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ADSORPTION OF PROTACTINIUM
ON UNFIRED VYCOR:
FINAL HOT-CELL EXPERIMENTS

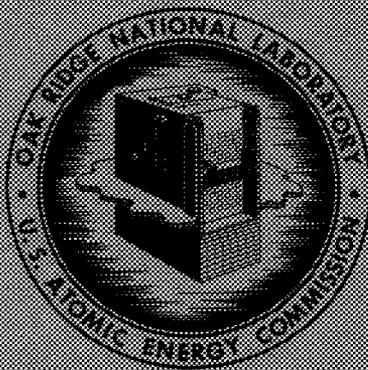
J. H. Goode
J. G. Moore

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ADSORPTION OF PROTACTINIUM ON UNFIRED VYCOR: FINAL
HOT-CELL EXPERIMENTS

J. H. Goode and J. G. Moore

Technicians:

L. A. Byrd
W. B. Howerton
R. C. Lovelace
G. E. Woodall

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ADSORPTION OF PROTACTINIUM ON UNFIRED VYCOR:
FINAL HOT-CELL EXPERIMENTS

J. H. Goode and J. G. Moore

ABSTRACT

Hot-cell experiments demonstrated the practicability of recovering ^{233}Pa from nitric acid solutions by adsorption on unfired, powdered Vycor. Sol-gel thorium that had been irradiated to about 5000 Mwd/metric ton and cooled 27 days was dissolved in 13 M HNO_3 --0.05 M HF --0.1 M $\text{Al}(\text{NO}_3)_3$, and the protactinium was preferentially adsorbed on unfired Vycor. (About 97% was adsorbed at a loading of 3.1 mg of ^{233}Pa per gram of glass.) It was eluted with 0.5 M oxalic acid, yielding product solutions with protactinium concentrations of about 1.5 mg/ml. Decontamination factors for zirconium-niobium, total rare earths, thorium, and uranium were 5.5, 4.8×10^3 , $\cong 1 \times 10^4$, and $\cong 5.7 \times 10^2$, respectively. The ^{233}U that would be present after the decay of the protactinium would contain only 0.1 to 0.5 ppm of ^{232}U .

Similar experiments showed that silica gel was also an effective adsorbent, although the capacity values and decontamination factors were lower than those obtained with the unfired Vycor. Zirconium phosphate (ZP-1) had only about half the capacity of unfired Vycor at 99% adsorption; in addition, oxalic acid elution of the protactinium adsorbed on ZP-1 was not feasible.

1. INTRODUCTION

The selective separation of ^{233}Pa ($t_{1/2} = 27.4$ days) from highly irradiated, short-decayed thorium or thorium-uranium mixtures would produce a potential source of isotopically pure ^{233}U , which is valuable because of its low content of ^{232}U , and, at the same time, remove a large fraction of the beta and gamma emitters associated with short-decayed thorium.

Previous hot-cell experiments¹ demonstrated the feasibility of a process for recovering ^{233}U from a nitric acid solution of highly irradiated, short-decayed ThO_2 - UO_2 by adsorbing ^{233}Pa on unfired

Vycor. Over 99% of the thorium-uranium from fuel rods that had been irradiated to 75,000 Mwd/metric ton and decayed 26 days was dissolved in refluxing 13 M HNO_3 --0.05 M HF, leaving a residue containing less than 0.1% of the uranium but up to 20% of the protactinium. The resulting solution was passed through a column of 60- to 80-mesh unfired Vycor, which adsorbed about 99.6% of the protactinium in the solution. Less than 0.1% of the adsorbed protactinium was removed when the column was washed with 10 M HNO_3 --0.1 M $\text{Al}(\text{NO}_3)_3$; 92% was recovered at a concentration equivalent to 5.5 times that of the feed solution by elution with 0.5 M oxalic acid. The final protactinium product was decontaminated from zirconium-niobium, ruthenium, and total rare earths by factors of 9, 2.87×10^3 , and 6.03×10^3 , respectively.

In these first experiments, the variables of importance for practical application were not examined. Thus, additional hot-cell experiments were made to study the effects of mesh size; flow rate; the capacity of unfired Vycor, silica gel, and zirconium phosphate for adsorbing protactinium; and the feasibility of eluting the latter from these adsorbents with oxalic acid.

In the first part of this report, the major results and conclusions of these experiments are summarized, and recommendations for possible future plant application are presented. The general procedures and results that could influence design criteria are discussed in the body of the report. Finally, the experimental details and observations are included in the Appendix.

The authors gratefully acknowledge the excellent and rapid analytical assistance given by the groups of C. E. Lamb and E. I. Wyatt, and the help of J. W. Ullmann, who arranged for fabrication, irradiation, and off-site handling of the fuel specimens.

2. SUMMARY

A series of ten hot-cell tests verified the practicability of using unfired Vycor for the recovery of protactinium from nitric

acid solutions of irradiated thoria. At a flow rate of $1.57 \text{ ml min}^{-1} \text{ cm}^{-2}$, columns containing 100- to 120-mesh Vycor, water-cooled to prevent boiling, could be loaded to 3.1 mg of protactinium per gram of glass with only 3% breakthrough. Washing with eight volumes of 10 M HNO_3 -- $0.1 \text{ M Al(NO}_3)_3$ removed most of the uranium and thorium and about 1.5% of the ^{233}Pa . On elution with 0.5 M oxalic acid, the remaining protactinium (98.5%) was recovered at an average concentration of 1.46 mg/ml, or about 25 times the feed concentration. The most concentrated fraction of eluate contained 2.86 mg of protactinium per milliliter and had to be diluted to prevent boiling. The protactinium product was found to be decontaminated from zirconium-niobium, total rare earths, thorium, and uranium by factors of 5.9, 5×10^4 , $\geq 1 \times 10^4$, and $\geq 5.7 \times 10^2$, respectively. The ^{233}U that would be obtained from decay of the ^{233}Pa in this solution would contain only 0.1 to 0.5 ppm of ^{232}U .

Radiation from one adsorption-elution cycle appeared to have little or no effect on the unfired Vycor; a second experiment using the same column showed essentially the same adsorption and eluting characteristics. Increasing the particle size from 100-120 to 60-80 mesh decreased the column loading from 2.5 to about 2 mg/g at 1% breakthrough. Increasing the flow rate from 1.57 to $3.14 \text{ ml min}^{-1} \text{ cm}^{-2}$ decreased the loading by 10 to 15%.

Similar tests were performed with 60- to 80-mesh silica gel and zirconium phosphate (Bio-Rad ZP-1). The columns were 0.6 cm in diameter and 11 cm long and contained about 4 g of the adsorbent. At a flow rate of 0.5 ml/min and 99% protactinium adsorption, the silica gel and the zirconium phosphate adsorbed about 2 and 1.3 mg/g, respectively. For comparison, under the same conditions, 60- to 80-mesh unfired Vycor adsorbed about 2.5 mg of ^{233}Pa per gram of glass.

Since the protactinium adsorbed on ZP-1 could not be eluted with oxalic acid, it was allowed to decay on the column, and the ^{233}U was removed with nitric acid. The protactinium on the silica gel, however, was easily eluted with oxalic acid; the elution characteristics

were very similar to those of unfired Vycor, although the product in this instance was not quite as pure. The protactinium product from the silica gel was decontaminated from zirconium-niobium, total rare earths, thorium, and uranium by factors of about 1.5, 8.6×10^2 , $\geq 1 \times 10^4$, and >100 , respectively.

Results of these experiments suggested the following design criteria for full-scale process application:

1. Adsorption columns should be filled with the smallest-sized Vycor compatible with pressure-drop limitations.
2. External and internal annular cooling would be required for loadings of greater than about 0.5 mg of ^{233}Pa per gram of Vycor for columns of critically safe dimensions.² A practical loading of 2.5 mg of protactinium per gram of glass at 1% breakthrough is possible for plant operation using flow rates of about $2 \text{ ml min}^{-1} \text{ cm}^{-2}$.
3. The concentration of the eluted product should either be maintained at about 1 mg of ^{233}Pa per milliliter or cooled to prevent boiling.
4. Engineering studies should be made of the design of adsorption columns with proper cooling capacity and of techniques for the improved washing of thorium and uranium from the loaded column.

3. RESULTS AND DISCUSSION

3.1 Feed Preparation

Feed solutions for these experiments were prepared from three Zircaloy-2-clad fuel rods (about 0.499 in. in diameter and 19 in. long) containing 300 g of sol-gel thoria vibratorily compacted to 88% of theoretical density.³ (This pure ThO_2 , irradiated to about 5000 Mwd/metric ton, was used to minimize the effects of macro concentrations of fission products that were present during the previous hot-cell tests.) These rods were cut into pieces sufficient to make one liter of feed solution about 0.6 $\underline{\text{M}}$ in thorium by refluxing

in boiling 13.2 M HNO_3 --0.1 M $\text{Al}(\text{NO}_3)_3$ --0.05 M HF for periods of up to 24 hr. During the first experiment the cladding sections were leached free of fuel in about 5 hr, but a large amount of the dislodged thorium remained undissolved. About 85% of the gamma emitters and 60% of the thorium were dissolved in 9 hr of boiling. Thereafter, an arbitrary 20- to 24-hr dissolution time was set. Maximum losses as insoluble residues amounted to 0.03% of the thorium and uranium and 0.32% of the protactinium. Data for the five dissolutions and the use of these feeds in the various experiments are summarized in Tables 1 and 2.

3.2 Capacity of Adsorbents

Each adsorbent was arbitrarily loaded to approximately 15% breakthrough to determine its capacity (Figs. 1-3); however, for plant operation, breakthroughs of less than 2% would be more desirable. At 98% adsorption, the 60- to 80-mesh and the 100- to 120-mesh unfired Vycor had capacities of 3 and 4.2 mg of protactinium per gram, respectively. The first run (A-1 in Fig. 1) shows a capacity of only 1 mg/g; this was the result of channeling caused by boiling at the beginning of the run. In succeeding runs, the columns were water-cooled to prevent this maloperation.

The capacity of the silica gel was slightly lower than that of the Vycor. Values of about 2.5 mg of protactinium per gram were obtained for two cycles of loading and elution on 60- to 80-mesh silica gel (Fig. 2).

Zirconium phosphate had a capacity of only 1.5 mg of protactinium per gram at 2% breakthrough; but, at flow rates of $1.27 \text{ mg min}^{-1} \text{ cm}^{-2}$, it continued to adsorb protactinium until the run was finally terminated at 20% breakthrough. At this point, 12.5 mg of protactinium per gram of ZP-1 had been adsorbed. Thus the zirconium phosphate, although capable of strongly adsorbing large quantities of protactinium, would require an extremely low flow rate to minimize losses to the effluent, and would probably be unsuitable in plant operation.

Table 1. Five Dissolutions of Irradiated Sol-Gel ThO₂ in Fluoride-Catalyzed Nitric Acid

Dissolution Number	1	2	3	4	5
Rod No.	T-6	T-6	T-5	T-5	T-8
Sample No.	A-3	B-1	D-1	E-1	F-1
Nvt	22.21 x 10 ²⁰	22.21 x 10 ²⁰	17.09 x 10 ²⁰	17.09 x 10 ²⁰	21.39 x 10 ²⁰
Decay, days	27	28	30	35	36
Vol, ml	1000	1000	1000	1000	1000
Dissolution Time, hr	9.0	24.0	24.8	24.0	21.0
HNO ₃ , M	11.35	11.09	11.76	11.35	11.09
Th, mg/ml	86.8	144.0	66.5	126.0	111.0
U, mg/ml	0.78	0.97	0.33	0.82	1.46
²³² U, ppm	170	150	123	107	253
Zr, mg/ml	0.10	2.0	0.01	0.11	3.03
Gross fission products (gamma), counts min ⁻¹ ml ⁻¹	2.00 x 10 ¹²	2.40 x 10 ¹²	1.20 x 10 ¹²	3.16 x 10 ¹²	1.09 x 10 ¹²
Zr-Nb (gamma), counts min ⁻¹ ml ⁻¹	6.43 x 10 ¹⁰	5.80 x 10 ¹⁰	3.05 x 10 ¹⁰	4.39 x 10 ¹⁰	1.96 x 10 ¹¹
Cs (gamma), counts min ⁻¹ ml ⁻¹	1.72 x 10 ⁹	4.31 x 10 ⁸	--	2.29 x 10 ⁸	<9 x 10 ⁸
Ru (gamma), counts min ⁻¹ ml ⁻¹	4.14 x 10 ⁹	1.72 x 10 ⁹	--	<3 x 10 ⁹	<6 x 10 ⁹
I (gamma), counts min ⁻¹ ml ⁻¹	2.04 x 10 ⁸	--	--	--	<2 x 10 ⁸
Total Rare Earths (beta), counts min ⁻¹ ml ⁻¹	2.60 x 10 ¹⁰	2.36 x 10 ¹⁰	1.38 x 10 ¹⁰	1.32 x 10 ¹⁰	3.97 x 10 ¹⁰
²³³ Pa, dis min ⁻¹ ml ⁻¹	3.85 x 10 ¹²	5.22 x 10 ¹²	2.48 x 10 ¹²	2.20 x 10 ¹²	3.78 x 10 ¹²
²³³ Pa, mg/ml	0.085	0.11	0.069	0.054	0.073

Table 2. ²³³Pa Adsorption-Elution Test Conditions

Feed - as shown in Table 1
 Wash - 10 M HNO₃-0.1 M Al(NO₃)₃
 Eluent - 0.5 M oxalic acid

Expt. No.	Cycle No.	Adsorbent	Mesh Size	Weight (g)	Flow Rates (ml cm ⁻² min ⁻¹)			Feed Comp. (Table 1)	Remarks
					Feed	Wash	Eluate		
A	1	Vycor	60-80	4	1.27	1.27	1.27	Diss. 1	Column boiled at start.
A	2	Vycor	60-80	4	1.27	1.27	Batch	Diss. 1	Column plugged after washing.
B	1	Vycor	100-120	4	1.27	1.27	1.27	a	
C	1	ZP-1	60-80	4	1.27	1.27	Batch	Diss. 2	Feed halted after 550 ml.
D	1	Silica Gel	60-80	4	1.27	1.27	1.27	Diss. 3	
D	2	Silica Gel	60-80	4	1.27	1.27	1.27	Diss. 3	
E	1	Vycor	100-120	7	1.57	0.78	0.78	Diss. 4	
E	2	Vycor	100-120	7	3.14	0.78	0.78	Diss. 4	
F	1	Vycor	60-80	7	1.57	0.78	0.78	Diss. 5	
F	2	Vycor	60-80	7	3.14	0.78	0.78	Diss. 5	

^a250 ml from Dissolution 1 + 770 ml from Dissolution 2.

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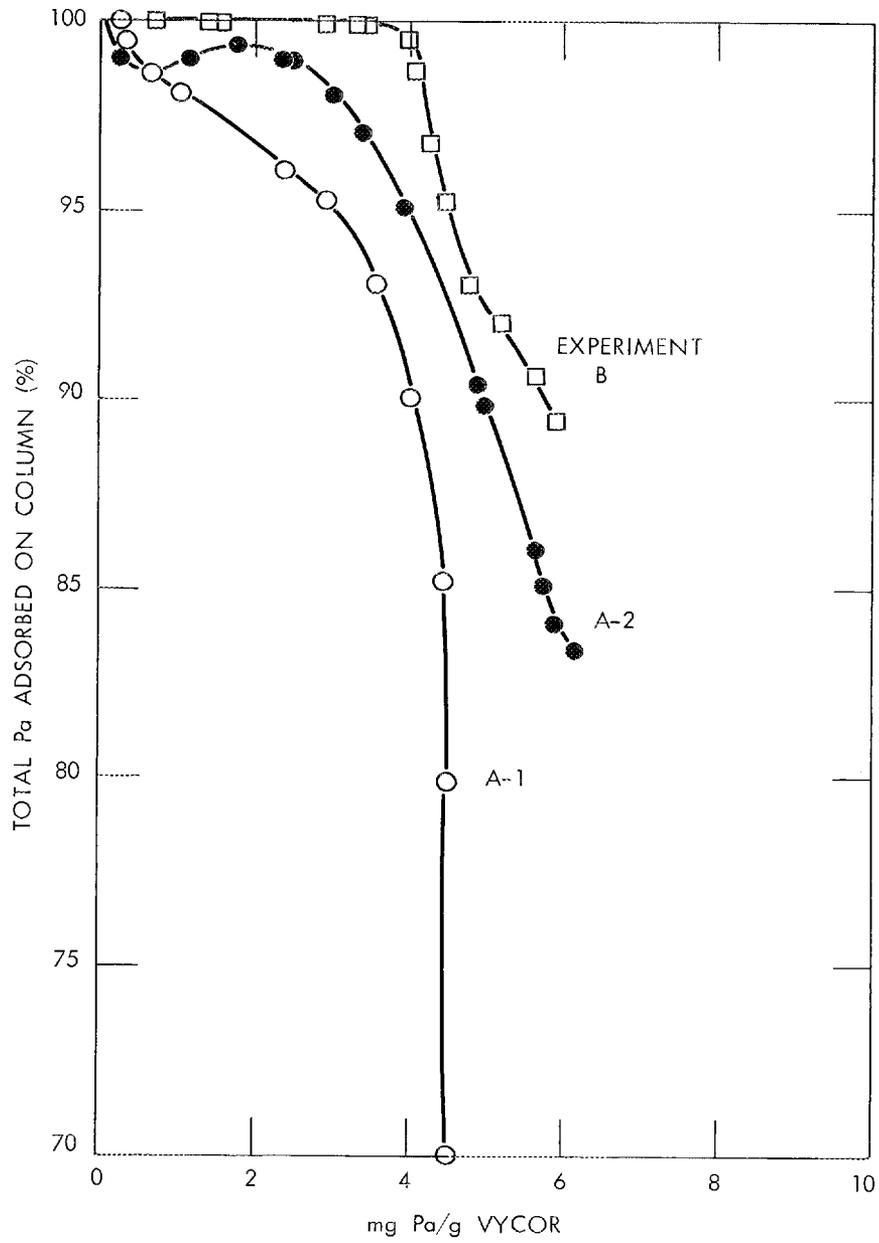


Fig. 1. Effect of ^{233}Pa Loading on Capacity of Unfired Vycor.

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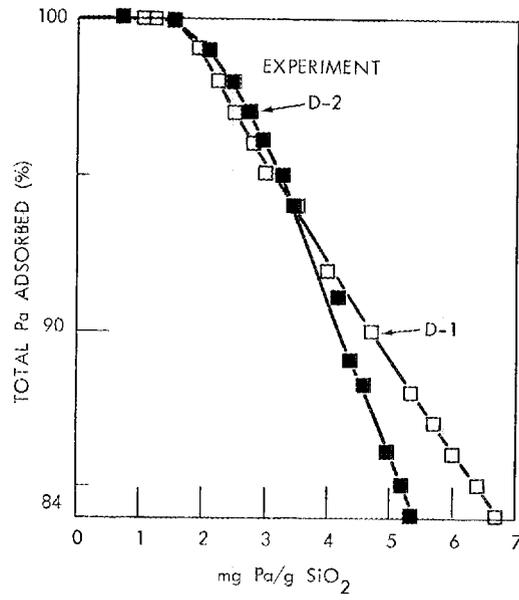


Fig. 2. Effect of ²³³Pa Loading on the Capacity of Silica Gel.

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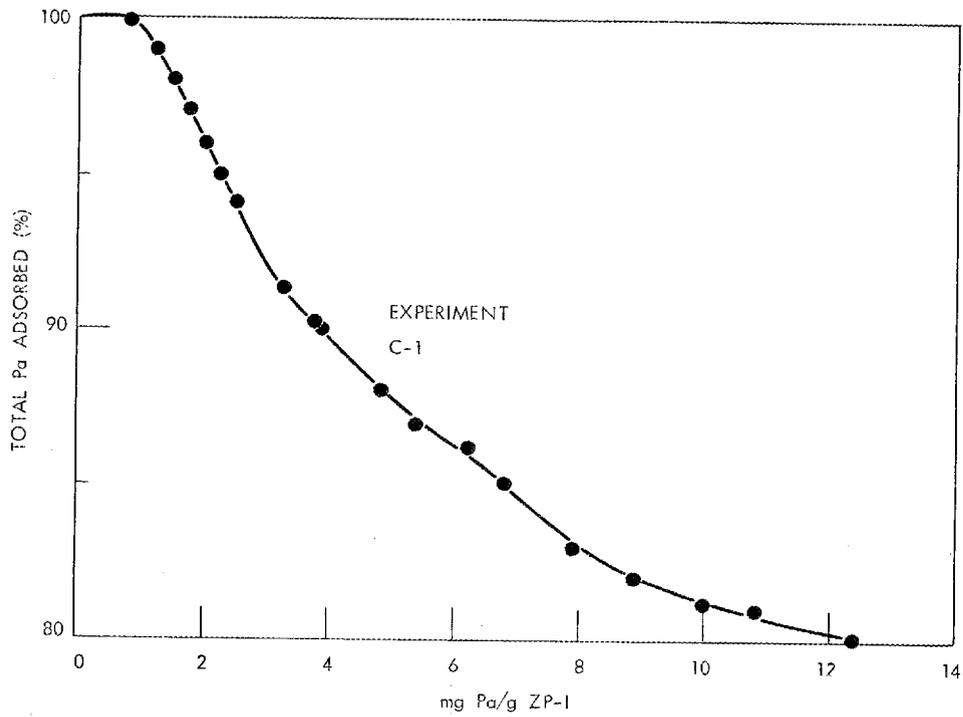


Fig. 3. Effect of ²³³Pa Loading on the Capacity of Zirconium Phosphate.

3.3 Effect of Flow Rate

A twofold increase in flow rate caused a slight decrease in the loading capacity of the Vycor (Figs. 4 and 5). However, it is apparent (Table 3) that, if only 95% adsorption of the protactinium were required on each cycle, water-cooled columns of 60- to 120-mesh Vycor could be loaded to greater than 2.5 mg of protactinium per gram of glass at flow rates up to $3 \text{ ml cm}^{-2} \text{ min}^{-1}$. Any flow rate greater than $1 \text{ ml cm}^{-2} \text{ min}^{-1}$ should be adequate for plant application.

3.4 Losses from Washing

Figure 6 shows the effect of loading rate on the losses of protactinium from the Vycor during washing of the column to remove fission products and thorium. Apparently, the protactinium that is loaded rapidly is not tightly bound to the Vycor and is easily displaced by the wash solution. Thus, 100- to 120-mesh Vycor that is loaded at 1.57 and $3.14 \text{ ml cm}^{-2} \text{ min}^{-1}$ and washed with eight column volumes of 10 M HNO_3 -- $0.1 \text{ M Al(NO}_3)_3$ at $0.78 \text{ ml cm}^{-2} \text{ min}^{-1}$, giving losses of about 1.5 and 1.9% of the protactinium respectively, appears to be most suitable for process operation. Under the same conditions, losses of 3.7 and 5.5% were obtained for 60- to 80-mesh Vycor.

About 5.1% of the protactinium was lost from silica gel (not shown) when it was loaded at $1.57 \text{ ml cm}^{-2} \text{ min}^{-1}$ and washed at $0.78 \text{ ml cm}^{-2} \text{ min}^{-1}$. Zirconium phosphate retained the protactinium tenaciously, with losses during washing of only 0.30%.

3.5 Elution from Columns

After the loaded columns were washed with 10 M HNO_3 -- $0.1 \text{ M Al(NO}_3)_3$ to remove thorium and uranium, the protactinium was eluted with 0.5 M oxalic acid. Tables 4 and 5 show the actual concentrations of protactinium in each sample, a "cumulative concentration" of protactinium for the first 20 ml of eluate, the ratio of the concentration of the protactinium in the cumulative product to that in the feed, and the total amount of protactinium eluted from Vycor and

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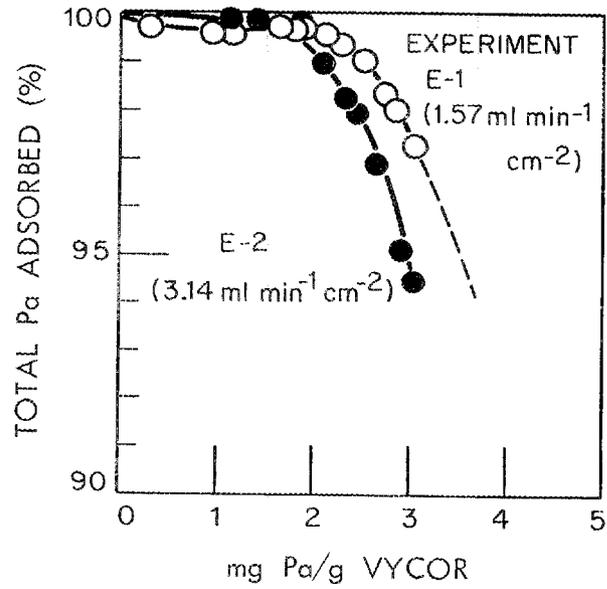


Fig. 4. Effect of Flow Rate on the Capacity of 60- to 80-Mesh Vycor for ^{233}Pa .

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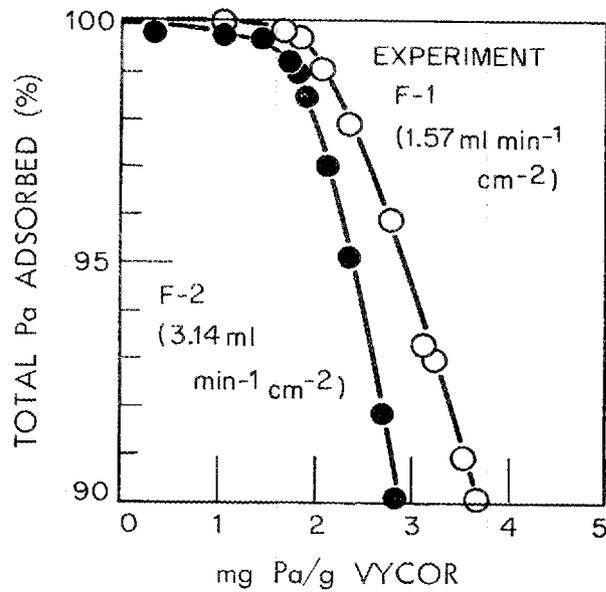


Fig. 5. Effect of Flow Rate on the Capacity of 100- to 120-Mesh Vycor for ^{233}Pa .

Table 3. Effect of Material and Flow Rate on the Loading of ^{233}Pa

Material	Mesh Size	Flow Rate ($\text{ml min}^{-1} \text{cm}^{-2}$)	Protactinium Loading ($\text{mg } ^{233}\text{Pa/g Adsorbent}$)				
			99% Retained	95% Retained	90% Retained	85% Retained	80% Retained
Vycor	60-80	1.27	2.5	4.5	5.0	5.8	7.0 ^a
Vycor	60-80	1.57	2.5	3.5	--	--	--
Vycor	60-80	3.14	2.0	3.0	--	--	--
Vycor	100-120	1.27	4.5	5.0	5.8	--	8.0 ^a
Vycor	100-120	1.57	2.1	2.9	3.7	--	--
Vycor	100-120	3.14	1.8	2.4	2.8	--	--
Silica Gel	60-80	1.27	2.0	3.3	4.5	5.8	--
ZP-1	60-80	1.27	1.3	2.3	3.9	6.8	12.4

^aEstimated.

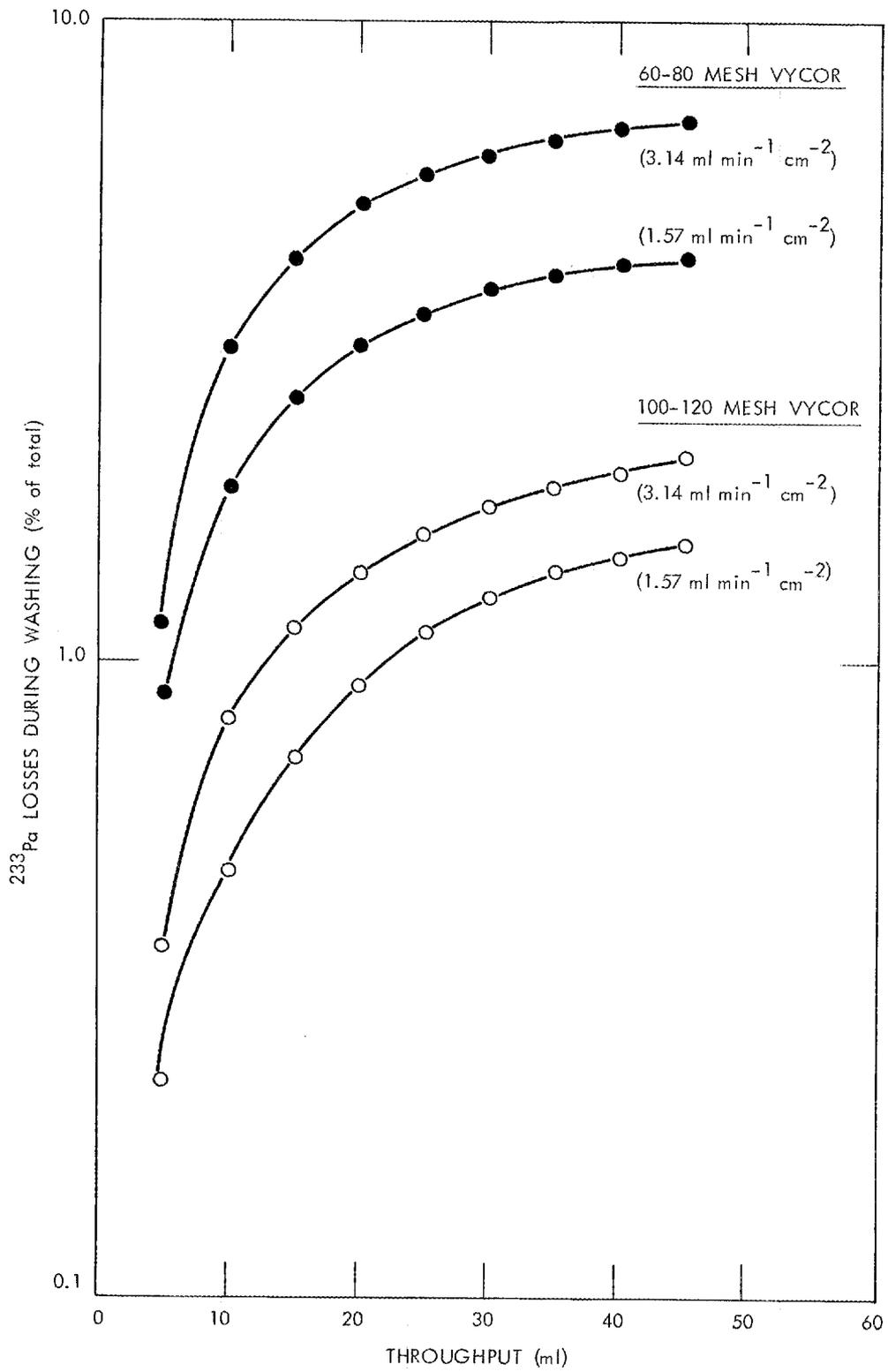


Fig. 6. Effect of Loading Rate on ^{233}Pa Losses During Washing of Column Prior to Elution.

Table 4. Continuous Elution of ^{233}Pa from Unfired Vycor with Oxalic Acid

Cumulative Vol (ml)	Sample Vol (ml)	^{233}Pa				^{233}Pa Eluted	
		dis min ⁻¹ ml ⁻¹	mg/ml	Cumulative Concentration (mg/ml)	Conc. in Cum. Product Conc. in Feed	Total (mg)	Percent Eluted
Elution A-1 (60- to 80-mesh Vycor)							
5	5	1.07×10^{14}	2.36	2.36	27.8	11.76	53.2
10	5	6.88×10^{13}	1.51	1.93	22.7	19.34	87.4
15	5	1.43×10^{13}	0.31	1.39	16.4	20.92	91.5
20	5	6.85×10^{12}	0.16	1.08	12.7	21.75	98.3
25	5	2.14×10^{12}	0.047	0.83	9.7	21.96	99.2
35	10	7.05×10^{11}	0.015	--	--	--	--
45	10	4.64×10^{10}	0.001	--	--	--	--
55	10	1.24×10^{10}	Negligible	--	--	--	--
65	10	1.42×10^{10}	Negligible	--	--	22.13	100.0
Elution B-1 (100- to 120-mesh Vycor)							
5	5	6.04×10^{13}	1.33	1.33	12.1	6.63	43.8
10	5	5.28×10^{13}	1.16	1.25	11.4	12.43	82.1
15	5	1.69×10^{13}	0.37	0.95	8.6	14.29	94.4
20	5	4.78×10^{12}	0.10	0.74	6.7	14.82	97.9
25	5	1.58×10^{12}	--	--	--	14.98	99.0
30	5	7.37×10^{11}	--	--	--	15.06	99.3
37.5	7.5	4.50×10^{11}	--	--	--	15.15	100.0

Table 5. Continuous Elution of ^{233}Pa from Silica Gel with Oxalic Acid

Elution D-1 (60- to 80-mesh SiO_2)

Cumulative Vol (ml)	Sample Vol (ml)	^{233}Pa				^{233}Pa Eluted	
		$\text{dis min}^{-1} \text{ ml}^{-1}$	mg/ml	Cumulative Concentration (mg/ml)	<u>Conc. in Cum. Product</u> <u>Conc. in Feed</u>	Total (mg)	Percent Eluted
5	5	1.78×10^{13}	0.79	0.79	11.4	1.95	7.7
10	5	1.90×10^{14}	4.18	2.48	35.9	22.80	90.5
15	5	1.79×10^{13}	0.80	1.93	28.0	24.77	98.4
20	5	2.15×10^{12}	0.05	1.45	21.0	25.04	99.5
25	5	7.85×10^{11}	--	--	--	--	--
30	5	3.18×10^{11}	--	--	--	--	--
40	10	7.66×10^{10}	--	--	--	--	--
50	10	1.71×10^9	--	--	--	--	--
60	10	3.98×10^{10}	--	--	--	25.19	100.0

silica gel. The results indicated that 98 to 99% of the protactinium adsorbed on each adsorbent was removed by the first 20 ml (approximately two column volumes) of oxalic acid. A sharp band of protactinium at a concentration about 25 times greater than that in the feed was eluted. The remainder of the protactinium was removed when the oxalic acid was displaced by 10 M HNO₃ prior to the next cycle of adsorption. Bubbles of gas formed in the eluate, and all products with concentrations greater than 1 mg of protactinium per milliliter required dilution to prevent boiling in the sample bottles. These characteristics must be considered in any plant design.

The protactinium eluted from the silica gel and Vycor was decontaminated from zirconium-niobium, rare earths, and thorium by factors of 6.6, from 2×10^3 to greater than 5×10^4 , and $\geq 1 \times 10^4$, respectively. Since one of the primary objectives of the process is to produce a source of high-purity ²³³U, the decontamination from ²³²U was measured by alpha pulse analysis for all feed and product solutions (Table 6). The results from runs F-1 and F-2, experiments that were more typical of process conditions, show that the uranium that was separated from the protactinium--oxalic acid product solution contained an average of 2.7 ppm of ²³²U after a two-week decay period. Further decay would reduce the ²³²U concentration in the final ²³³U product to 0.1 to 0.5 ppm.

Although zirconium phosphate can strongly adsorb large quantities of protactinium, it does not appear to be a useful process material. Because previous laboratory experiments had shown that the protactinium adsorbed on it could not be eluted with oxalic acid, the loaded column from the hot-cell experiment was stored for three months to allow the ²³³Pa to decay to ²³³U. At the end of this period, recovery of the uranium was attempted by elution with nitric acid; however, the adsorbent had deteriorated into a putty-like mass, and only 47.3% of the calculated amount of ²³³U was recovered by leaching with 10 M HNO₃. The specificity of the ZP-1 for protactinium was demonstrated by the 99.7% isotopic purity of the ²³³U in this product solution. Unfortunately,

the leached residue was lost, and completion of a material balance was impossible.

Table 6. Decontamination of ^{233}U Product from ^{232}U in Adsorption-Elution Experiments

Run No.	^{232}U Concentration (ppm)		Decontamination Factor
	Feed	Product	
A-2	170	2.3	74
C-1	152	1.3	117
E-1	130	2.7	48
E-2	107	5.3	20
F-1	253	2.6	97
F-2	196	2.8	70

4. REFERENCES

1. J. G. Moore et al., Adsorption of Protactinium on Unfired Vycor: Initial Hot-Cell Experiments, ORNL-3773 (April 1965).
2. E. L. Nicholson, ORNL, personal communication.
3. A. R. Olsen et al., Irradiation Behavior of Thorium-Uranium Alloys and Compounds, ORNL-TM-1142 (June 1965).
4. A. R. Olsen, ORNL, personal communication.

APPENDIX

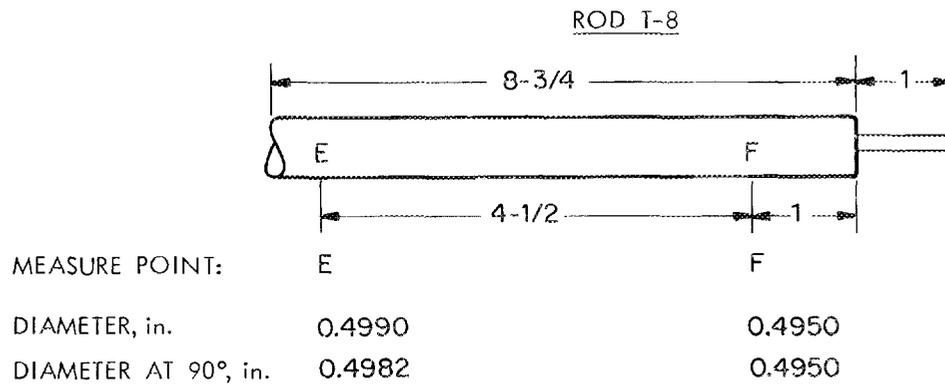
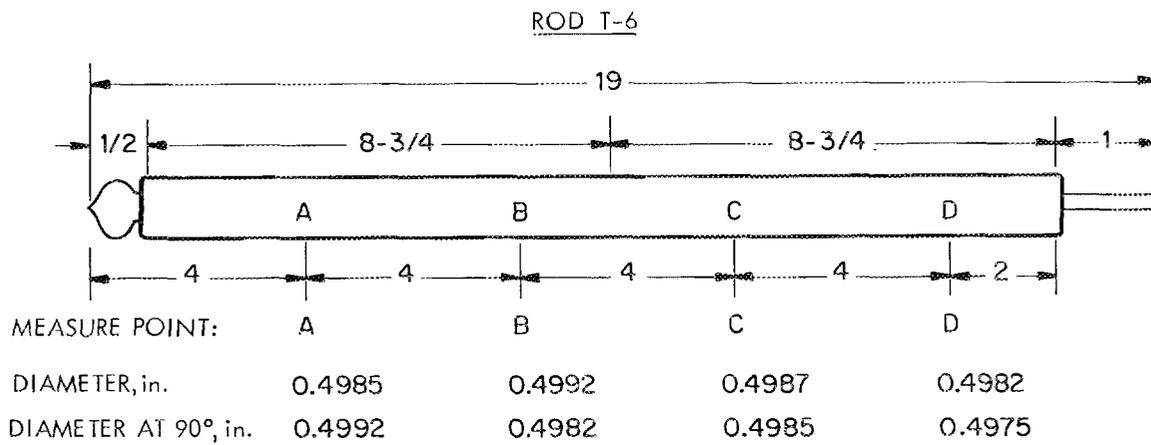
The following section describes the apparatus, analytical procedures, and other details of each of the hot-cell experiments. Included are tables and graphs showing the quantities of protactinium, zirconium-niobium, and rare earths in the effluent samples from the various types of columns.

Fuels and Adsorbents

The fuel rods were irradiated to about 5000 Mwd/metric ton in the ETR from February 6, 1965 to December 6, 1965 (ORNL experiments 43-90, -91, and -92) at an average unperturbed flux of 2.6×10^{14} . The calculated nvt for rod T-6 (43-91), used in experiments A, B, and C, was 22.10×10^{20} ; that for rod T-3 (43-90), experiments D and E, was 17.09×10^{20} ; and that for rod T-8 (43-92), experiment F, was 21.39×10^{20} .⁴ At discharge, each rod contained an estimated 0.97 g of ^{233}Pa and 1.05 g of fission products. A series of measurements of the diameter of each fuel rod were made with a micrometer using the model 8 manipulators. No significant irradiation-caused swelling could be detected (Fig. 7). The rods were then sectioned, dissolved, and processed after a decay period of less than 36 days. The solutions obtained contained small, rapid-settling black particles from the outside of the cladding and lighter white "flakes" that appeared to come from the inside surface of the Zircaloy. Continued attack by the dissolvent removed all of the coatings from the cladding, leaving shiny, silver-colored surfaces.

About 0.75 g of a hydrated residue filtered from rod T-5 dissolver solutions contained 42 mg of zirconium, 68 mg of thorium, 0.62 mg of uranium, and 0.30 mg of ^{233}Pa . This is equivalent to losses (to the residue) of 0.03% of the thorium and uranium and 0.36% of the protactinium. The losses from rod T-6 were only one-eighth of those from rod T-5. Sections of the leached cladding (20 to 35 g) from both rods, which were dissolved in H_2SO_4 -HF mixtures, contained practically no uranium, thorium, or protactinium.

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ROD T-5

DIAMETER OF ROD T-5 IS LESS THAN 0.500-in. ALONG ENTIRE LENGTH.

Fig. 7. Measurement of Diameters of Irradiated Zircaloy-Clad ThO_2 Rods.

Mass spectrometric analyses of the uranium from three of the dissolver solutions were made after a decay period of 2-1/2 months to determine the burnup and isotopic purity of the uranium (Table 7).

Table 7. Uranium Mass Analyses of Dissolver Solutions

Dissolving No.	Rod No.	Composition (%)					
		$^{232}\text{U}^a$	^{233}U	^{234}U	^{235}U	^{236}U	^{238}U
4	T-5	<0.035	95.04	3.02	0.12	0.005	1.82
2	T-6	--	94.51	3.95	0.19	0.008	1.34
5	T-8	<0.035	91.87	6.82	0.49	0.028	0.79

^aSome interference from thorium at mass 232.

The unfired Vycor was obtained as a powder from the Corning Glass Works and was screened to separate the 60- to 80-mesh and 100- to 120-mesh fractions. Columns were prepared after weighing the glass and conditioning it with 10 M HNO_3 . The silica gel (60 to 80 mesh) was obtained from the Fisher Scientific Company, and the Bio-Rad ZP-1 zirconium phosphate was obtained from the Bio-Rad Laboratories of Richmond, California.

Apparatus

The fuel segments were dissolved in a 2-liter Pyrex flask (Fig. 8) equipped with a downdraft condenser to minimize loss of protactinium and other fission products. The off-gas train consisted of a packed bed of activated charcoal and silver-plated copper mesh for iodine removal and a caustic scrubber attached to the building vessel off-gas system.

Adsorption columns were of two sizes (Fig. 9): 0.6 cm diam x 11 cm long, containing 4 g of adsorbent, and 0.9 cm diam x 17 cm long, containing 7 g of adsorbent. Each column was fed by an "upflow"

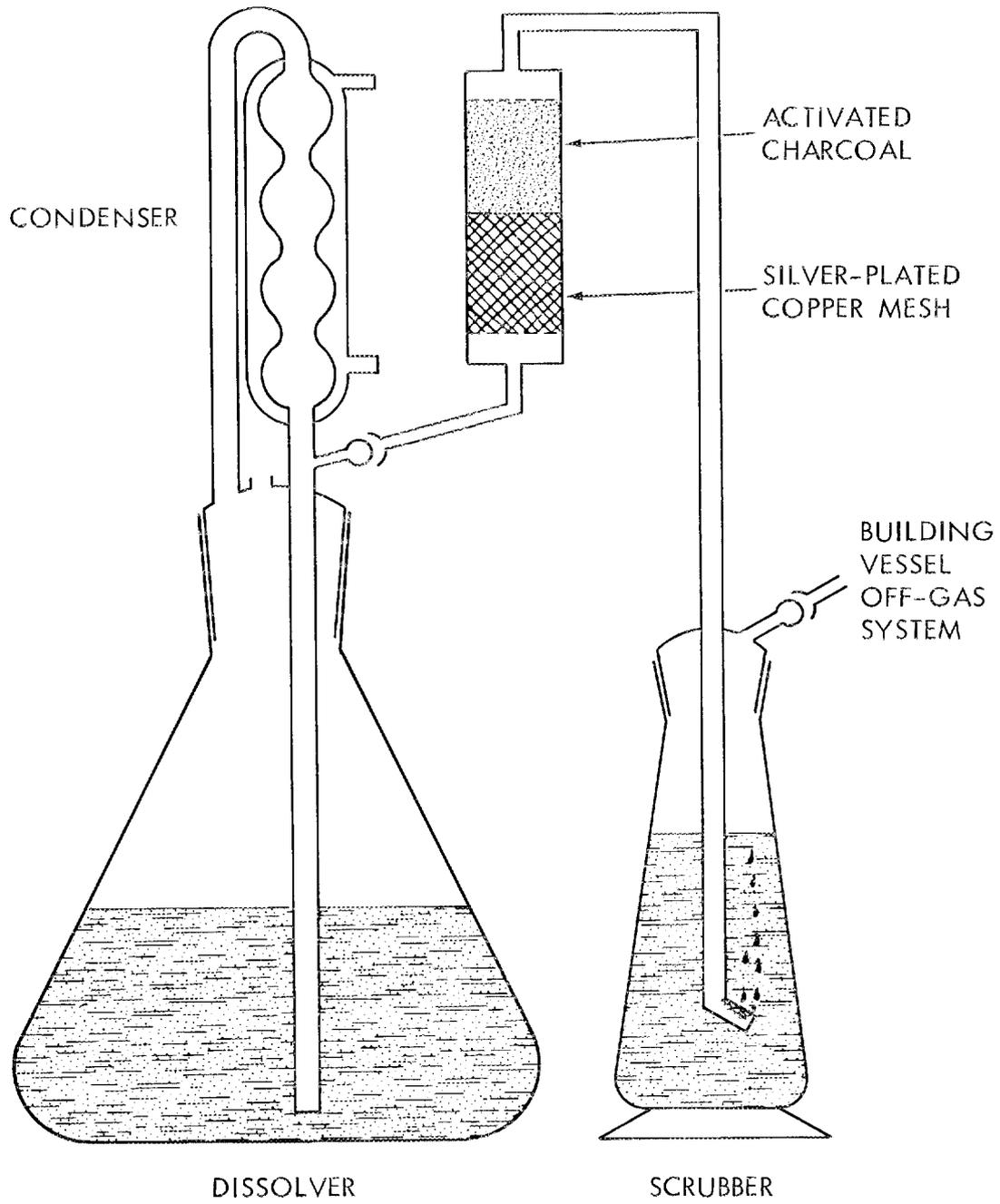


Fig. 8. Dissolver and Off-Gas Train for Dissolution of Zircaloy-Clad ThO_2 .

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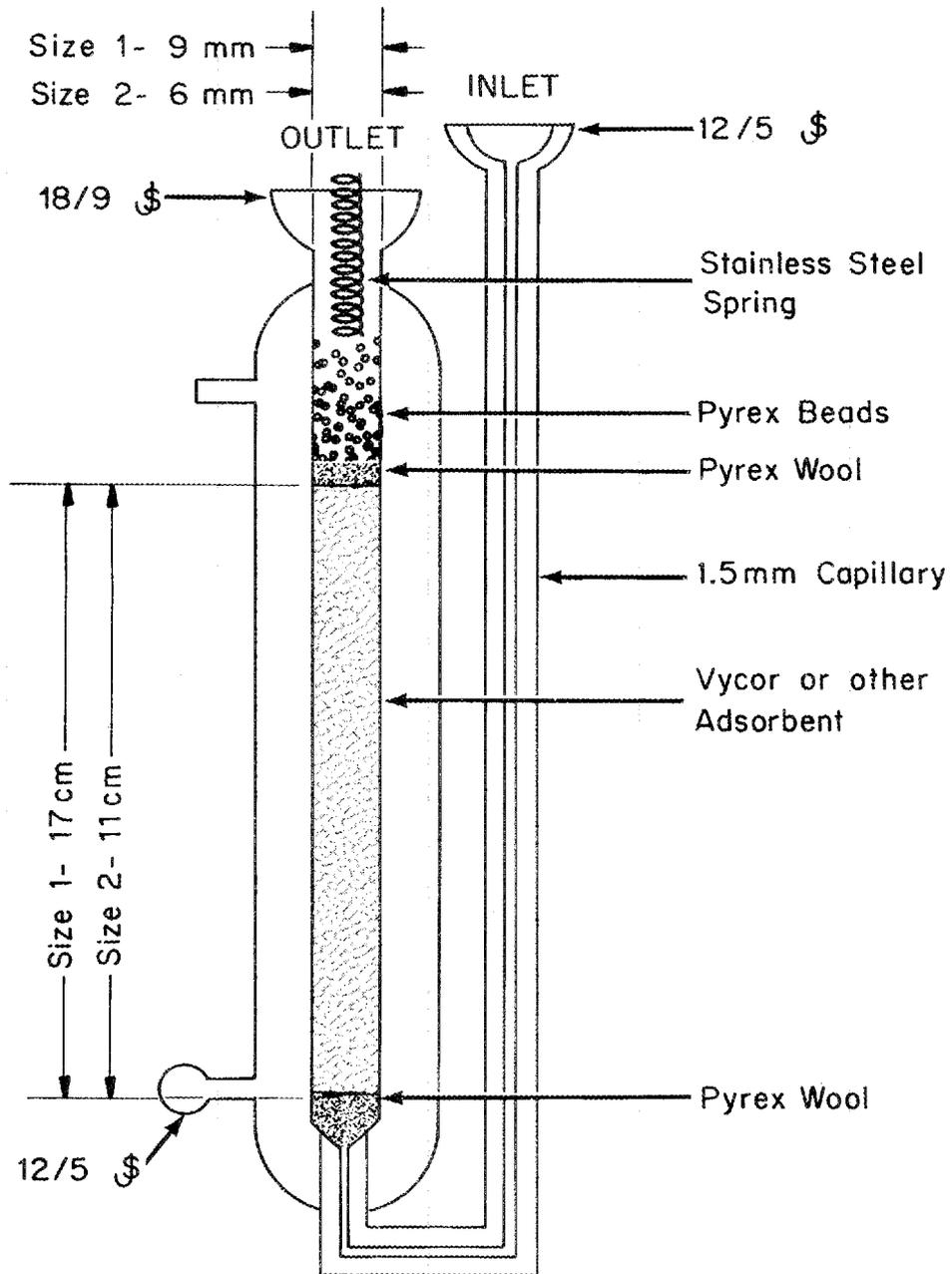


Fig. 9. Water-Cooled Columns for Protactinium Adsorption.

to minimize any effect of gassing and was provided with a water jacket for cooling. Standard 1- or 2-liter Pyrex vacuum flasks and polyethylene Büchner filter funnels containing 7.0-cm-diam No. 40 filter paper were used for feed clarification.

The feed solutions were displaced from a 1300-ml Pyrex and stainless steel vessel with Amsco 125-82, a hydrocarbon diluent, which was pumped into the cell with a Lapp model LS-20 Microflow Pulsafeeder pump. The wash and eluent solutions were displaced from a 150-ml Pyrex and stainless steel vessel by a similar pump.

The entire volume of column effluent was collected as 5- or 10-ml samples in 1/2-oz polyethylene bottles fitted with screw caps.

Analytical Procedures

Thorium was determined by EDTA titration of dilutions of the feed and effluent samples containing large amounts of ^{233}Pa ; uranium was determined fluorometrically from the same dilution. The oxalate product solutions were analyzed colorimetrically for thorium, and fluorometrically for uranium. After the ^{233}Pa had decayed to ^{233}U , the uranium from the batch elution tests was determined colorimetrically. Emission spectroscopic methods were used to analyze for zirconium. The ^{232}U : ^{233}U ratio was ascertained by alpha pulse analysis of uranium separated from the feed and product samples. Standard methods were used for the radiochemical analyses.

Experimental Details

The series of hot-cell tests demonstrating the adsorption, washing, and elution of ^{233}Pa from columns of 60- to 80-mesh or 100- or 120-mesh unfired Vycor, zirconium phosphate, and silica gel are summarized in Table 8, with more detailed descriptions of the individual runs given below.

Table 8. Summary of ²³³Pa Adsorption and Elution Experiments.

Run No.	Bed Wt.	Bed Material	Feed Flow (ml min ⁻¹ cm ⁻²)	Pa in Feed ^a (mg)	Pa Adsorbed ^b on Column		Pa in Column Raffinate ^b		Pa in Column Wash Solution ^b		Pa Eluted, Conc. Fract. ^c		Pa Eluted, Total		Decontamination Factors ^e		
					(mg)	(%)	(mg)	(%)	(mg)	(%)	(mg)	(%)	(mg)	(%)	²³² U	Zr-NbY	TRE β
A-1	4 g	60-80 Vycor	1.27	29.59	21.93	74.2	7.66	25.9	0.65	2.2	21.75	73.5	22.13	74.9	---	6.7	2 × 10 ³
A-2	4 g	60-80 Vycor	1.27	29.66	24.73	83.5	4.93	16.6	---	---	26.09	---	27.89	94.0	74	100	n.a.
B-1	4 g	100-120 Vycor	1.27	26.37	23.58	89.4	2.81	10.7	0.69	2.6	14.82	56.2	15.15	57.5	n.a. ^f	n.a.	n.a.
C-1	4 g	60-80 ZP-1	1.27	61.89	49.52	80.0	12.37	19.9	0.21	0.3	18.00	---	23.40 ^d	38.1	117	n.a.	n.a.
D-1	4 g	60-80 SiO ₂	1.27	31.65	26.69	84.4	4.96	15.7	1.38	4.4	25.04	79.2	25.19	79.6	48	2	2 × 10 ³
D-2	4 g	60-80 SiO ₂	1.27	31.54	25.15	79.7	6.39	20.5	1.81	5.7	20.56	---	20.79	65.9	---	5.8	>1 × 10 ⁴
E-1	7 g	100-120 Vycor	1.57	22.08	21.47	97.2	0.61	2.8	0.33	1.5	22.36	---	22.56	102.2	77	5.9	5 × 10 ⁴
E-2	7 g	100-120 Vycor	3.14	22.53	21.28	94.4	1.25	5.5	0.44	1.9	20.40	---	20.55	91.2	20	6.5	5 × 10 ⁴
F-1	7 g	60-80 Vycor	1.57	31.90	27.71	86.8	4.19	13.1	1.18	3.7	25.08	---	26.55	83.2	97	8.4	2 × 10 ⁴
F-2	7 g	60-80 Vycor	3.14	33.25	26.57	79.9	6.68	20.1	1.84	5.5	22.21	---	23.61	71.0	70	6.5	>6 × 10 ³

^aBased on average feed analyses and approximate volumes ±10%.

^bBased on effluent analyses and approximate volumes ±10%.

^cConcentrated fraction: First 20 ml of eluted product.

^dLeached ZP-1 sample lost -- no analysis possible.

^eConcentration in feed/concentration in product.

^fn.a. = no analysis.

50

Unfired Vycor Experiments

Run A (4 g of 60 to 80 mesh). This test was designed to determine the capacity of the Vycor adsorbent for ^{233}Pa and thus did not represent the best conditions for operation.

Decanted, but unfiltered, feed from dissolution 1 was pumped through a 4-g column at a rate of $1.27 \text{ ml cm}^{-2} \text{ min}^{-1}$. The Vycor turned black, bubbles of gas formed in the column, and the solution boiled at the bottom of the column. A flow of cooling water to the jacket relieved the situation, and the experiment was continued. Figure 10 shows the ^{233}Pa , $^{95}\text{Zr-Nb}$, and rare-earth concentrations in the column effluents during a loading-wash-elution cycle (A-1) followed by a second loading and wash cycle (A-2). The column was plugged by dense, black solids from the unfiltered feed during the second washing. Since the first-cycle oxalate-stripped products (containing 1.51 to 2.35 mg of ^{233}Pa per milliliter) gassed and/or boiled vigorously, they were diluted with an equal volume of oxalic acid.

Run B (4 g of 100 to 120 mesh). This run was designed to determine the capacity of smaller-sized Vycor. A mixture of 770 ml of decanted feed from dissolution 2 and 230 ml of feed from Run A was pumped at the rate of $1.27 \text{ ml cm}^{-2} \text{ min}^{-1}$ through a water-cooled column containing 100- to 120-mesh unfired Vycor. The column appeared to partially plug during the experiment, but it was possible to load the Vycor with 240 ml of feed, wash, and elute the column once (Fig. 11).

The ^{233}Pa product contained a white, fluffy precipitate, probably thorium oxalate resulting from poor washing.

Run E (7 g of 100 to 120 mesh). Runs E and F were designed to test the effects of flow rate on column loading. Filtered feed from dissolution 4 was loaded onto the Vycor at the rate of $1.57 \text{ ml cm}^{-2} \text{ min}^{-1}$; the column was washed and then eluted at the rate of $0.78 \text{ ml cm}^{-2} \text{ min}^{-1}$. A second loading cycle was accomplished, using a flow rate of $3.14 \text{ ml cm}^{-2} \text{ min}^{-1}$; it was followed by washing and elution at $0.78 \text{ ml cm}^{-2} \text{ min}^{-1}$. Figure 12 summarizes the run.

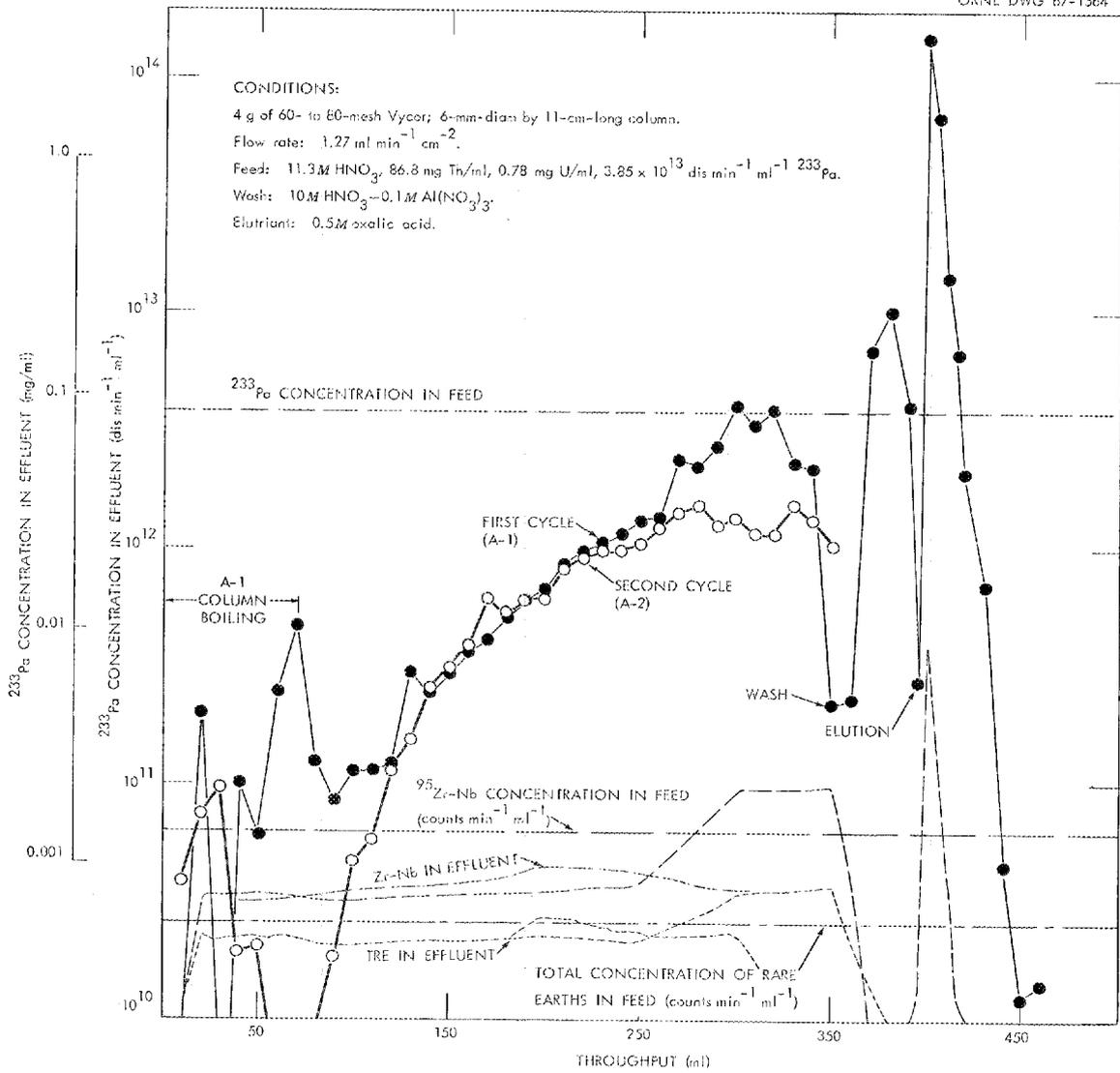


Fig. 10. Separation of ^{233}Pa on Unfired Vycor - Series A.

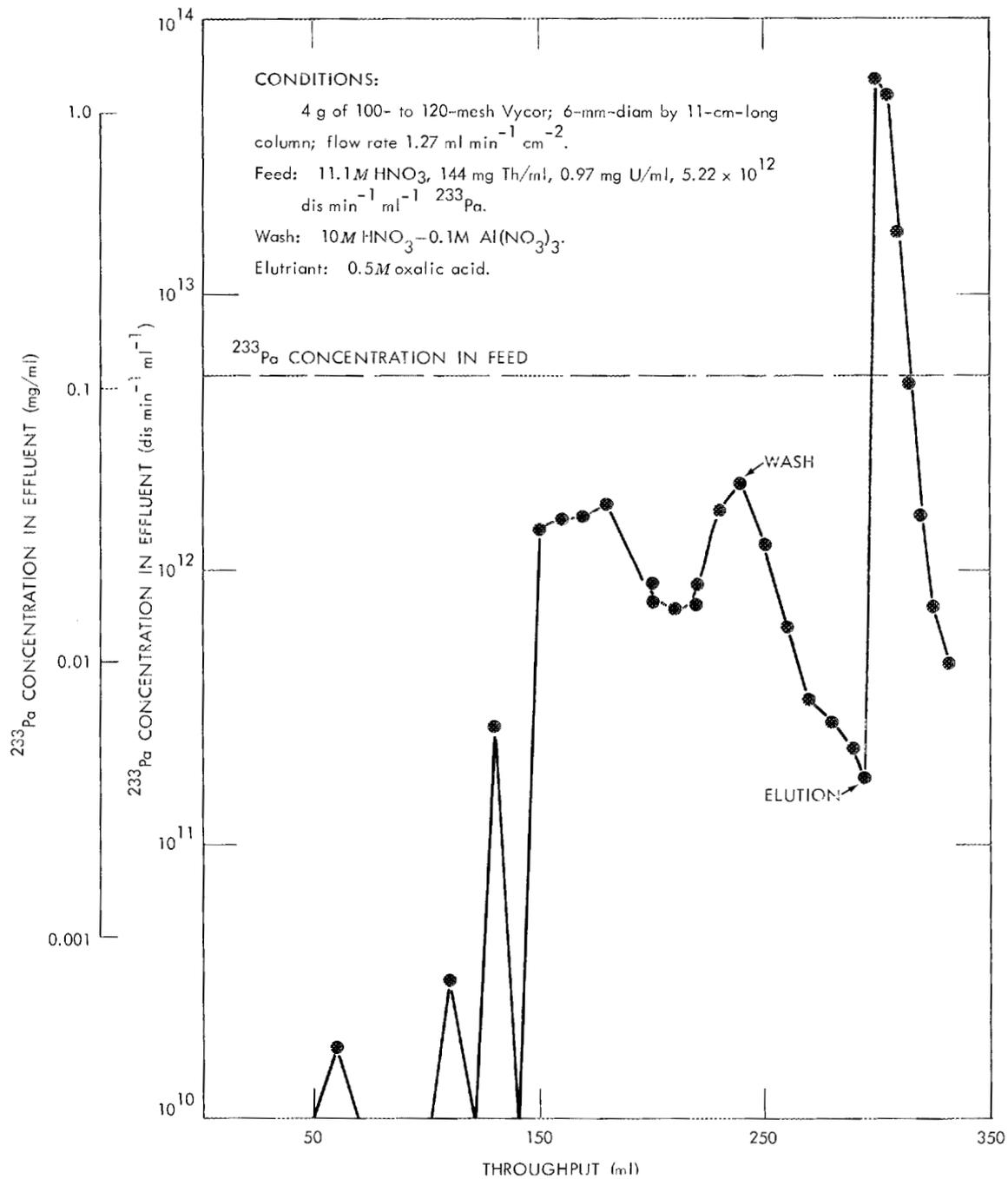


Fig. 11. Separation of ^{233}Pa on Unfired Vycor - Series B.

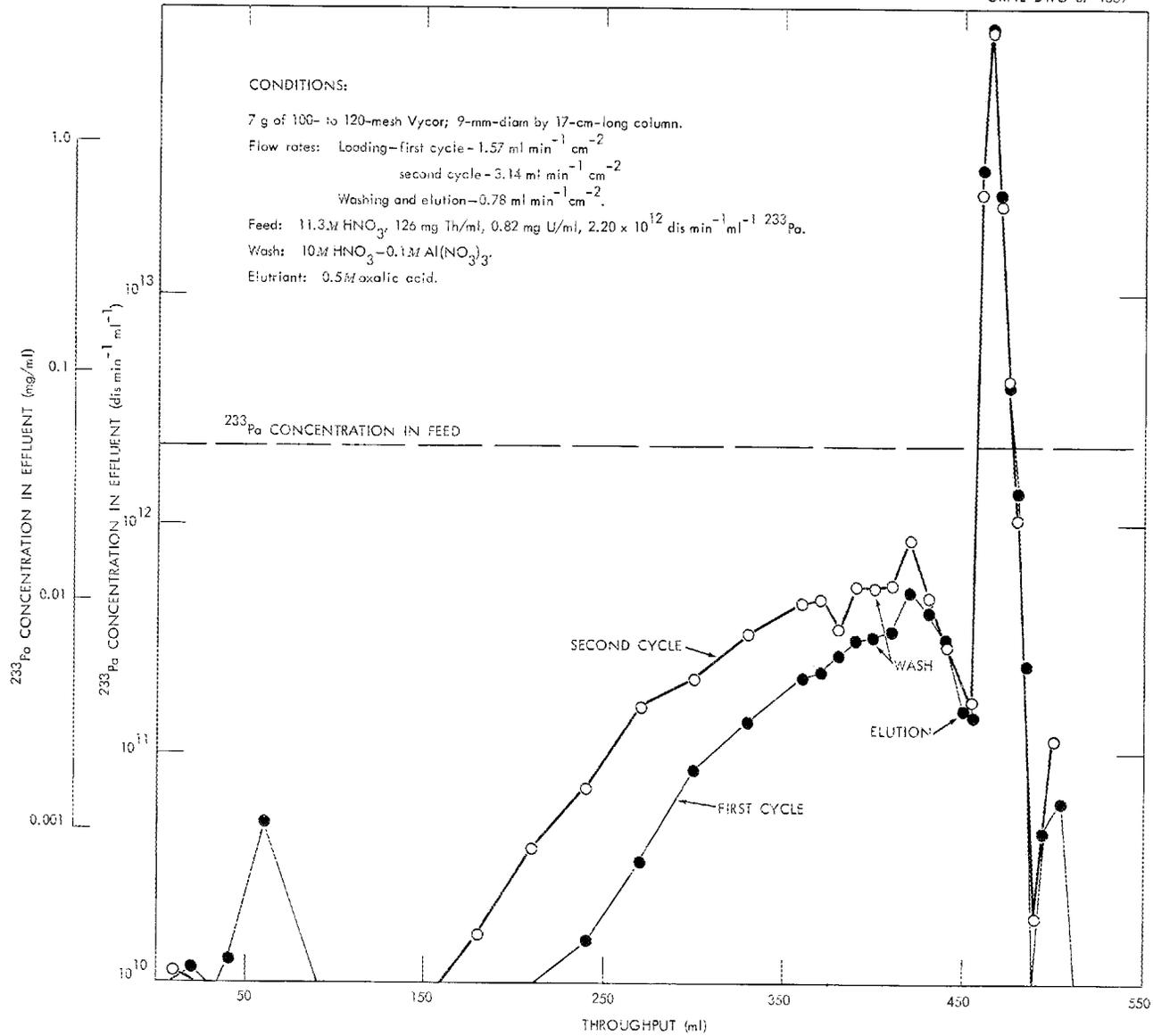


Fig. 12. Separation of ^{233}Pa by Adsorption on Unfired Vycor - Series E.

Run F (7 g of 60 to 80 mesh). The 9-mm-diam column was loaded with filtered feed from dissolution 5 at the rate of $1.57 \text{ ml cm}^{-2} \text{ min}^{-1}$, washed, and then eluted at $0.78 \text{ ml cm}^{-2} \text{ min}^{-1}$. A second cycle was loaded at $3.14 \text{ ml cm}^{-2} \text{ min}^{-1}$, washed, and eluted at $0.78 \text{ ml cm}^{-2} \text{ min}^{-1}$. (These products also contained a white precipitate.) Figure 13 summarizes the experiment.

Experiments with Other Adsorbents

Run D (4g of 60- to 80-mesh silica gel). A small column, filled with 4 g of 60- to 80-mesh silica gel, was loaded, washed, and eluted at the rate of $1.27 \text{ ml cm}^{-2} \text{ min}^{-1}$ for two cycles (Fig. 14), using filtered feed from dissolution 3. The silica gel in the column resembled fluffy clouds during passage of the feed and contained many gas bubbles, but there was apparently no channeling or other effect on operation as determined by flow-rate checks and radioactivity-level measurements of the column effluent.

Run C (4 g of 60- to 80-mesh zirconium phosphate). The maximum capacity of zirconium phosphate was to be determined by pumping feed from dissolution 2 through 4 g of water-cooled 60- to 80-mesh zirconium phosphate at $1.27 \text{ ml cm}^{-2} \text{ min}^{-1}$ until the effluent activity reached the level of the feed activity, that is, 100% breakthrough. After 550 ml had been passed, the effluent activity was still about one-half of that of the feed, a level reached when only about 100 ml of feed had been run (Fig. 15). The loading was then stopped, and the column was washed with 30 ml of 10 M HNO_3 -- $0.1 \text{ M Al(NO}_3)_3$ and stored in a crude calorimeter consisting of a 1.5-liter silvered-Pyrex Dewar flask, containing one liter of water, capped with an aluminum-foil-clad 1/2-in.-thick cork stopper. The estimated 50 mg of ^{233}Pa on the column heated the water and flask from 21 to 38°C during the first 48 hr of storage and maintained this temperature for 24 additional hours. These rough measurements indicated a liberation of 0.084 watt of energy (theoretical = 0.12 w) from the ^{233}Pa . Prior to introduction of the water, the ^{233}Pa on the column heated the air in the empty flask from 24.5 to 41°C over a 9-hr period.

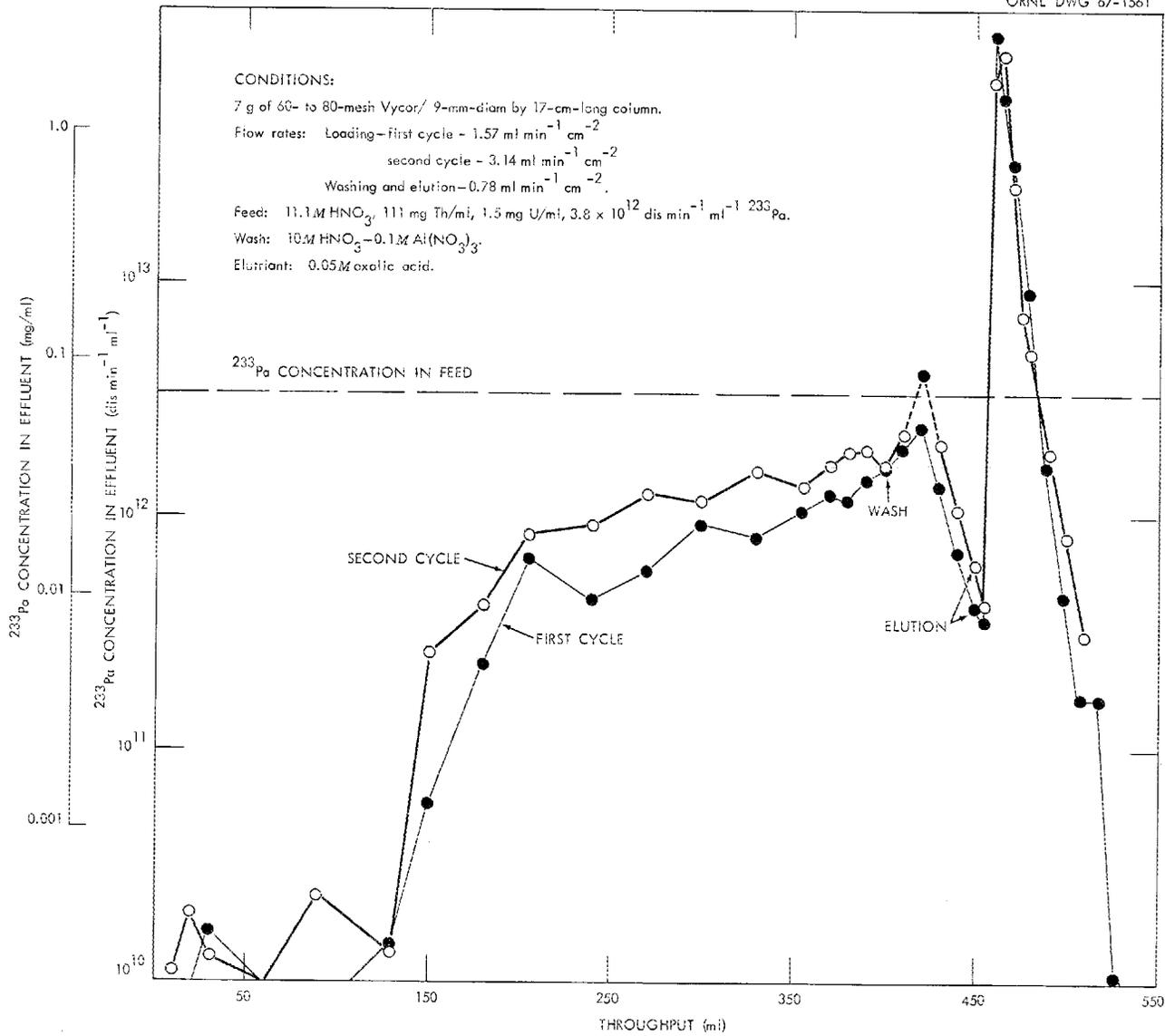


Fig. 13. Separation of ^{233}Pa by Adsorption on Unfired Vycor - Series F.

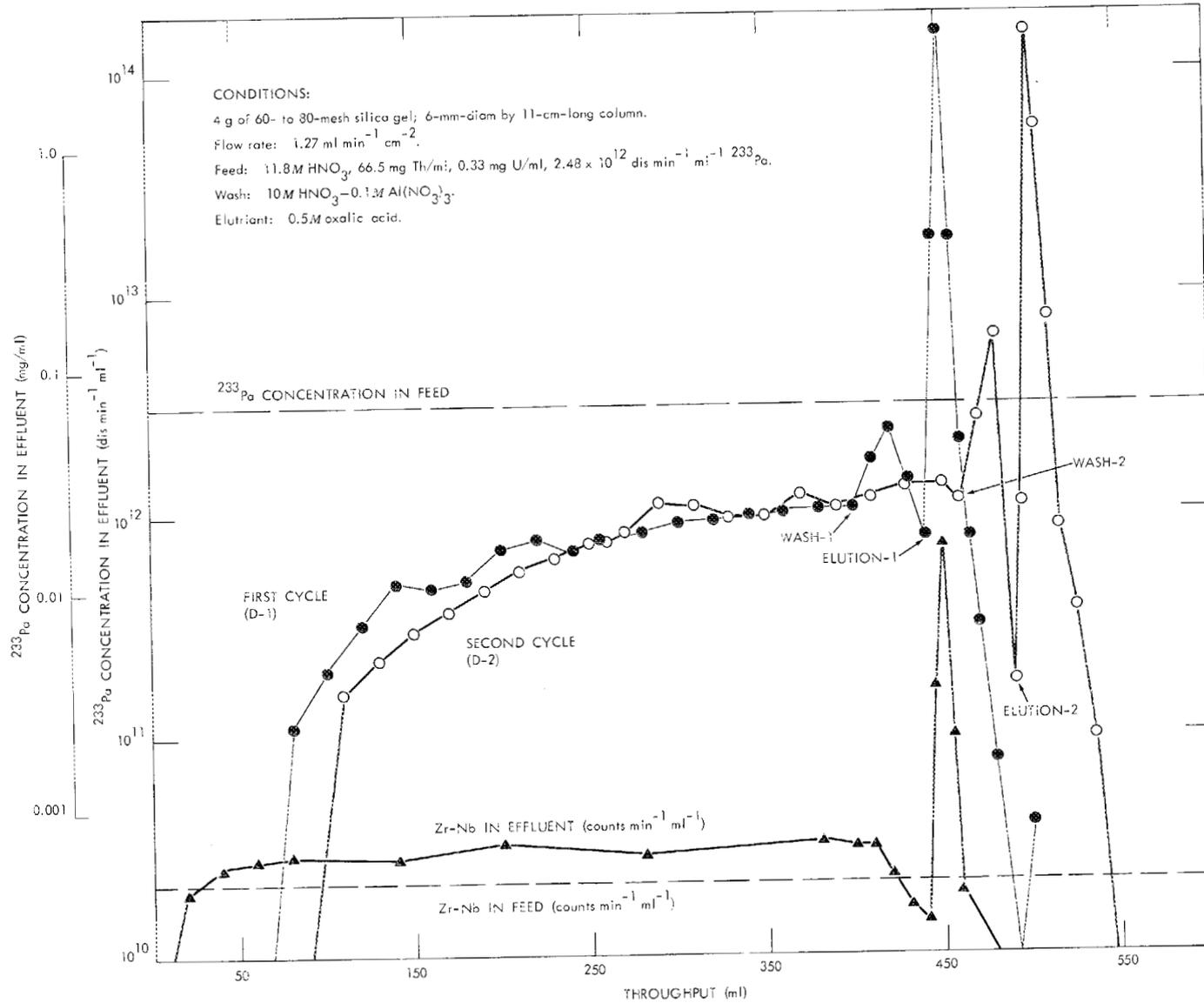


Fig. 14. Separation of ^{233}Pa on Silica Gel - Series D.

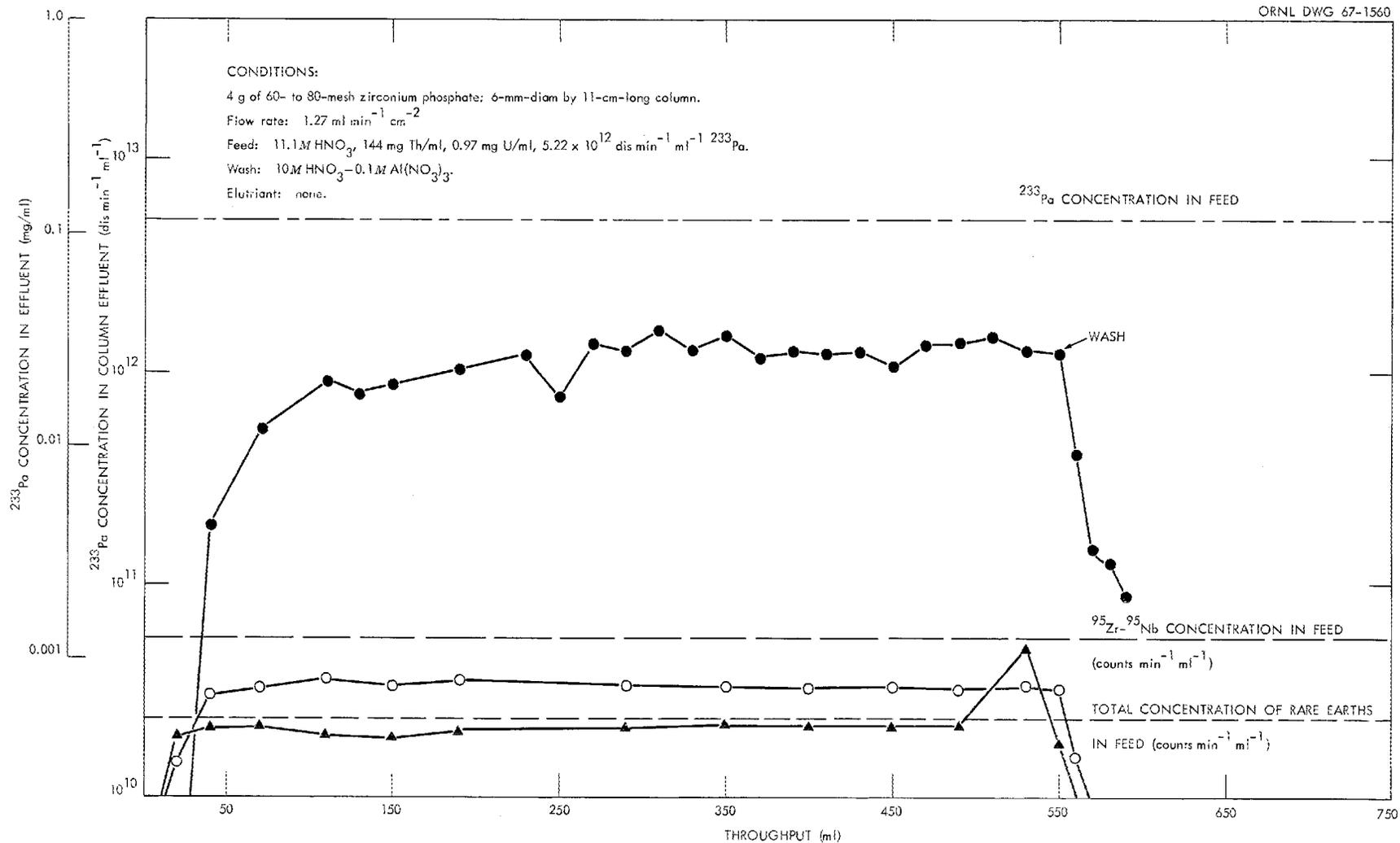


Fig. 15. Adsorption of ^{233}Pa on Zirconium Phosphate - Series C.



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