In some of the alpha-pulse-height analyses, ^{244}Cm was added to the solutions as an internal standard. In many cases, sealed samples were counted repeatedly over a period of time to measure the rate of production or decay of the daughters of ^{232}U . These daughters could be identified by their respective half-lives.

4.2 Experimental Procedure

Except where indicated, experiments were made using ion exchange columns 2 to 5 mm in diameter and 20 to 50 mm long. Passage of solution through a column generally was expressed in terms of the number of column volumes (CV) passed. A column volume is defined as the apparent volume occupied by the wet resin. Many of the data were correlated using a retention parameter defined as min/CV. The void volume of the columns was not determined; nevertheless, since the resin spheres were of uniform size, the calculated value of 40% should be fairly accurate. Thus, the actual residence time of a solution in a column can be estimated as:

$$\text{residence time} = 0.4 (\text{retention parameter}).$$

In this work, flow rates through the column were varied to give retention parameters in the range of 1 to 8 min/CV.

In order to obtain the desired flow rates through the resin columns, small positive-displacement metering pumps, which produced pressure drops across the resin columns of 20 to 150 psi, were used. Since no gases were involved, we assumed that the pressure did not influence the reaction rate or equilibrium values. In many ways, the increased pressure on the system simplified operation.¹⁷ For example, when a gas was inadvertently introduced into the resin column, it was either quickly swept through the column or was dissolved. In some experiments, the progress of the sorption front of thorium or uranium on the resin was observed by use of ultraviolet light. These observations demonstrated that, with pressurized columns, there was little tendency for the solutions to "channel" (i.e., the sorption front was very sharp). Unless the columns were pressurized, the flow rate through the fine resin would have been too low to be practical.

4.3 Distribution Coefficients for Thorium, Radium, and Lead, Using Uranyl Nitrate Solution and Uranium-Saturated Resin

The distribution coefficient data available from the literature⁹ had been determined with hydrogen-form resin and with the metal ions present in the aqueous solution at very low concentrations. As noted in Sect. 3, thorium and barium were strongly sorbed in comparison to uranium. In our system, however, the values of interest are those obtained when the metal ions in solution are in equilibrium with resin saturated with uranium. Thus experiments were performed under these conditions to determine whether the ions sorbed in the same manner as with hydrogen-form resin, and to obtain an estimate of the potential separation factors.

Distribution coefficients (defined in Sect. 3) were determined at 25°C by equilibrating an aqueous solution of the composition 0.2 M HNO₃, 130 g of ²³³U per liter (²³²U content ~ 8 ppm), and 130 ppm of thorium with Dowex 50W-X12 (200- to 400-mesh) resin. This resin was found to have a capacity of 0.595 g of ²³⁸U per gram of dry resin, or 0.274 g of ²³⁸U per milliliter of wet resin. The ratio of resin to solution was varied from 0.2 to 120 mg/ml. After equilibration for 24 hr, a measured volume of the aqueous phase was removed and an alpha-pulse-height

analysis was made quickly, using an internal ^{244}Cm standard. The concentration of each element in the resin was calculated from the difference between its initial concentration in solution and the concentration measured after equilibration. The ^{220}Rn and ^{216}Po were assumed to be in equilibrium with their parent, ^{224}Ra , and the ^{212}Bi and ^{212}Po in equilibrium with ^{212}Pb . The ^{220}Rn and ^{216}Po analyses were used to confirm the value for the radium. Since ^{212}Pb does not emit an alpha particle, the ^{212}Bi and ^{212}Po counts were assumed to represent lead.

Data obtained from these equilibrations are shown in Fig. 6 as plots of the percentage of the total amount of the element in the system sorbed by the resin vs the amount of resin used per milliliter of aqueous phase. As seen, the order of sorption is the same as observed with hydrogen-form resin (Fig. 5); that is, thorium is the most strongly sorbed and uranium is the most weakly sorbed. The data also indicate that, by proper choice of conditions, large fractions of the thorium, radium, and lead, along with only a small fraction of the uranium, in a given system may be sorbed on a small amount of uranium-saturated resin. Further, these data show that the Th-Ra and Th-Pb separation factors are about the same as those obtained with hydrogen-form resin. However, it should be emphasized that the data and conclusions apply only to the case in which the resin is saturated with uranium and the other metal ions are present in solution at very low concentrations.

4.4 Effect of Uranium Concentration in Feed on Thorium Sorption

Since the distribution coefficient data presented in Sect. 4.3 showed that thorium, radium, and lead could be separated from uranium, a few scouting experiments were made to determine the effect of uranium concentration in the aqueous phase on the amount of thorium sorbed by the resin at the time that thorium was first detected in the effluent. These experiments were not sufficiently systematized to define a correlation, but they did show that uranium concentration had a marked effect. In each test, uranium breakthrough occurred when only 0.27 g of uranium had been sorbed per milliliter resin. When the solution had the composition 112 g of uranium per liter, 0.67 g of thorium per liter, and 0.09 M HNO_3 , about 6 g of uranium per milliliter

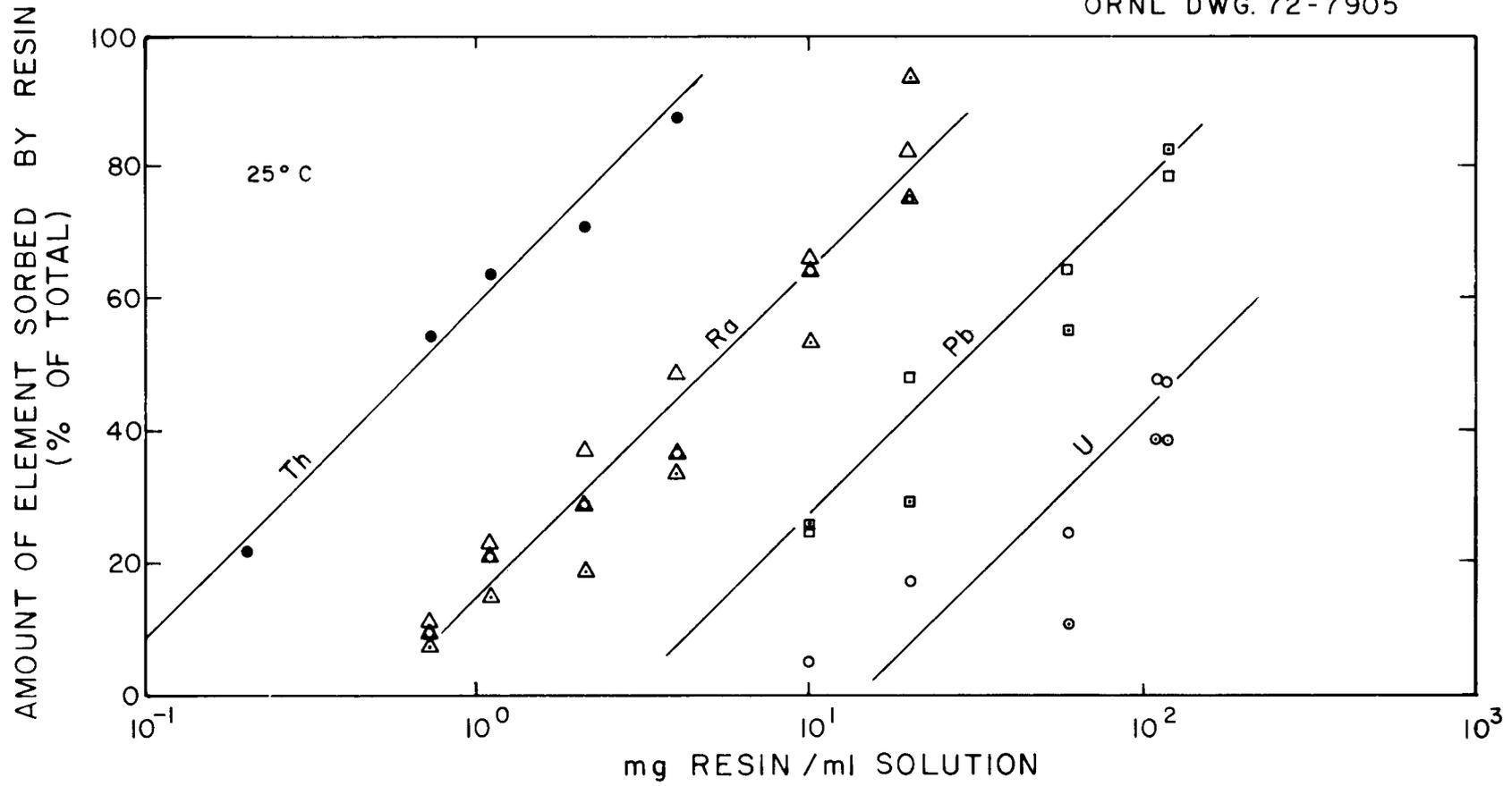


Fig. 6. Sorption of Thorium, Radium, and Lead on Uranium-saturated Dowex 50W-X12. ●, ^{228}Th ; △, ^{220}Rn ; △, ^{216}Po ; △, ^{224}Ra ; □, ^{212}Bi ; □, ^{212}Po ; ○, ^{233}U ; ○, ^{232}U .

of resin could be passed through a column before thorium could be detected in the effluent. The thorium loading at this point was about 30% of theoretical. When the aqueous phase contained 168 g of uranium and 1 g of thorium per liter and was 0.14 M in HNO_3 , thorium breakthrough occurred after passage of about 2.2 g of uranium per milliliter, with a thorium loading of about 10% of theoretical. With a solution that contained 337 g of uranium and 2 g of thorium per liter and was 0.28 M in HNO_3 , thorium breakthrough occurred almost immediately after uranium breakthrough. Thorium loadings higher than 30% of theoretical were obtained with solutions containing less than 100 g of uranium per liter; however, a uranium concentration of about 100 g/liter was considered acceptable since the size of processing equipment is minimized by use of solutions having the highest possible uranium concentration.

4.5 Effect of Solution Acidity on Resin Capacity for Thorium

As indicated earlier (Fig. 5), both the distribution coefficients with hydrogen-form ion exchange resin and the separation of uranium from lead, barium, and thorium increased as the acidity of the solution was decreased. This effect of acidity was confirmed in a series of experiments made using feeds containing 112 g of uranium and 0.66 g of thorium per liter, and various acid concentrations. The objective of each of these experiments was to determine the amount of thorium sorbed on a uranium-form resin column at the time thorium was first detected in the column effluent. The data obtained (Fig. 7) showed that about two and one-half times as much uranium could be processed on a column when the solution was 0.1 M in HNO_3 than when it was 0.7 M in HNO_3 . Solution acidity is, therefore, an important parameter in a processing scheme and should be kept as low as practical to permit the highest possible thorium loading.

4.6 Effect of Resin Cross-Linkage on Ion Sorption and Separations

The data of Bonner and Smith¹⁶ illustrate the increase in distribution coefficients of uranyl, barium, and lead ions with increasing resin cross-linkage in a perchlorate system. However, more data were needed to determine whether similar results would

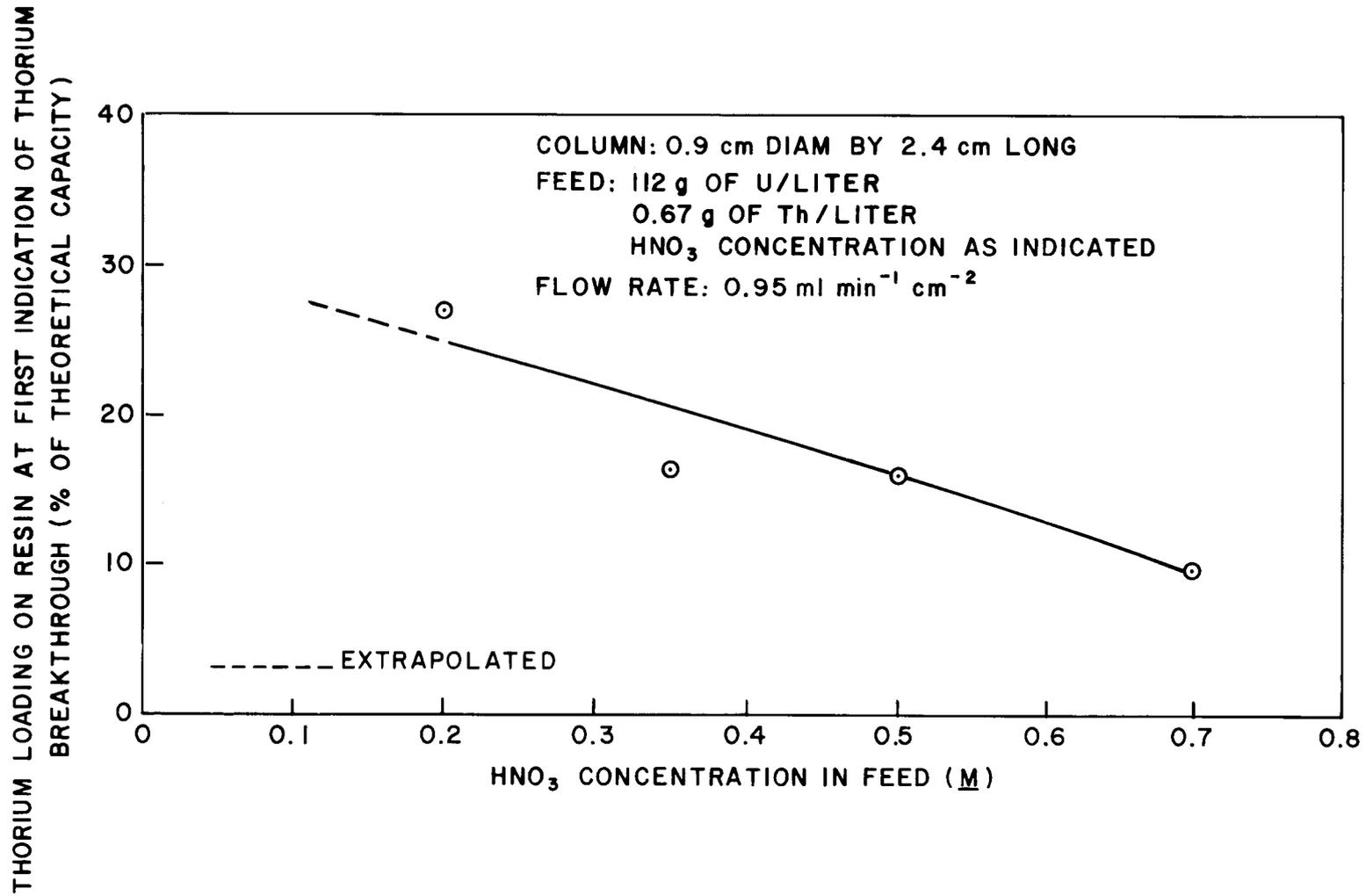


Fig. 7. Effect of Acid Concentration on the Removal of Thorium from UO₂(NO₃)₂.

be obtained for a nitrate system.

In our experiments, $^{233}\text{UO}_2(\text{NO}_3)_2$ solutions were passed through columns containing either 8% or 12% cross-linked AG-50W resin, using the flowsheet conditions shown in Fig. 1. In each case, the product solution was allowed to stand 3 days, to permit the short-lived nuclides to decay, before it was analyzed for uranium and ^{208}Tl . The thallium decontamination factor was found to be less than 10 when 8% cross-linked resin was used but increased sharply to about 300 with the 12% cross-linked resin. The greatly improved decontamination factor achieved with the 12% cross-linked resin was attributed to an increase both in the resin capacity and in the separation factor. These tests confirmed that use of the more highly cross-linked resin yielded more efficient separations.

4.7 Effect of Fluoride on Decontamination of ^{233}U

The presence of up to 300 ppm of fluoride in the ^{233}U did not cause a noticeable decrease in the decontamination of uranium from ^{208}Tl in tests conducted using the flowsheet conditions given in Fig. 1. However, the decontamination factor decreased from about 150 to 15 when the solution contained 1000 ppm. Other workers¹⁷ reported failure of a similar ion exchange separation process due to the presence of fluoride. Evaluation of their data by this author indicated that the observed decrease in capacity could be mostly accounted for by the high uranyl nitrate concentration used in their process (180 g of uranium per liter). The results of the present study show that ^{233}U containing up to 300 ppm of fluoride can be decontaminated easily by cation exchange. The ^{233}U from the solvent extraction recovery plants normally contains less than this amount of fluoride.

4.8 Elution of Uranium and Thorium with Nitric Acid

In most ion exchange processes, it is desirable to reuse the resin. To accomplish this in our system, it is necessary to remove the sorbed uranium, the daughters of ^{232}U , and some of the thorium from the resin between runs. Water does not elute any

of these species; hence, it can be used to displace uranyl nitrate solution from a resin column. Both uranium and thorium can be eluted with nitric acid. Uranium is eluted easily with 1.5 *M* HNO₃ at 25°C; however, the elution of thorium requires more stringent conditions. Consequently, the effects of HNO₃ concentration and temperature on thorium elution were studied.

Preliminary studies at 25°C showed that nitric acid, even in concentrations as high as about 7.5 *M*, was not very effective in eluting thorium. Therefore, subsequent experiments were conducted at 60°C, the highest practical temperature. (At higher temperatures, chemical attack of the resin by nitric acid becomes severe.) Unless otherwise stated, the experiments were conducted with small (capacity, 1 to 3 ml) columns filled with Bio-Rad AG-50W-X8 (200- to 400-mesh) resin. Half of the resin in the column was saturated with thorium containing ²³⁴Th tracer; the remaining resin was in the acid form.

In tests made at 60°C with a constant retention parameter of 2 min/CV, nitric acid at concentrations below about 5 *M* was found to be ineffective for eluting thorium. Elution with 5 to 9 *M* HNO₃ (Fig. 8) was satisfactory, with 6 *M* appearing to be about optimum. Nitric acid concentrations higher than 9 *M* were not considered because of their excessively high rate of attack on the resin. The curves in Fig. 8 do not originate at zero volume because, in these experiments, the volume of acid required to displace the water initially in the resin column, the feed pump, and the connecting lines was not accurately known. It is possible, then, that the beginning of actual elution may have been displaced by as much as a column volume. For this reason, the slope of the elution curve gave a better indication of the efficiency of an elution procedure than the number of column volumes of acid required to obtain a given percentage of thorium removal.

Tests with 6 *M* HNO₃ and a 1-ml column at 60°C showed that the amount of thorium eluted by a given amount of acid increased as the residence time of the acid in the column was increased (Fig. 9). This is equivalent to saying that the amount eluted increased as the flow rate through the column was decreased. Adjustment of the flow rate so that the retention parameter was increased from 1 min/CV to 8 min/CV

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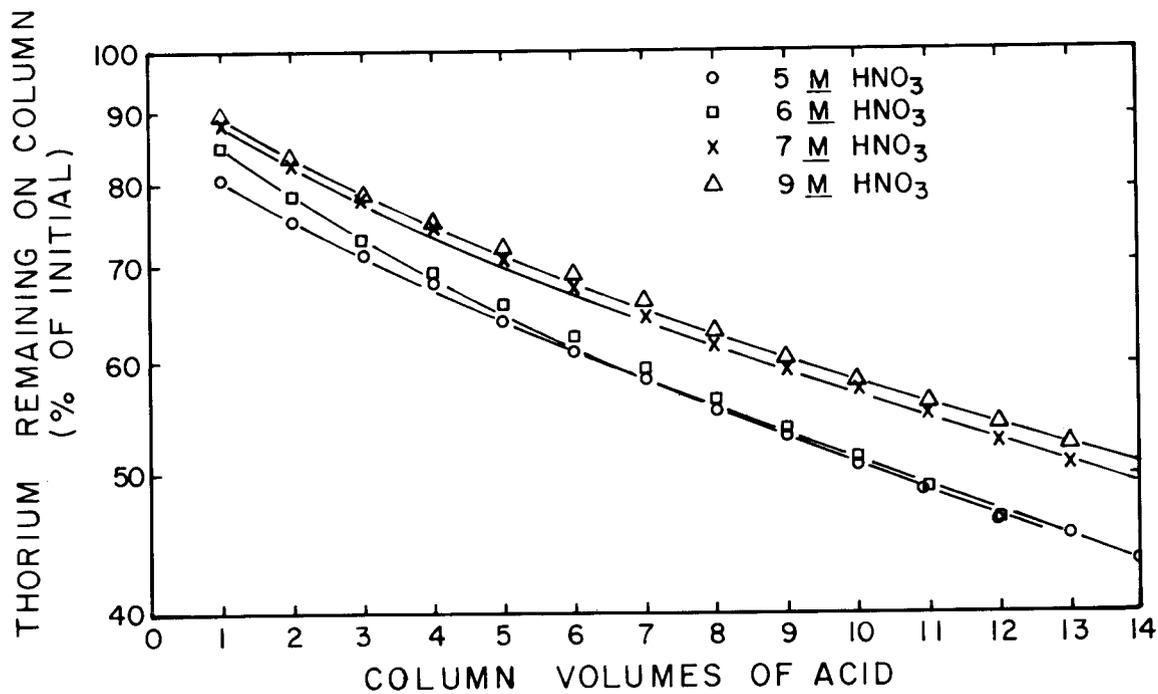


Fig. 8. Effect of Acid Concentration on the Elution of Thorium from Ion Exchange Resin. Retention Parameter: 2 min/CV. Bio-Rad AG-50W-X8 (200-400 mesh) half-saturated with thorium.

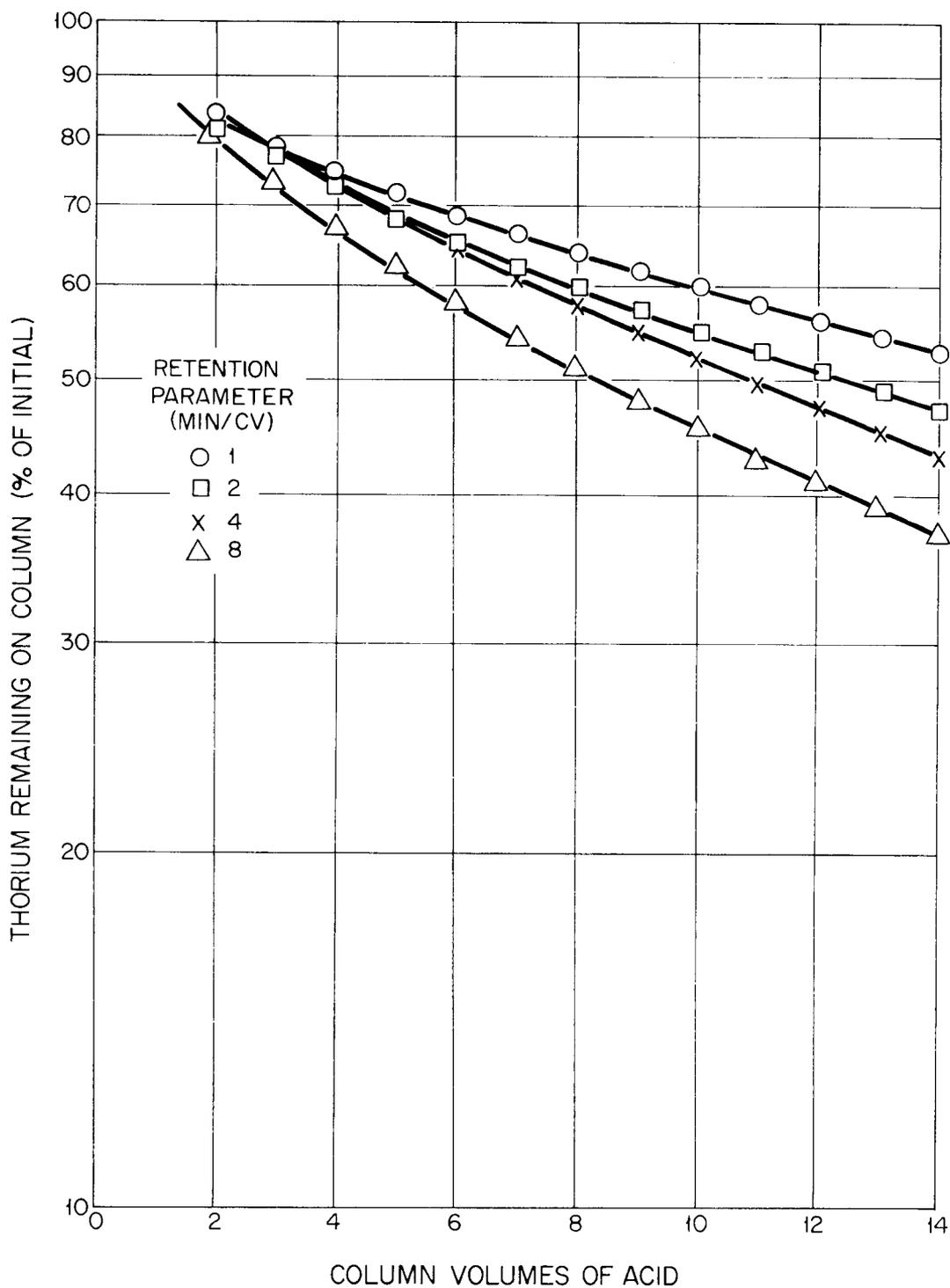


Fig. 9. Effect of Retention Parameter on the Elution of Thorium from Ion Exchange Resin at 60°C. Initial thorium loading on resin was 50% of theoretical. Eluent, 6 M HNO₃.

significantly increased the extent of thorium elution.

In another series of experiments with 6 *M* HNO₃ at 60°C, the length of the resin column was varied significantly while the retention parameter was fixed at 4 min/CV. In these experiments, varying amounts of resin were added to a column of uniform diameter and the flow rate was adjusted proportionally. The data (Fig. 10) showed that, within analytical uncertainty, the amount of thorium eluted was dependent on the retention but independent of the column length. This result suggests that elution behavior in large columns can be predicted from data obtained in small columns by using the retention parameter for the scale-up.

The effect of retention parameter on the volume of acid and the time required to elute 50% of the thorium was determined at 60°C with 6 *M* HNO₃, using 1-ml columns. (These data were taken from Fig. 9.) As shown in Fig. 11, the number of column volumes of acid required to elute 50% of the thorium decreased from about 16 to about 10 as the retention parameter was increased from 1 min/CV to about 4 min/CV; however, increasing the retention parameter from 4 min/CV to 8 min/CV had only a small additional effect on the volume of acid required. These data show that rapid elution can be achieved by passing a large volume of acid through the column at a high flow rate. However, setting the retention parameter at 4 min/CV appears to offer a reasonable compromise between the volume of acid and the time required to elute 50% of the thorium.

Inspection of each of the elution curves revealed that, after about 50% of the thorium had been eluted from the resin, elution of the remaining thorium was a semilogarithmic function of the amount of eluent that was passed through the column. This behavior occurred only when the thorium concentration in the resin was well below the saturation value. The volume of eluent required to reduce the amount of thorium on a column to any desired level below 50% can be calculated from an equation of the following form:

$$\log F = \log (50) + kV_{50} - kV ,$$

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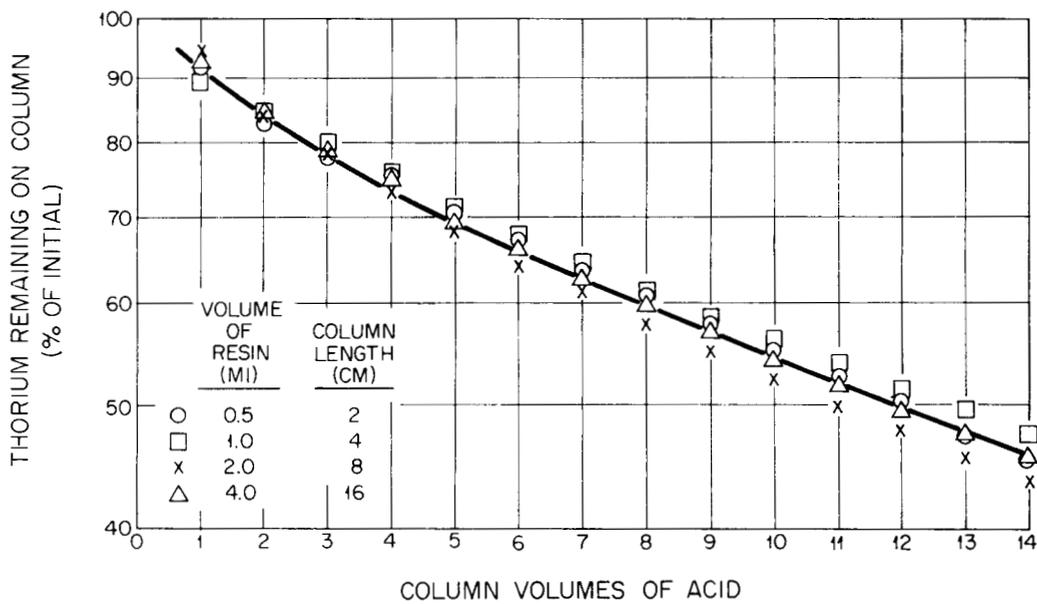


Fig. 10. Effect of Varying the Length of the Resin Column and Flow Rate So That the Retention Parameter Was Constant at 4 min/CV. Eluent, 6 M HNO₃ at 60°C.

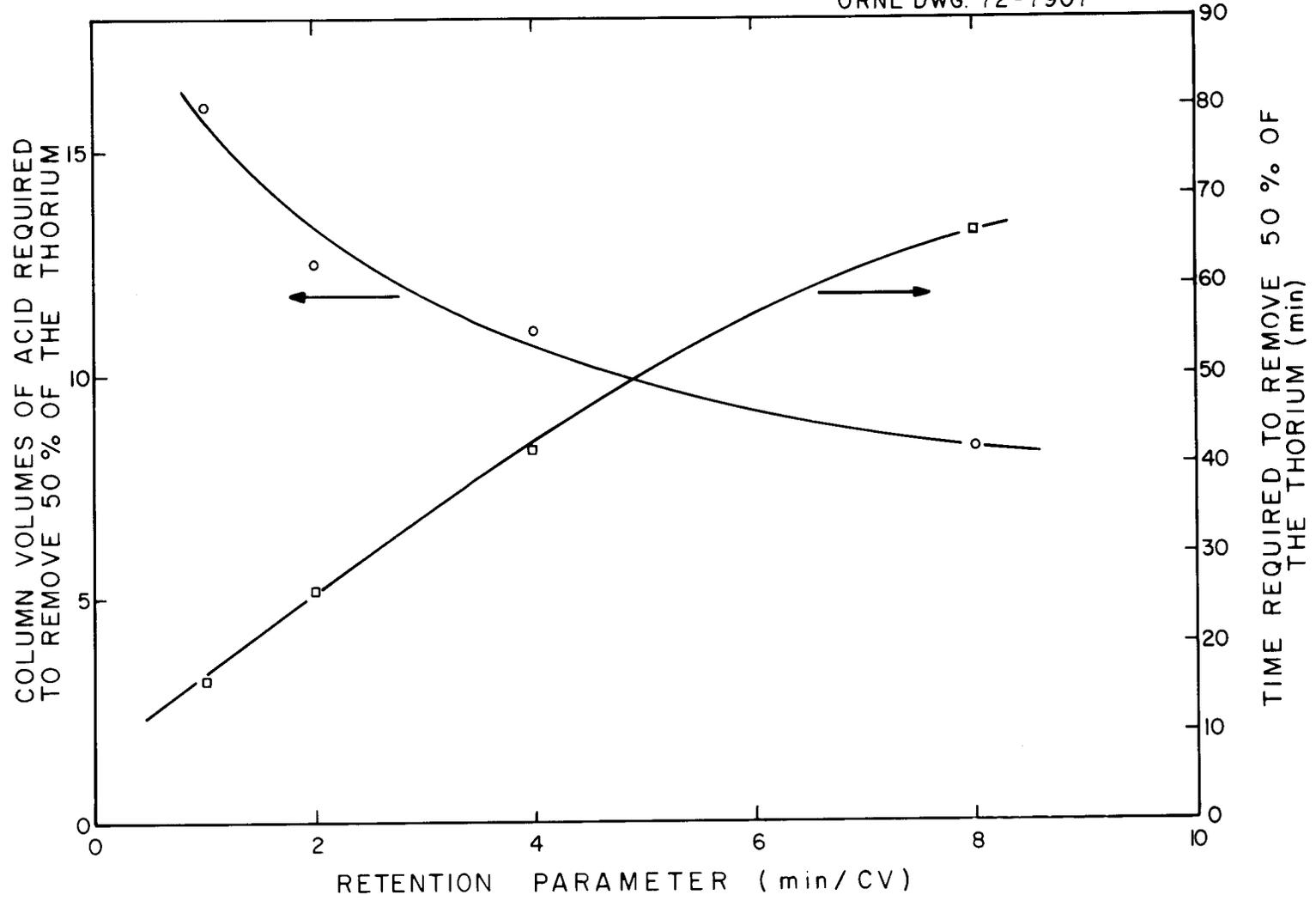


Fig. 11. Effect of Retention Parameter on the Volume of Acid and the Time Required to Elute 50% of the Thorium from Resin with 6 M HNO₃ at 60°C.

where

F = percent of original thorium remaining on resin,

V_{50} = number of column volumes of acid required to elute 50% of the thorium,

V = number of column volumes required to attain F ,

k = slope of the plot of $\log F$ vs V when $F > 50\%$.

The k for the elution of thorium from the resin used in these experiments with 6 M HNO_3 and a retention parameter of 4 min/CV was 0.021. It should be emphasized that the above equation is valid only for predicting behavior after 50% of the thorium has been removed from the column.

In all experiments, it was found that nitric acid eluted both lead and radium from the resin much more easily than thorium.

4.9 Column Scaling

Small columns containing about 1 to 5 ml of resin were used in most of the laboratory studies of the ion exchange process. Experiments demonstrated that laboratory data for both sorption and elution could be reproduced in large columns, provided the flow rate was such that the same retention parameter was used for the large and small columns.

In a series of experiments, a solution that contained 112 g of uranium and 0.67 g of thorium per liter and was 0.09 M in HNO_3 was passed through 0.9-cm-diam columns varying in length from 3.4 to 27 cm; the retention parameter was held constant at 3.5 min/CV. In each experiment, the thorium loading of the columns at the point of thorium breakthrough was 0.133 g of thorium per milliliter of resin, which is 30% of theoretical capacity. The constant loading, regardless of column length, is shown by a plot of the data in which a straight line passes through the origin (Fig. 12). Under the flow conditions defined by this retention parameter, the ions in the resin were apparently very nearly at equilibrium with those in the solution since there was no significant increase in the thorium loading when the retention parameter was decreased by a factor of 3. If the thorium loading had been determined

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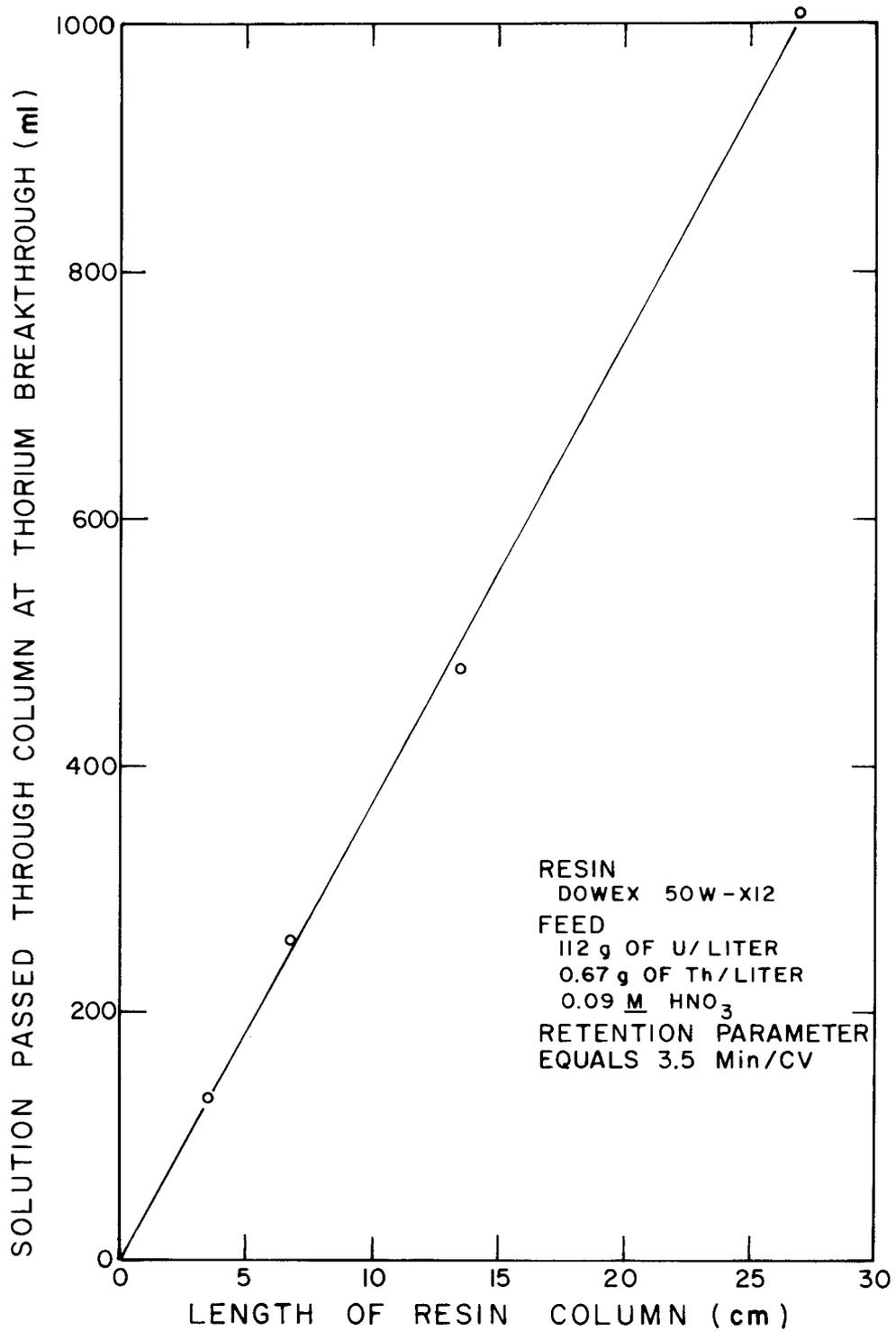


Fig. 12. Effect of Column Length on the Thorium Loading Capacity of a Resin Column.

by the rate of diffusion in the resin, the shorter retention time would have decreased the amount of thorium sorbed by the resin. Higher flow rates (i.e., shorter retention times) would have increased the pressure drop across the resin columns and, because the production rate at this flow was acceptable, the higher flow rates were not investigated.

When columns of constant length were eluted under different flow conditions (see Sect. 4.8), the percentage of thorium that was removed per column volume of eluent increased as the retention parameter was increased (Fig. 9). However, the amount eluted was dependent only on the retention parameter and not on the column length (Fig. 10). Thus, loading and elution conditions can be scaled by using resin capacity to determine column size and using the retention parameter (min/CV) to determine flow rate. Both sorption and elution behavior were correlated by this parameter alone when the resin was of small diameter and uniformly sized. Later, plant operations using 5 liters of resin (scale-up factor > 1000) duplicated laboratory results to within operational and analytical variations.

4.10 Effects of Flow Rates and Column Geometry on Pressure Drop

A series of laboratory experiments at 25°C showed that the pressure drop (ΔP) across the cylindrical ion exchange columns used in this study could be expressed by equations of the form

$$\Delta P = \frac{(\text{constant})(\text{feed flow rate})(\text{length of column})}{(\text{cross-sectional area of column})} .$$

Different constants were obtained, depending on the particle size of the resin and the size distribution of the resin beads. This effect was found in a series of laboratory experiments made with different resins, column lengths that varied from 1 to 66 cm, and solution flow rates that varied from 5 to 20 ml min⁻¹ cm⁻². With each type and/or size of resin, a plot of ΔP vs [(ml/min)(cm/cm²)] was linear (Fig. 13). Under fixed column and flow conditions, the lowest pressure drops were obtained with AG-50W-X12 (200- to 400-mesh) resin. This was one of the primary factors leading to the selection of this resin for the plant.

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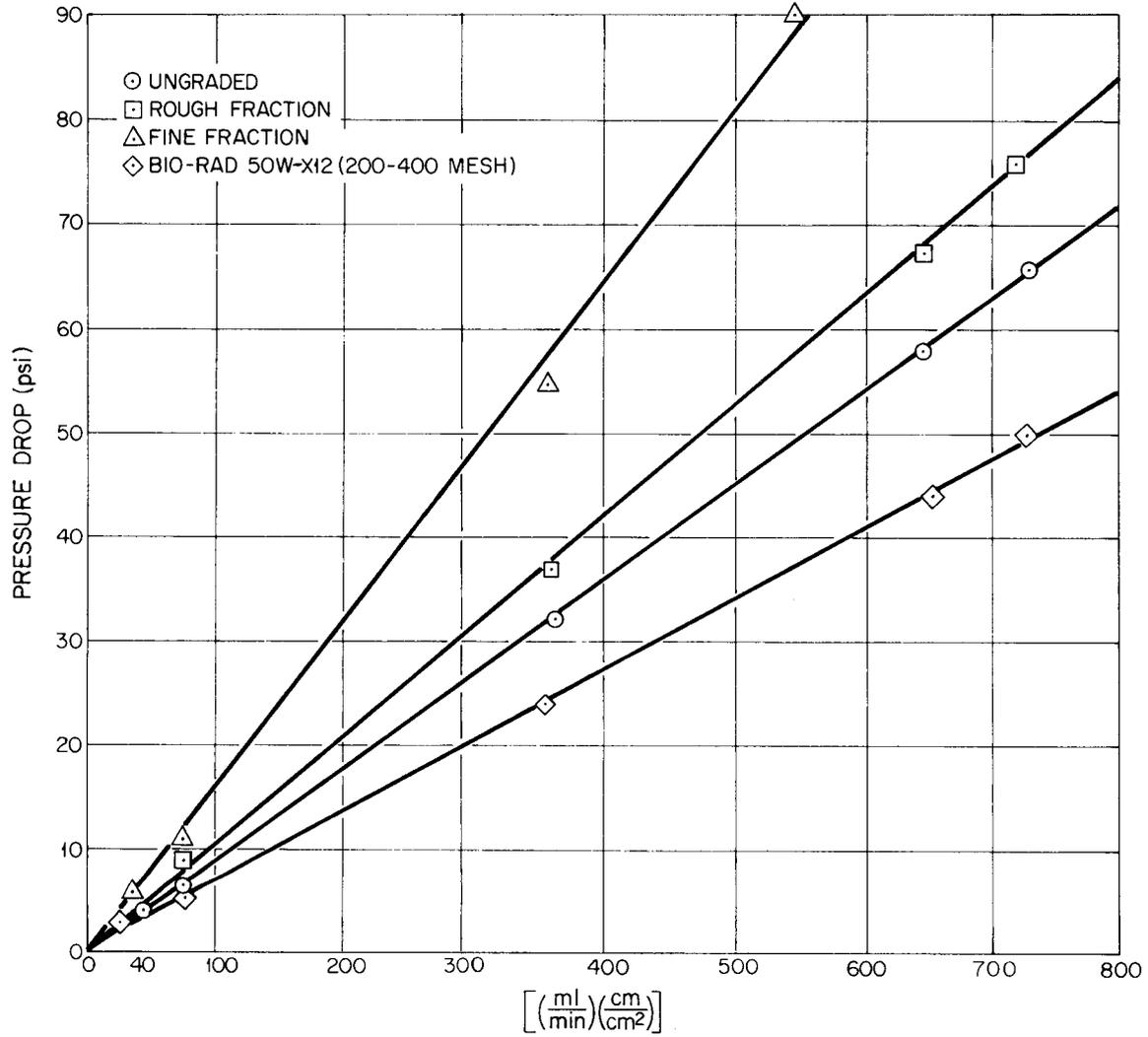


Fig. 13. Pressure Drops Produced at 25°C with Different Types and Sizes of Resin Under Various Flow Conditions. The columns were 0.9 cm in diameter and varied from 1 to 66 cm in length.

Pressure drop data were also obtained in large columns (3 in. in diameter, 17 to 26 in. long) to test the linearity of ΔP -vs- $[(\text{ml}/\text{min})(\text{cm}/\text{cm}^2)]$ plots over a wider range of conditions than could be obtained with laboratory-scale columns. These data were obtained with AG-50W-X12 (200- to 400-mesh) resin, and were in excellent agreement with the results of the laboratory-scale experiments (Fig. 14). Note that data obtained with two columns in series were in accord with data obtained with single columns. This is not surprising since the ΔP due to the piping between two columns in series is very small. The excellent correlation shown in Fig. 14 illustrates that the performance of large columns containing small, uniformly sized resin can be predicted from data obtained with small, laboratory-scale columns.

4.11 Development of a Resin Column for Use with Reverse Flow

A resin retention system was developed for use with columns in which the feed flows up and the eluent flows down through the resin bed. Columns previously designed for this operation have employed mechanical means (such as a spring) for keeping the resin bed fixed and preventing fluidization of the bed during reverse flow.¹⁸ The use of fine, uniformly sized resin and a high-pressure drop across the resin bed made a simpler design possible. The resin column was equipped with stainless steel frits at each end to contain the resin in the column. The space between the two frits was nearly filled with resin, leaving only enough free space to ensure that the resin in its most-expanded form did not exceed the space provided. With columns of this design, we demonstrated that, when flow was reversed, the resin bed merely slid up and down the column in the form of a compact cylinder. No detectable mixing of the resin occurred.

This operation was demonstrated with a 3-in.-diam, 2-ft-long glass column filled with resin. Part of the resin had been converted to the copper form to give it a distinctive green color. The column was loaded with the resin such that there were several 1/2-in. bands of the green resin near each end and at the center of the column. Water was pumped alternately down and up through the column at flow rates which covered the proposed operating range. As the resin bed slid up and down the

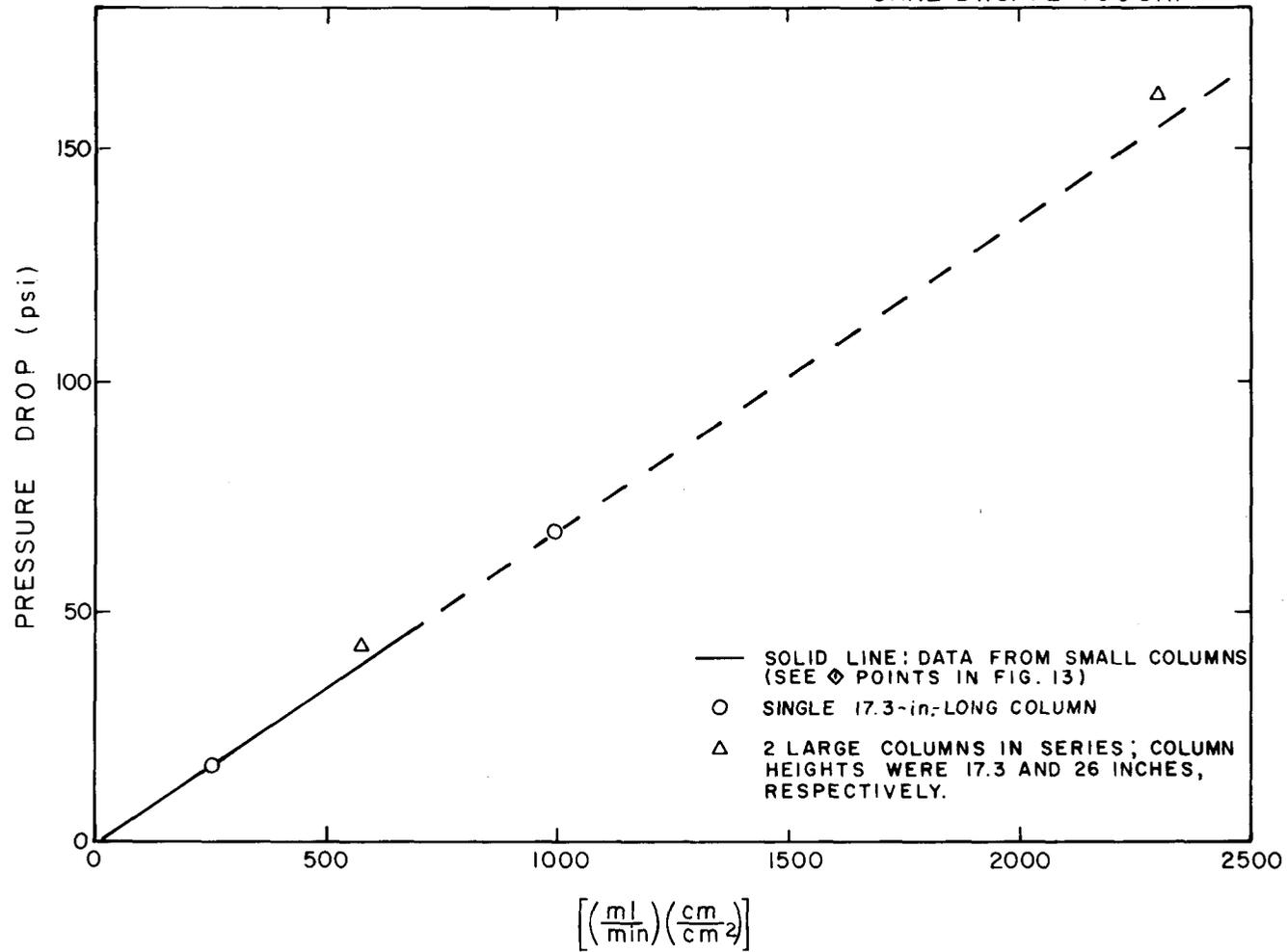


Fig. 14. Comparison of Pressure Drop Data Obtained with AG-50W-X12 (200-400 mesh) Resin at 25°C, Using Both Laboratory-Scale and Large Columns. Diameter of large columns = 3 in.

column, movement of the green bands could be easily measured. No mixing of the resin was detected visually after many pumping cycles.

5. LABORATORY DEMONSTRATION OF FLOWSHEET

Based on the data presented in the previous sections, a flowsheet for the separation of ^{233}U containing a few ppm of ^{232}U from ^{228}Th and ^{224}Ra was designed for use in plant operations (see Fig. 1). This flowsheet was purposely kept conservative to facilitate the initial evaluation in engineering equipment. Laboratory experiments to test the flowsheet were conducted at about 1/1000 plant scale.

As indicated in Sect. 2, the resin was divided into two columns in actual plant operation; however, a single 2-ml column was used in most of the laboratory experiments. The resin was obtained from the same batch that ultimately was used in the plant. The feed solutions contained 100 to 110 g of uranium per liter, 5 ppm to 2 g of thorium per liter, and were 0.1 M acid-deficient to 0.4 M in H^+ . Since equipment was not available for backflow elution of the resin at elevated temperatures, fresh resin was used in each loading experiment.

In experiments using ^{233}U to confirm column capacity, uranium broke through the 2-ml resin column (corresponding to the first column of the flowsheet) at about feed concentration after passage of about 0.25 g of uranium per milliliter of resin (i.e., after passage of 5 ml of feed). This is in excellent agreement with the results obtained in the scouting experiments discussed in Sect. 4.4. The ^{212}Pb broke through after passage of about 1 g of uranium per milliliter of resin. The ^{224}Ra had just started to break through the resin at the end of each experiment, that is, after passage of 95 ml of feed, which corresponds to 4.8 g of uranium per milliliter of resin. No evidence of thorium breakthrough was noted in any of the runs. When 5 ml of resin was used (corresponding to the two columns in the flowsheet), there was no indication of radium breakthrough.

After the residual feed solution had been displaced from the column with water, a scan of the alpha energies of the composited product solution showed that, immediately

following a typical experiment, the daughters of ^{212}Pb were present at about the same concentration as in the feed but that the ^{228}Th and ^{224}Ra and their short half-lived daughters, ^{220}Rn and ^{216}Po , were absent (Fig. 15). After 4 days, none of the ^{232}U daughters could be detected. The gamma activity of the ^{208}Tl in the product immediately after processing was nearly as great as that of the feed (see Fig. 2). However, the ^{208}Tl decayed rapidly, at a rate approximately equivalent to the decay of the ^{212}Pb , and after 3 days was only about 0.3% of its equilibrium value. The activity then increased at the rate that would be expected from the re-growth of ^{228}Th and its daughters.

Uranium, radium, and lead were eluted from the resin columns at 25°C with varying concentrations of nitric acid. The flow of eluent was cocurrent with that of the feed. Eight column volumes of 6 M HNO_3 removed nearly all of the uranium and lead and about 90% of the radium. As expected, only a small percentage of the thorium was removed by this elution procedure. As described previously (Sect. 4.8), thorium can be satisfactorily removed from the resin by elution at an elevated temperature. Therefore, no thorium elution data were obtained in the laboratory tests of the flowsheet.

Since most of the thorium is sorbed on the first part of the resin that the feed flows through, countercurrent elution is more efficient than cocurrent elution. If the eluent flowed in the same direction as the feed, part of the thorium would be sorbed on the resin throughout the column and would, therefore, be removed with subsequent uranium products. In countercurrent elution, the thorium is pushed back toward the head of the resin column on each cycle, thereby delaying its breakthrough with the product.

6. PLANT DEMONSTRATION OF FLOWSHEET*

Three runs have been made in plant equipment to demonstrate the process and to aid in defining the limitations of the flowsheet on an engineering scale. The design

*Operations were under the direction of Ralph G. Nicol.

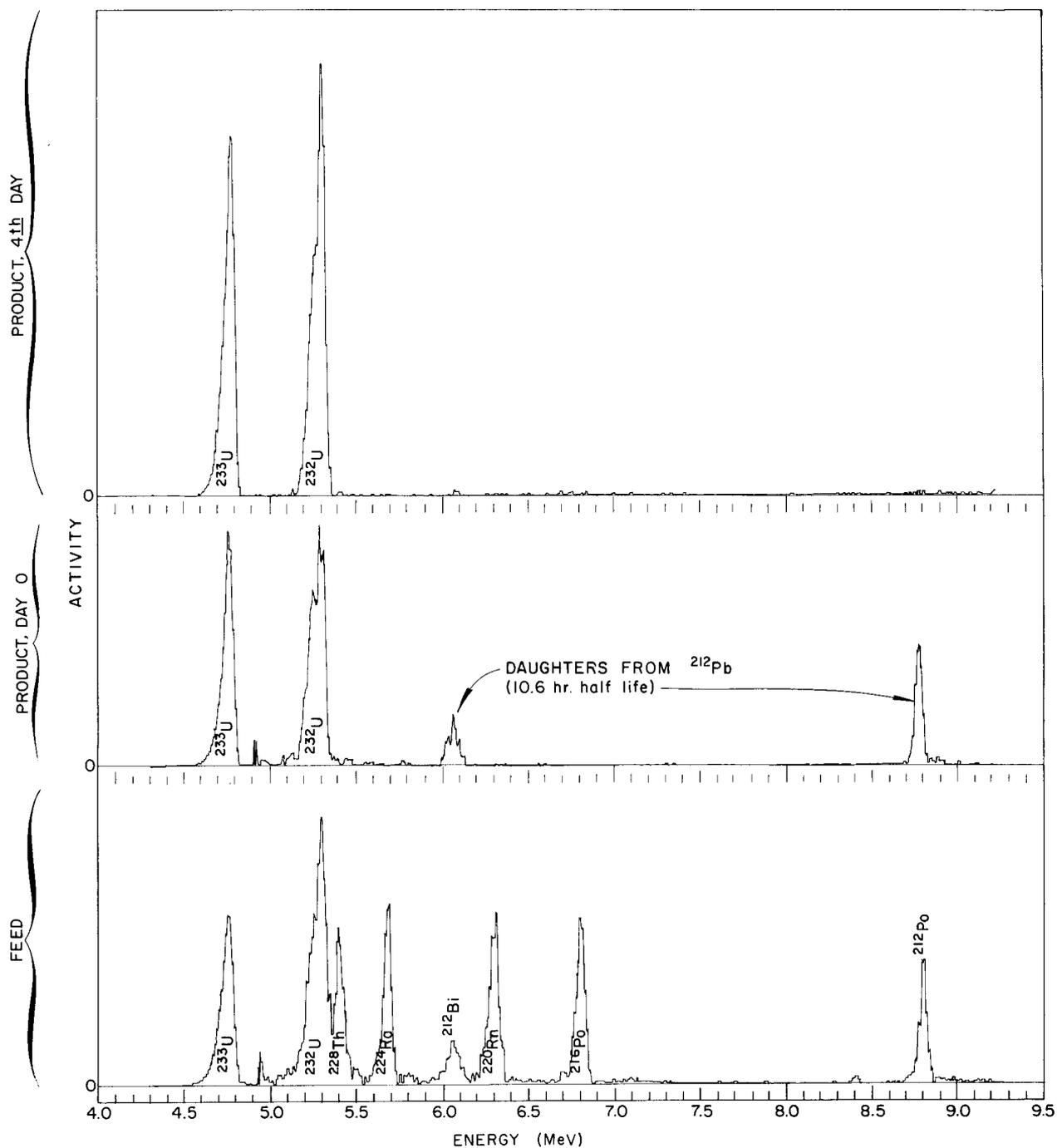


Fig. 15. Alpha Energy Spectrum of ^{233}U Solution Containing 8 ppm of ^{232}U Before and After Passage Through Ion Exchange Column of AG-50W-X12 (200 to 400 mesh) at 25°C.

and installation of the plant equipment and the details of these runs will be described in a report currently being prepared by operations personnel. The present report, therefore, includes only sufficient data to confirm that the plant operated as predicted by the laboratory experiments.

The ion exchange equipment (Fig. 16) was assembled and tested on a single rack before being installed in a remote cell; therefore, there was a minimum of in-cell installation time. This rack is 6-1/2 ft high and 4-1/2 ft wide and contains the ion exchange column, valves, pressure transmitters, etc., required for processing 17.5 kg of ^{233}U .

The feeds used in the three runs were, respectively: (1) 17.5 kg of ^{233}U containing less than 10 ppm of thorium (storage time, 140 days after previous processing); (2) 15 kg of ^{233}U containing 1000 ppm of thorium (storage time, 217 days); and (3) 17.5 kg of ^{233}U containing 1000 ppm of thorium (storage time, 282 days). The feed to the third run was as severe a test of the process as would be experienced in plant operation. Each run was made using the flowsheet shown in Fig. 1.

The product solutions from each run had essentially the same composition and met the decontamination requirements. After a decay period of 3 days, the gamma activity was less than 0.2% of the equilibrium value; and during the following 3 weeks, it remained at less than the 2% of equilibrium value that is required for processing without gamma shielding (Fig. 17). Elution with 6 *M* HNO_3 at 60°C removed nearly all of the uranium, radium, and lead as well as about 50% of the thorium from the resin columns after each run. The eluent contained about 9% of the uranium and was recycled to solvent extraction for recovery. At the end of the three runs, elution (see Appendix I for details) with an ammonium acetate-acetic acid solution removed about 99% of the thorium that was retained by the resin.

The first resin column was equipped with a radiation scanner, which determined the activity at any point along the axis of the first resin column. This instrument was very useful for measuring the thorium band front, the radiation exposure of the resin, and the efficiency of the elution procedure.

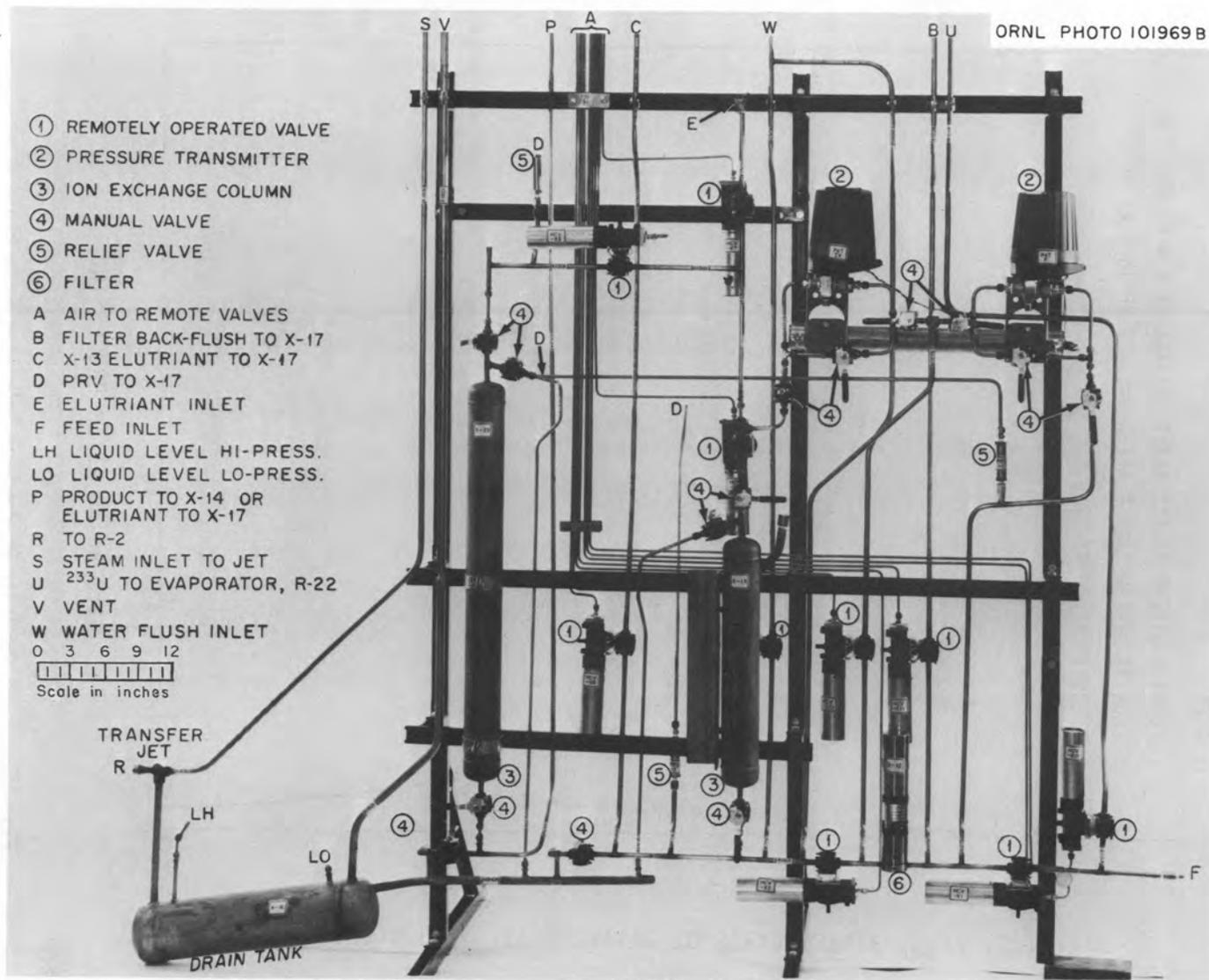


Fig. 16. Ion Exchange Plant Equipment.

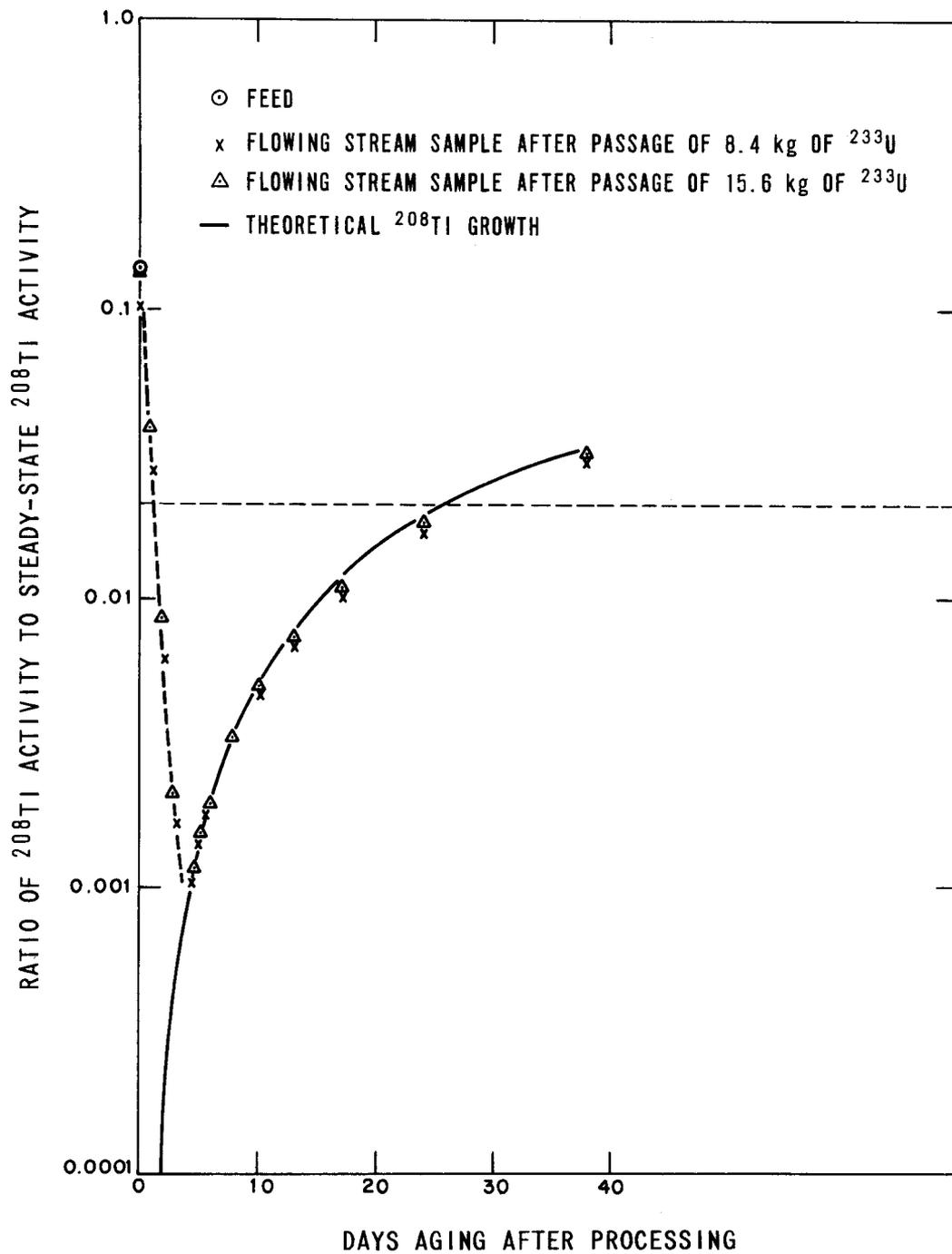


Fig. 17. ^{208}Tl Activity in Product Solutions From Plant Runs.

The processing time for each run, including all sorption and elution steps, was less than 18 hr.

7. ACKNOWLEDGMENTS

The author is very grateful for the help and encouragement which he received in the development of this program. Roy C. Lovelace performed most of the laboratory experiments with skill and dedication. The analyses were made by groups from the ORNL Analytical Chemistry Division under the supervision of W. R. Laing and J. H. Cooper. Rex E. Leuze made a critical review of the program at a crucial point in the development and offered helpful suggestions. Frank E. Harrington and members of the Pilot Plant Section helped to point out and evaluate the engineering data required for plant operation. Fred Nelson's (Chemistry Division) expertise in the theory of ion exchange was heavily relied upon and generously given throughout the program. L. M. Ferris made valuable contributions to the preparation of this report.

The pilot plant demonstration of this process was under the direction of R. E. Brooksbank and J. R. Parrott. F. E. Harrington was responsible for the scale-up and design; W. R. Whitson for construction, testing and installation; R. G. Nicol for operations; and W. T. McDuffee and W. L. Pattison for data accumulation and evaluation. All of the data with engineering-sized equipment was made in the Pilot Plant facility.

8. APPENDIX I: ELUTION OF THORIUM BY ACETATE COMPLEXING

In previous processing of ^{233}U to remove thorium,¹⁸ an acetate-citrate mixture was used to elute the uranium and thorium from the resin column. However, work conducted during the present study showed that thorium was eluted from the resin much more effectively by mixtures of ammonium acetate and acetic acid (Fig. 18). A search of the literature failed to supply information about possible thorium acetate complexes. Thus our study was made on a trial-and-error basis.

A series of experiments was made to determine the optimum ratio and concentrations of ammonium acetate (NH_4Ac) and acetic acid (HAc). Solutions were prepared by mixing a stock solution of NH_4Ac , the concentration of which was 90% of saturation (analyzed 9.28 M acetate, 8.83 M NH_4^+ , and 0.42 M acid), with glacial acetic acid. The data presented in Fig. 19 show that, after an initial period during which the resin was apparently converted from the acid to the ammonium form, an approximately equimolar ratio of NH_4Ac to HAc was the most effective combination. At this ratio, when at least 98% of the thorium was to be removed, the most effective eluent appeared to be one in which both the NH_4Ac and HAc concentrations were in the range of 4 to 4.5 M (Fig. 20).

The rate at which thorium is eluted is thought to be almost completely limited by the diffusion of the thorium from the ion exchange resin beads. This hypothesis is supported by the fact that thorium removal increased very rapidly with increasing temperature (Fig. 21). Temperatures of less than 70°C were studied in order to avoid possible damage to the resin. These data illustrate that the elution of thorium is satisfactory over a wide range of acetate concentrations. At the conditions selected, 4.55 M NH_4Ac -- 3.85 M HAc and 60°C , 90% of the thorium was removed with less than two column volumes of eluent and 99% was removed with about four volumes (Fig. 22).

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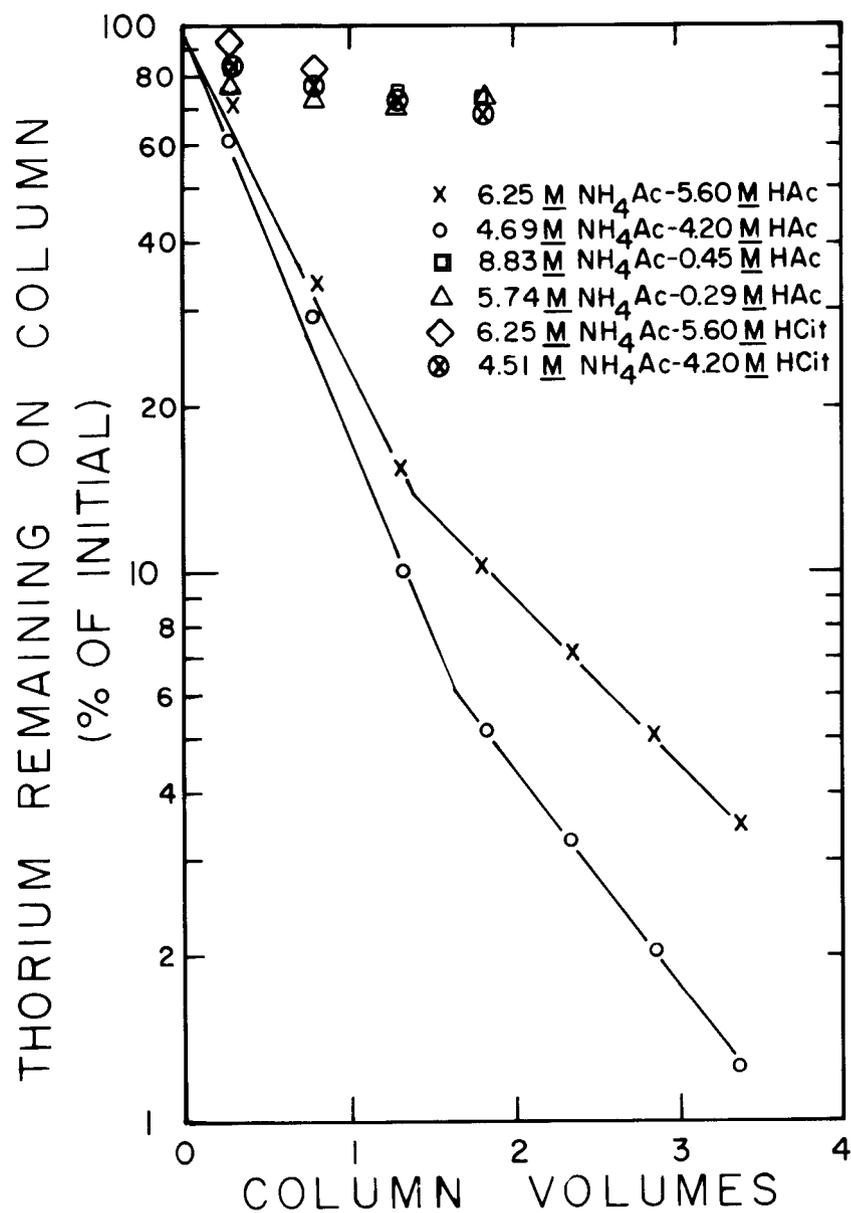


Fig. 18. Elution of Thorium with Various Combinations of Ammonium Acetate, Acetic Acid, and Citric Acid.

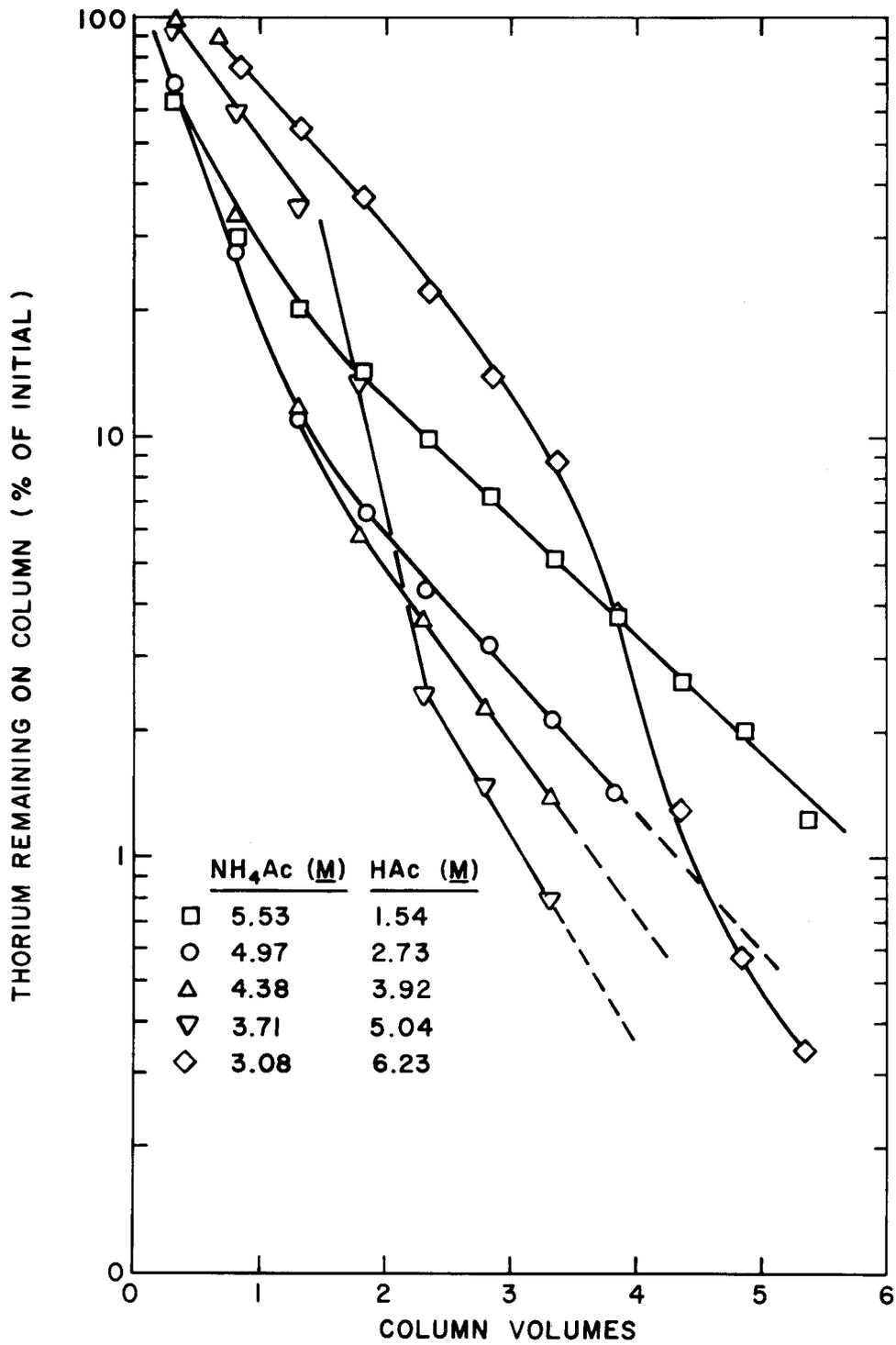


Fig. 19. Effect of Ammonium Acetate-to-Acetic Acid Ratio on the Elution of Thorium. Temperature, 60°C.

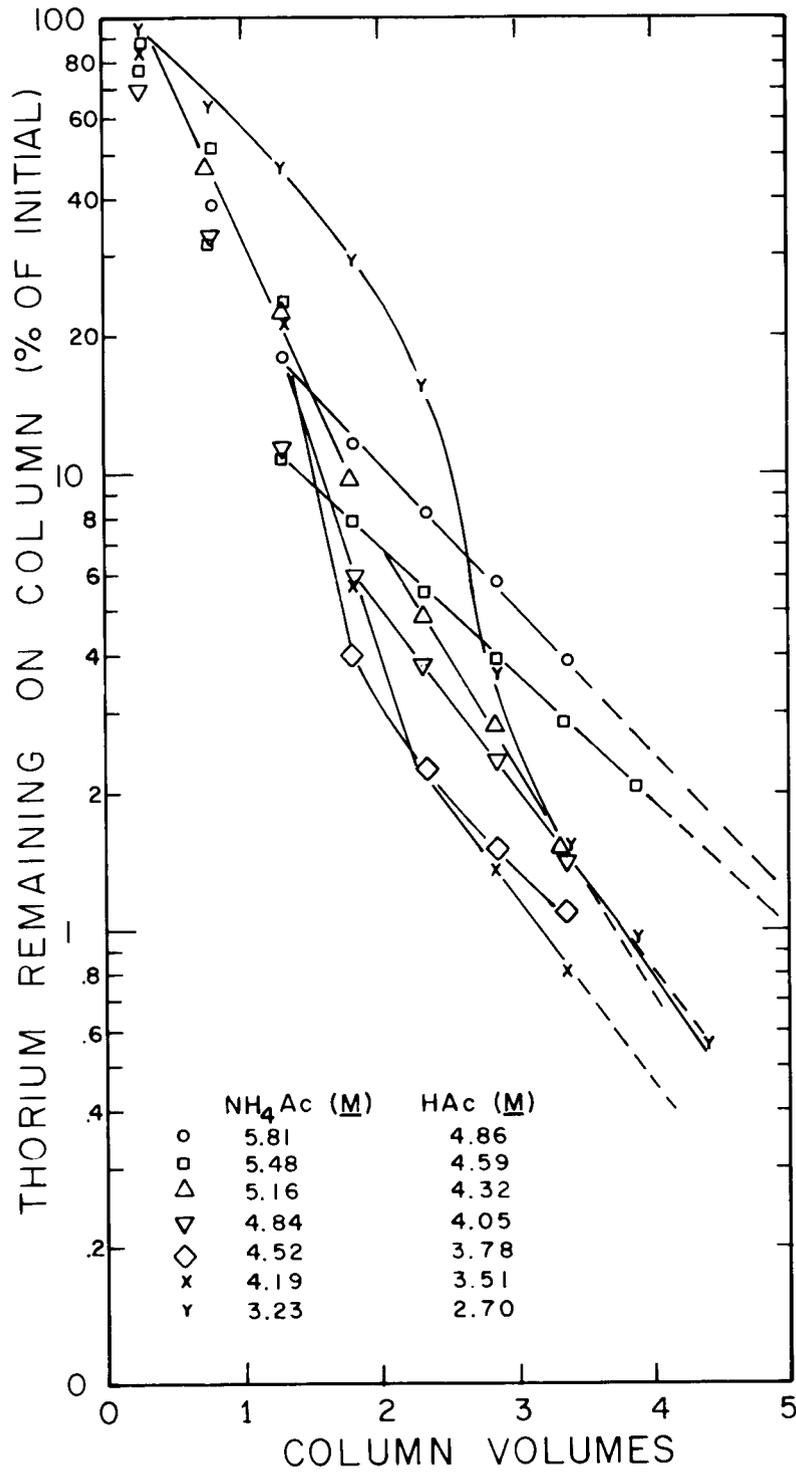


Fig. 20. Effect of NH_4Ac and HAc Concentrations on the Elution of Thorium with Approximately Equimolar Ratios of Ammonium Acetate and Acetic Acid. Temperature, 60°C .

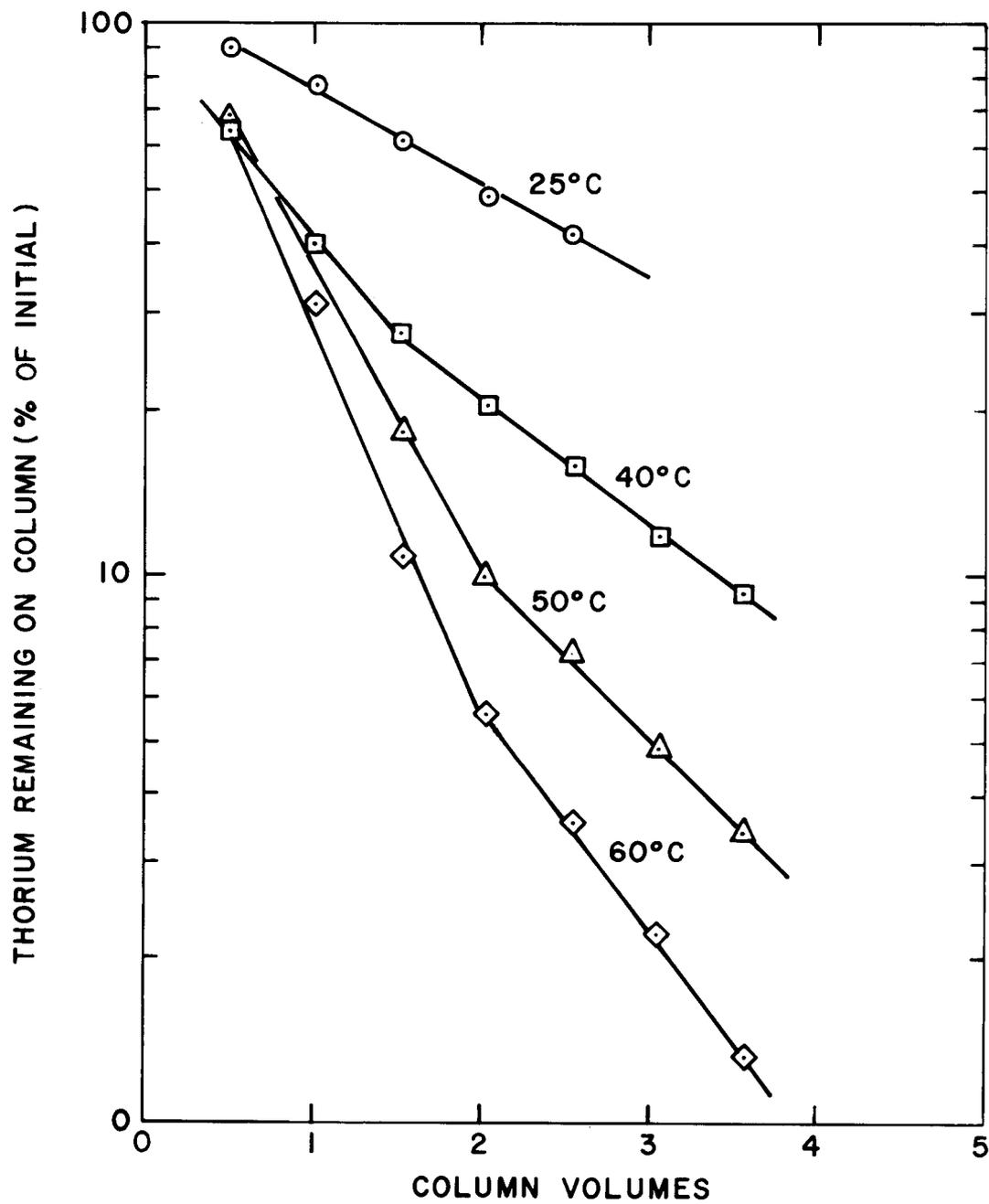


Fig. 21. Effect of Temperature on the Elution of Thorium with 4.69 *M* Ammonium Acetate--4.20 *M* Acetic Acid.

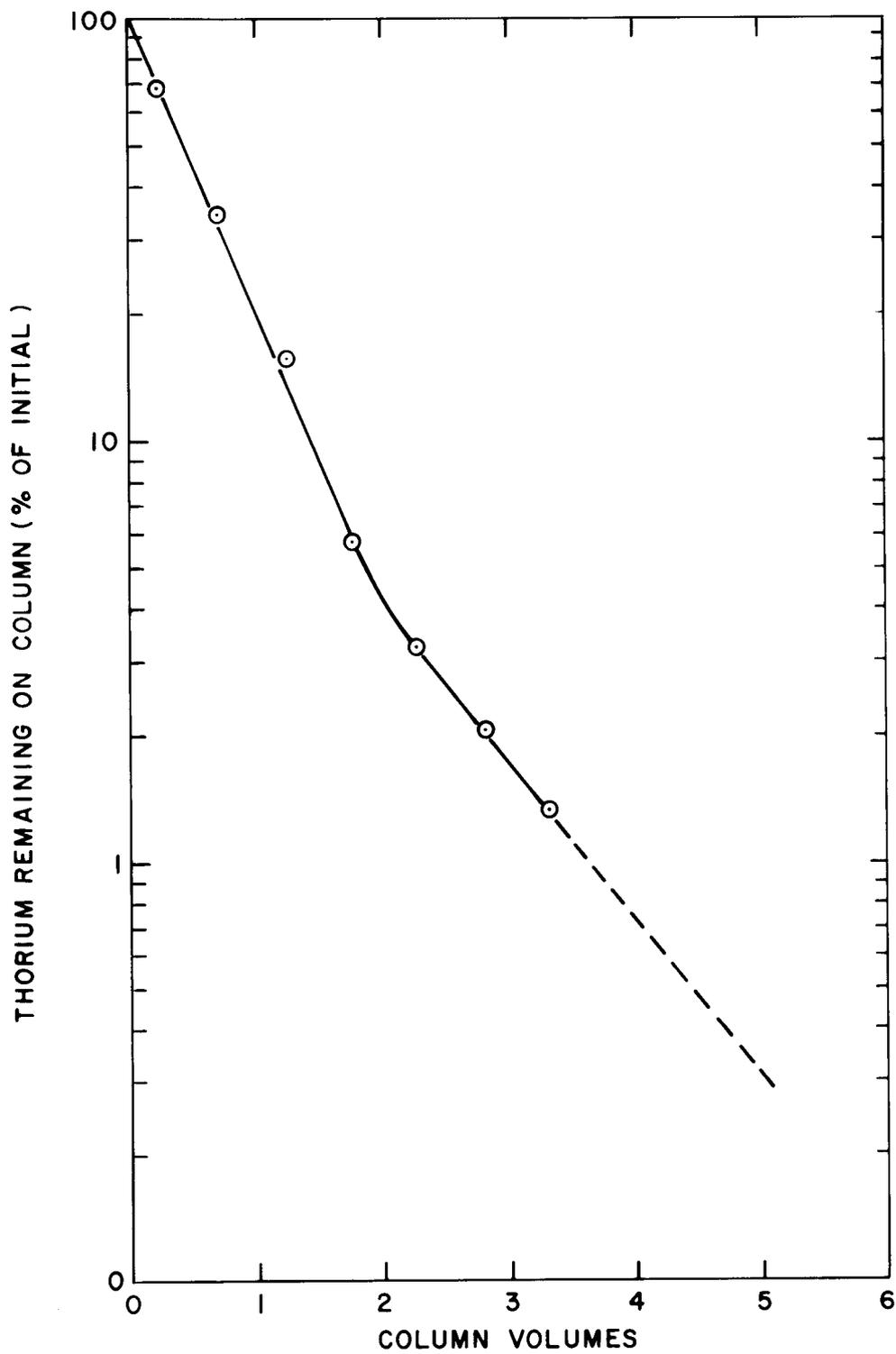


Fig. 22. Elution of Thorium with 4.55 *M* Ammonium Acetate--3.85 *M* Acetic Acid at 60°C.

9. APPENDIX II: SOLVENT EXTRACTION OF URANIUM FROM ACETATE SOLUTIONS

One of the concerns about the use of acetate to recondition the ion exchange columns was that the presence of this ion would make recovery of the ^{233}U by solvent extraction more difficult. However, experiments demonstrated that uranyl nitrate is readily extracted by 15% TBP from acidic solutions containing high concentrations of acetate.

When $0.042\text{ M UO}_2(\text{NO}_3)_2$ -- 5.40 M HAc -- $6.45\text{ M NH}_4\text{Ac}$ was equilibrated with an equal volume of 15% TBP, essentially none of the uranium was extracted. Nitric acid was then added to the solution to bring its composition to $0.034\text{ M UO}_2(\text{NO}_3)_2$ -- 0.5 M HNO_3 -- 8.08 M HAc -- $4.4\text{ M NH}_4\text{NO}_3$. At this point, the uranium became highly extractable; the distribution coefficient (organic/aqueous) was about 15.

The results of these studies indicate that uranium remains strongly complexed by acetate until sufficient nitric acid is added to destroy the acetate complex and convert the uranium to nitrate complexes. After this is accomplished, the uranium becomes highly extractable.

10. APPENDIX III: CALCULATED DEGRADATION OF ION EXCHANGE RESIN BY RADIATION FROM SORBED ^{228}Th AND ITS DAUGHTERS

As shown in the preceding sections, nearly all of the ^{228}Th and ^{224}Ra and part of the ^{212}Pb which are associated with ^{232}U in a feed solution can be sorbed on cation exchange resin. The reconditioning of the resin with 6 M HNO_3 at the end of a flowsheet (Fig. 1) run removes nearly all of the radium and lead but only about 50% of the thorium. Under steady-state flowsheet conditions, the resin after loading will contain about twice the amount of thorium in a single feed, while the resin after reconditioning will contain only half of this amount. The irradiation of the resin will increase rapidly as the daughters of the ^{228}Th grow back (limited by the 3.6-day half-life of ^{224}Ra). After about 30 days for each curie of ^{228}Th , there will be a curie each of alpha activity from ^{224}Ra , ^{220}Ra , and ^{216}Po , 0.36 curie of alpha activity from ^{212}Bi , 0.64 curie of alpha activity from ^{212}Po , as well as additional radiation from beta and gamma emitters. A 1-year-old batch of feed containing 17.5 kg of ^{233}U will contain about 0.5 curie of ^{228}Th , about 2 curies of other alpha emitters (for a total of 2.5 curies of alpha), and about 1 curie of beta plus gamma radiation. Calculations by Arnold¹⁴ indicate that this activity would result in an exposure of the resin to approximately 7.4 rads/sec.

Studies by I. R. Higgins¹⁹ showed that the irradiation of wet Dowex 50 resin to 3.8×10^8 rads in a ^{60}Co unit resulted in a decrease in capacity of 13 to 30% but no other serious changes in the resin. Experience with processing curium and californium, using Dowex 50W-X8 in a chloride system, showed satisfactory operation after exposures to greater than 10^9 rads.²⁰ If we make the conservative assumption that the AG-50W-X12 (200- to 400-mesh) resin will provide satisfactory service up to a dose of 1×10^8 rads, the resin would have an operating life of about 5 months for processing 1-year-old feed, assuming that the ^{228}Th is constantly in equilibrium with its daughters. The actual life of the resin would probably be much longer than this. Resin failure would probably be indicated by decreasing decontamination of the product and by a radiation scanner showing the movement of the thorium band up the first resin column. Thus the resin column could be replaced before operational difficulties occurred.

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