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

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Chemical Development Section B

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ABSTRACT

A process for recovering ^{233}Pa by adsorbing it on unfired Vycor glass was demonstrated using thorium-uranium fuel specimens that had been irradiated to 75,000 Mwd/metric ton in an average neutron flux of 2×10^{14} and allowed to decay 26 days. Over 99% of the fuel dissolved in refluxing 13 M HNO_3--0.05 M HF, leaving a residue containing less than 0.1% of the uranium and up to 20% of the protactinium. The protactinium losses could be minimized by cyclic dissolution in a process application.

About 99.6% of the protactinium was adsorbed from a solution, which contained 69 mg/ml Th, 1.80 mg/ml U, 30 mg/liter ^{233}Pa, 10.1 M HNO_3, 0.05 M HF, 0.1 M $Al(NO_3)_3$, and 1.7×10^{11} counts min^{-1} ml^{-1} gross gamma by passing the solution through a bed 0.9 cm in diameter and 17 cm long, containing 8 g of 60- to 80-mesh unfired Vycor glass. The flow rate was 1 ml/min. Less than 0.1% of the adsorbed protactinium was removed by washing the column with 10 M HNO_3--0.1 M $Al(NO_3)_3$. Ninety-two percent of the protactinium was recovered at a concentration equivalent to 5.5 times the protactinium concentration in the feed solution. The product had been decontaminated from zirconium-niobium, ruthenium, and total rare earths by factors of 9, 2.87×10^3 and 6.03×10^3, respectively.

Several gross inconsistencies were observed in results from protactinium analyses. These difficulties indicate that the analytical procedures for protactinium and the stability of solutions containing protactinium in the presence of macro concentrations of fission products need to be reinvestigated. Further hot-cell experiments will be necessary to determine the capacity of unfired Vycor and the maximum protactinium concentration factors obtainable with the process.

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1. INTRODUCTION

One of the major difficulties associated with the processing of thorium-uranium reactor fuels is due to the presence of ^{233}Pa. This 27.4-day precursor of ^{233}U accounts for a large fraction of the beta

and gamma radioactivity associated with short-decayed thorium. Generally, such fuels are allowed to decay at least 150 to 180 days before processing to allow most of the protactinium to decay to ^{233}U and to diminish the radioactivity to a level that can be accommodated by the processing facility. Significant improvements could be effected by separating the protactinium prior to processing the thorium and uranium. Not only would the decay period be shortened since a substantial fraction of the activity would have been removed, but the recovered protactinium would be a source of isotopically pure ^{233}U.

Previous papers[1,2] presented data that showed that protactinium is preferentially adsorbed by pulverized, unfired Vycor glass from nitric acid solutions. Laboratory data indicated that reactor fuel may be dissolved in 13 M HNO_3 that is about 0.04 M in F and up to 0.1 M in $Al(NO_3)_3$ and that the protactinium can be removed by passing the resulting solution through a column of unfired, powdered Vycor glass. The effluent is then adjusted so that the thorium and uranium may be recovered by the usual solvent extraction methods. The feasibility of the process was verified in laboratory tests with tracer quantities of ^{233}Pa and in glovebox experiments with ^{231}Pa in simulated process solutions. However, since the thorium-uranium fuels presently under consideration are to be irradiated to about 100,000 Mwd/metric ton of U-Th, it was necessary to determine the effectiveness of the Vycor adsorption process for recovering protactinium from solutions containing high concentrations of fission products and high specific radioactivity.

The feasibility of the process was verified in hot-cell experiments described in this report using thorium-uranium pellets that had been irradiated to about 75,000 Mwd/metric ton and allowed to decay only 26 days before processing. The effect of flowrate and feed composition on the effectiveness of the column were studied. Although inconsistencies were encountered in determining protactinium concentrations, analysis of the column effluent showed that up to 99.6% of the protactinium was adsorbed from process solutions containing as much as 50 mg of ^{233}Pa per liter. About 92% of the protactinium was recovered and decontaminated by factors greater than 1000 from all the major contaminants except zirconium-niobium.

The authors gratefully acknowledge the excellent and complete analytical support given by D. C. Canada, C. F. Goeking, and their associates in the Analytical Chemistry groups headed by C. E. Lamb and E. I. Wyatt, respectively.

2. REAGENTS, APPARATUS, AND ANALYTICAL PROCEDURES

2.1 Reagents

The feed solutions used in the hot-cell experiments were prepared from one irradiated fuel pin containing seven pellets of 5% urania-95% thoria. They had been irradiated to about 75,000 Mwd/metric ton at an average neutron flux of 2×10^{14} in the Engineering Test Reactor (ETR) by Phillips Petroleum Company of Idaho Falls, Idaho. The fuel pin (ORNL 43-42), containing 23.8 g Th and 1.1 g of 93.2% enriched uranium, was placed in the ETR June 27, 1960, and discharged during the shutdown at the end of cycle 65 on July 8, 1964.[3] Calculations indicated that, at discharge, the pin contained about 83 mg of ^{233}Pa, 100 curies of ^{131}I, and 1.3 g of fission products in addition to the residual thorium and uranium.[4] The pin was allowed to decay 26 days before processing to diminish the amount of iodine released when dissolving the pellets. The runs were started August 3 and completed August 6. To simplify the calculations, all protactinium analyses were corrected to August 3.

The unfired Vycor used in the adsorption columns was obtained from Corning Glass Works, Corning, New York, as a powder finer than 60 mesh. The material was screened, and aliquots of the 60- to 80-mesh fraction were used to prepare the adsorption columns.

2.2 Apparatus

The fuel specimens were dissolved in a 250-ml round-bottom flask (Fig. 1) heated to reflux temperatures with a heating mantle. The off-gas system for the dissolver consisted of a water-cooled updraft condenser followed by a de-entrainer and three iodine-removal traps. The first two traps were 8- by 2-1/8-in. beds containing about 175 g of silver-plated copper mesh and 250 g of activated charcoal, respectively. Finally, the

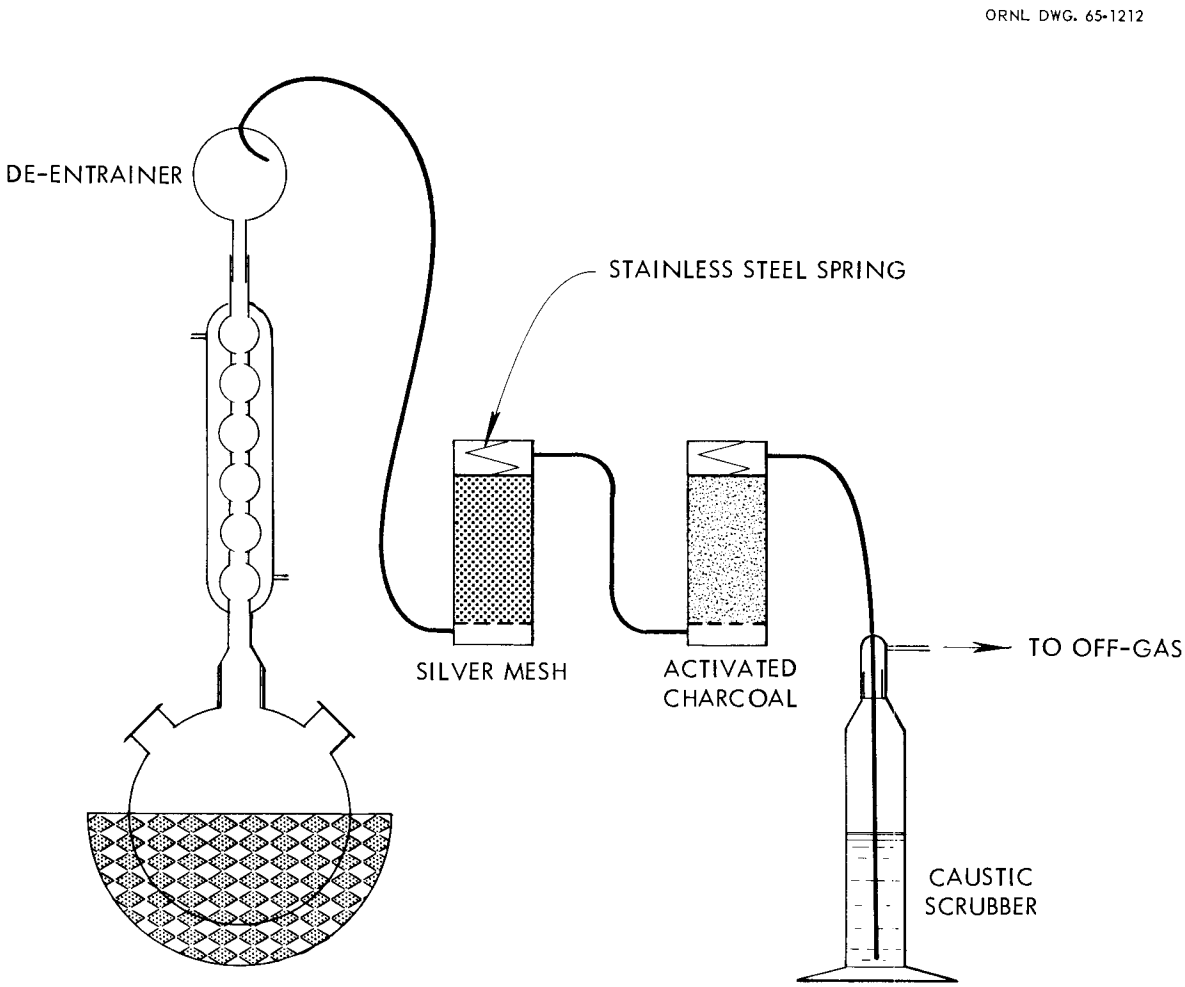

Fig. 1. Dissolver and Iodine-Removal System.

gas passed through a caustic scrubber containing 125 ml of 7 M NaOH before going to the cell's off-gas line.

The adsorption columns (Fig. 2) were about 0.9 cm in diameter and contained a 17-cm bed of 8 g (dry weight) of 60- to 80-mesh unfired Vycor held in place with Pyrex wool. In addition, 3-mm-diam Pyrex glass beads were placed on top of the bed and held in place with a stainless steel spring. The aqueous feed was forced to flow upwards through the column by displacing the feed from a 125-ml reservoir with Amsco 125-82. The flowrate was adjusted by controlling the pumping rate of the Amsco to the reservoir. Amsco was prevented from entering the adsorption line by maintaining an adequate aqueous level through the runs. Provisions were made so that additional feed, wash, and elution solutions could be added to the reservoir. A fresh Vycor column was attached to the feed reservoir for each experiment (Fig. 2).

2.3 Analytical Procedures

Two methods were used to determine the amount of protactinium in the solutions. Because of the high specific activity of the solutions, samples were diluted with 11 M HNO_3--0.05 M HF by factors of 100,000 to 200,000 before analysis. Dilutions were made in three or four steps using polyethylene containers and polyethylene pipettes. If the protactinium activity in the diluted solution represented 10 to 20% of the gross gamma activity, the disintegration rate of the ^{233}Pa was determined directly with a multichannel gamma-ray spectrometer. For samples containing a smaller percentage of protactinium activity, one of two extraction procedures was used to separate the protactinium prior to determining the disintegration rate. In the first procedure, the sample was made 7 N in HCl; two or three drops of saturated oxalic acid was added; and the protactinium was extracted into a 4:1 mixture of diisopropyl ketone and n-heptone. After the organic was washed with 7 N HCl, the protactinium was stripped from the organic phase with 1 N HCl--0.5 N HF. A gamma count was then made on this solution to determine the protactinium content.

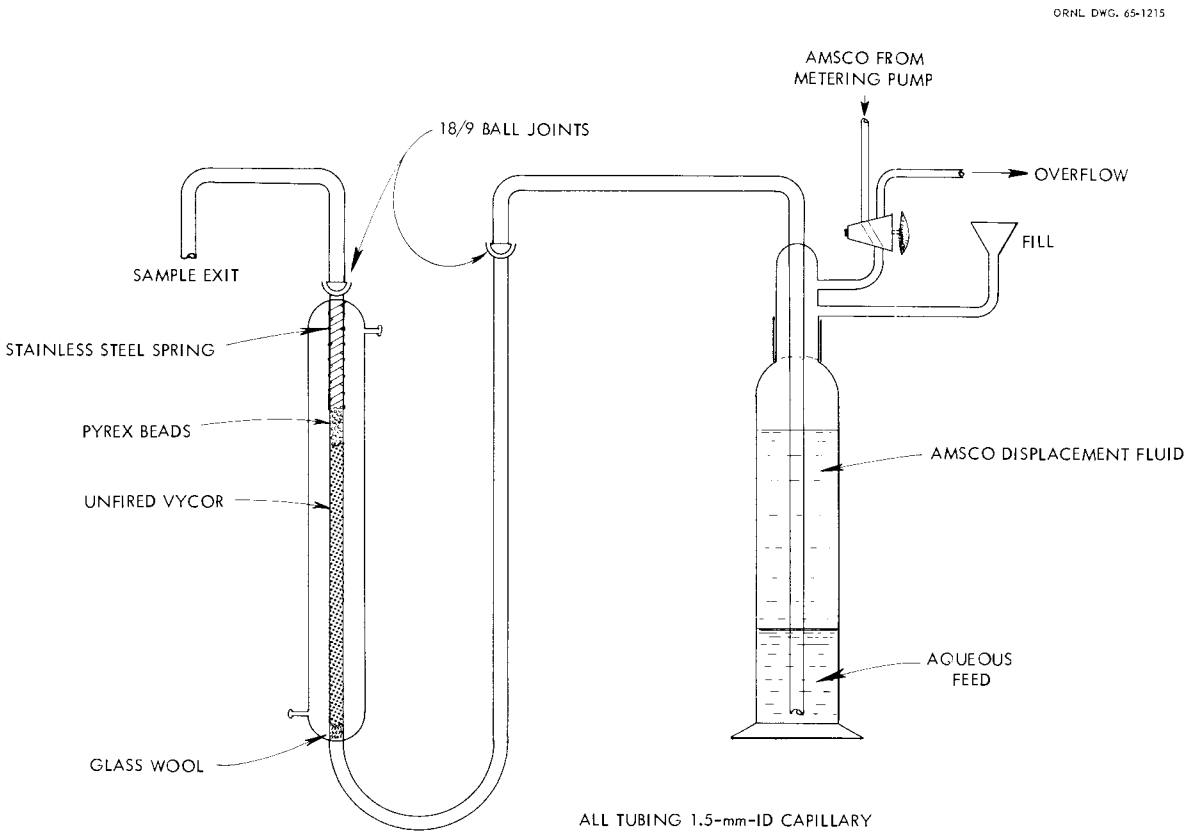

Fig. 2. Adsorption System.

In the second method, the protactinium was extracted by diisobutyl carbinol from 9 N H_2SO_4--6 N HCl that contained a few drops of 30% H_2O_2. The organic was washed with H_2SO_4-HCl, and the protactinium was then stripped from the organic with 6 M H_2SO_4--6 M HF. In both methods a small percentage of the gross niobium was extracted with the protactinium. For some of the solutions, such as the effluents, the niobium-to-protactinium ratio was so great that even this small amount of niobium which coextracted completely masked any protactinium radioactivity that might have been present.

3. DISSOLUTION OF FUEL PELLETS

The results obtained by dissolving the irradiated pellets in 13 M HNO_3--0.05 M HF indicate that cyclic dissolving will be necessary to minimize protactinium losses during large-scale processing. Three dissolutions were made by leaching the pellets from segmented sections of the fuel pin. The end plugs of the 4.5-in.-long pin were removed by sawing with an abrasive disk, then the remainder of the pin was cut with tubing cutters into segments containing two, two, and three pellets, respectively. There was no apparent dusting, and the pellets remained with the cladding until they were dissolved. The three dissolutions were refluxed 8, 8.5, and 20 hr with sufficient dissolvent to yield solutions containing 117, 103, and 69 mg/ml of Th, respectively. More than 99% of the pellets and 99.9% of the uranium and thorium dissolved in all three cases. However, up to about 20% of the protactinium remained with the residue (Table 1). Additional protactinium could be dissolved with fresh Thorex dissolvent. About 83% of the protactinium in the residue from run B was dissolved by refluxing for 24 hr with fresh Thorex dissolvent, showing that losses could be minimized by using a cyclic dissolving procedure. Such procedures have been examined with long-decayed thorium-uranium fuels and found feasible.[5]

The residue remaining after the pellets were dissolved was a black, highly radioactive solid. The 60-mg residue from the first run measured over 10,000 r/hr at a distance of 2 in. The residues were dissolved in

Table 1. Dissolution of Short-Decayed Thoria-Urania in Refluxing 13 M HNO_3--0.05 M HF

Run	Time (hr)	Total Wt (g)					
		Pellets + Cladding	Cladding	ThO_2-UO_2 in Sol'n.	Residue		
					Solid	Pa	U
A	8	11.5	3.3	7.92	0.0601	0.00091	0.0001
B	8.5	11.2	3.1	8.20	0.0479	0.00082[a]	---
C	20	16	4.4	11.30	0.0563	0.00059	0.00003

[a]0.68 mg obtained by digesting solid in fresh Thorex dissolvent prior to dissolving in 8 M HF--6 M HCl.

hot 8 M HF--6 M HCl for analysis. A gamma-ray spectrum showed the presence of protactinium, ruthenium, and zirconium-niobium. In addition, a spectrographic analysis showed strong lines for Th, Si, Ti, and Mo.

A protactinium material balance for the three runs indicated that either the solutions were not stable or that present protactinium analytical procedures are inadequate for such highly radioactive solutions. A more complete discussion of these possibilities will be found in Section 5. The total amount of protactinium found was only 30 to 40% of the 43 mg calculated to be present in the seven pellets at the time of the experiments, according to irradiation history and burnup data.[4] A review of reactor operations revealed nothing that would account for this discrepancy.[3] Two analytical values were available for the total protactinium in the system: a composite value obtained by totaling the amount of protactinium in the effluents, washes, eluates, and glass after the adsorption runs, and the protactinium value obtained by direct analysis of the feed solution. The composite values were in agreement with the pellet solution in the last run only. In the first two experiments, the composite accounted for only 60% of the protactinium value obtained by analysis of the feed. Unfortunately, there was not sufficient sample to allow analytical rechecks on the feeds after this discrepancy was discovered. An additional 0.3 mg of protactinium was found by washing the empty cladding and all the equipment used in the dissolution, including

condenser, de-entrainer, lines, and traps with hot HCl-HF solution. This brought the total amount of protactinium to 13.2 and 17.3 mg for the composite and feed analytical values, respectively. The composite values were used in all calculations and were considered to be the more reasonable values since the amounts of protactinium per pellet calculated with these numbers were in better agreement and because these analyses, in the presence of lower amounts of other radioactivity, are probably more accurate (Table 2).

4. ADSORPTION AND ELUTION OF PROTACTINIUM

According to effluent analyses, more than 99.4% of the protactinium was adsorbed on the unfired Vycor in each run. Washing the columns with 10 M HNO_3--0.1 M $Al(NO_3)_3$ removed about 0.1% or less of the adsorbed protactinium. More than 95% was eluted with 0.5 M oxalic acid, leaving less than 5% on the Vycor. In each of the adsorption runs, the aqueous feed was about 10 M in HNO_3 and 0.05 M in HF. The first two runs were made at flow rates of 0.3 ml/min and about 1 ml/min, respectively, with no aluminum present in the feed to complex the fluoride. The third run was also made at 1 ml/min, and the feed was 0.1 M in $Al(NO_3)_3$. More than 99% of the protactinium was adsorbed in each experiment (Table 3).

Figure 3 shows the behavior of protactinium and zirconium-niobium in the first run. The feed solution containing 117 mg/ml Th, 2.92 mg/ml U, 0.050 mg/ml ^{233}Pa, 10.3 M HNO_3, 0.05 M HF, and 3.94×10^{11} counts min^{-1} ml^{-1} gross gamma was passed through the column at 0.27 ml/min. The column was loaded to 0.5 mg of ^{233}Pa per gram of glass and adsorbed 99.8% of the protactinium. Although over 95% of the protactinium was stripped from the column with 0.5 M oxalic acid, it was at an average concentration of only about 70% of that of the feed. This poor elution may have happened because a small amount of Amsco accidentally was allowed to go through the column during the latter part of the adsorption run. About 30% of the zirconium-niobium was adsorbed from the feed during the adsorption cycle, but 61% of this was removed during the wash, leaving only 12% of the total zirconium-niobium activity on the column (Fig. 3).

Table 2. Protactinium Material Balance

Run	^{233}Pa (mg)							
				Total			Mg/Pellet	
	By Analysis	Composite[a]	Residue	By Analysis	Composite	Calculated	By Analysis	Composite
A	4.82[b]	3.03	0.91	5.73	3.94	12.3	2.86	1.97
B	5.26	3.09	0.82	6.08	3.91	12.3	3.04	1.96
C	4.60	4.44	0.59	5.19	5.03	18.4	1.73	1.68
A+B+C	14.68	10.56	2.32	17.00[c]	12.88[c]	43.0		

[a]This value was determined after the adsorption runs and consists of the total amount of protactinium in the effluents, washes, strips, and that remaining on the unfired Vycor.

[b]Average of values for two samples of same feed; values were 4.23 and 5.41 mg ^{233}Pa.

[c]An additional 0.3 mg of protactinium was found by washing the equipment and cladding after all runs were completed making the analysis and composite totals 17.3 mg and 13.2 mg, respectively.

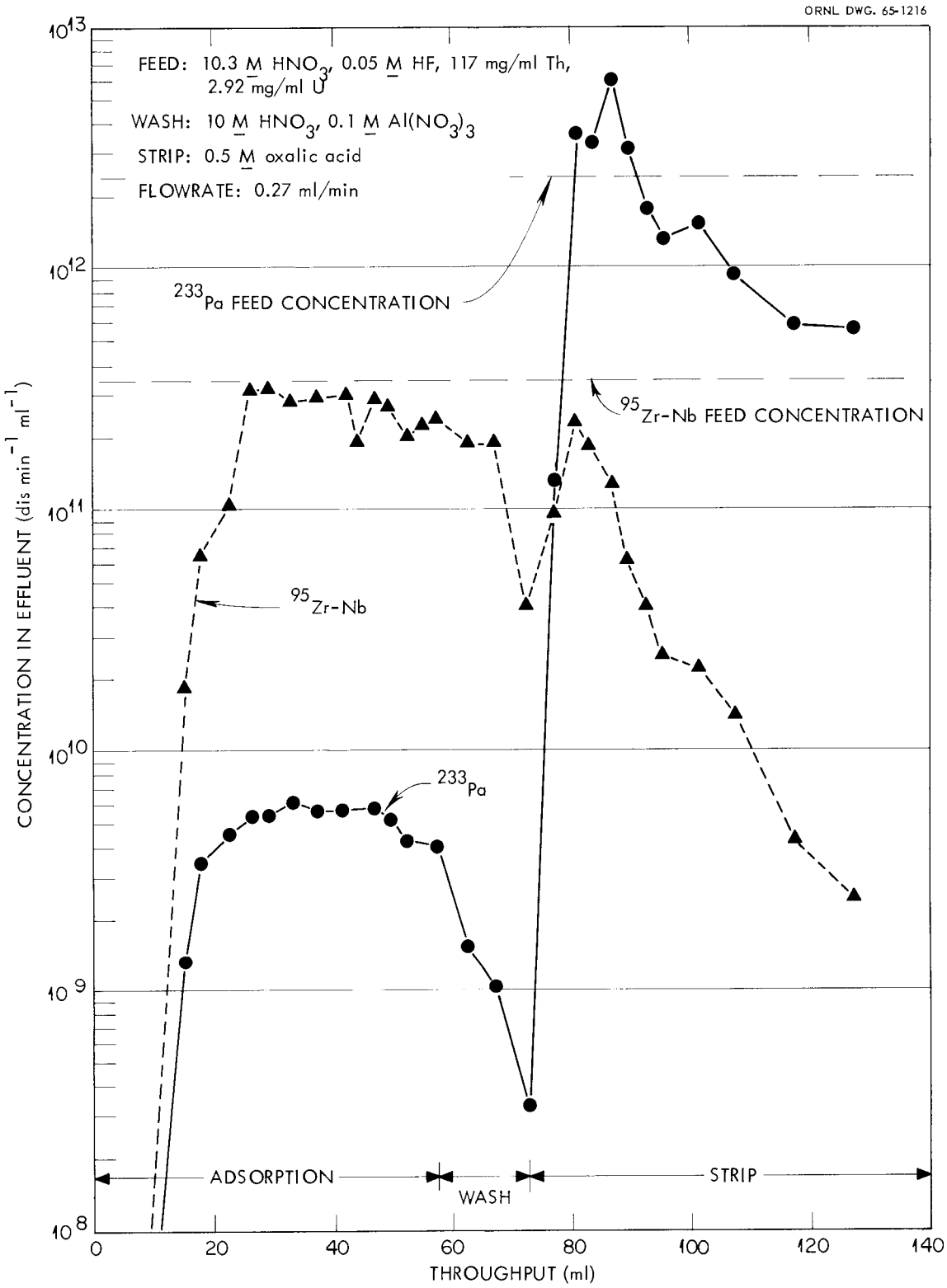

Fig. 3. Concentration of ^{233}Pa and ^{95}Zr-Nb in Column Effluents of Run A.

Table 3. Adsorption and Elution of Protactinium

Run	A	B	C
Feed solution			
HNO_3, M	10.3	10.3	10.1
HF, M	0.05	0.05	0.05
$Al(NO_3)_3$, M	0	0	0.1
Th, mg/ml	117	103	69
U, mg/ml	2.92	2.50	1.80
Pa, mg/ml	0.052	0.046	0.032
Avg. flow rate, ml/min	0.27	0.89	0.97
Protactinium, %			
Adsorbed	99.8	99.4	99.6
Washed	0.01	0.09	0.10
Stripped	95.3	99.05	97.7
Left on column	4.69	0.86	2.2

The results from the second run showed that increasing the flow rate from 0.3 to 0.9 ml/min produced very little change in protactinium adsorption. In this experiment, the feed contained 103 mg/ml Th, 2.50 mg/ml U, 0.046 mg/ml Pa, 10.3 M HNO_3, 0.05 M HF, and 3×10^{11} counts min^{-1} ml^{-1} of gross gamma. Two changes were made from the first experiment: the flowrate was increased to 0.9 ml/min and the oxalate strip solution was allowed to contact the column 30 min at the beginning of the elution cycle. The column was loaded to 0.6 mg ^{233}Pa per gram of glass, and 99.4% of the protactinium was adsorbed. About 99% of the protactinium was eluted from the column — 80% at a concentration equivalent to three times the protactinium concentration in the feed. As in the first run, about 30% of the zirconium-niobium was adsorbed during the adsorption cycle, but 67% was removed in washing, leaving only 10% in the total eluate. There was some indication that much of the zirconium-niobium which remained was eluted during the first stages of the elution cycle (Fig. 4).

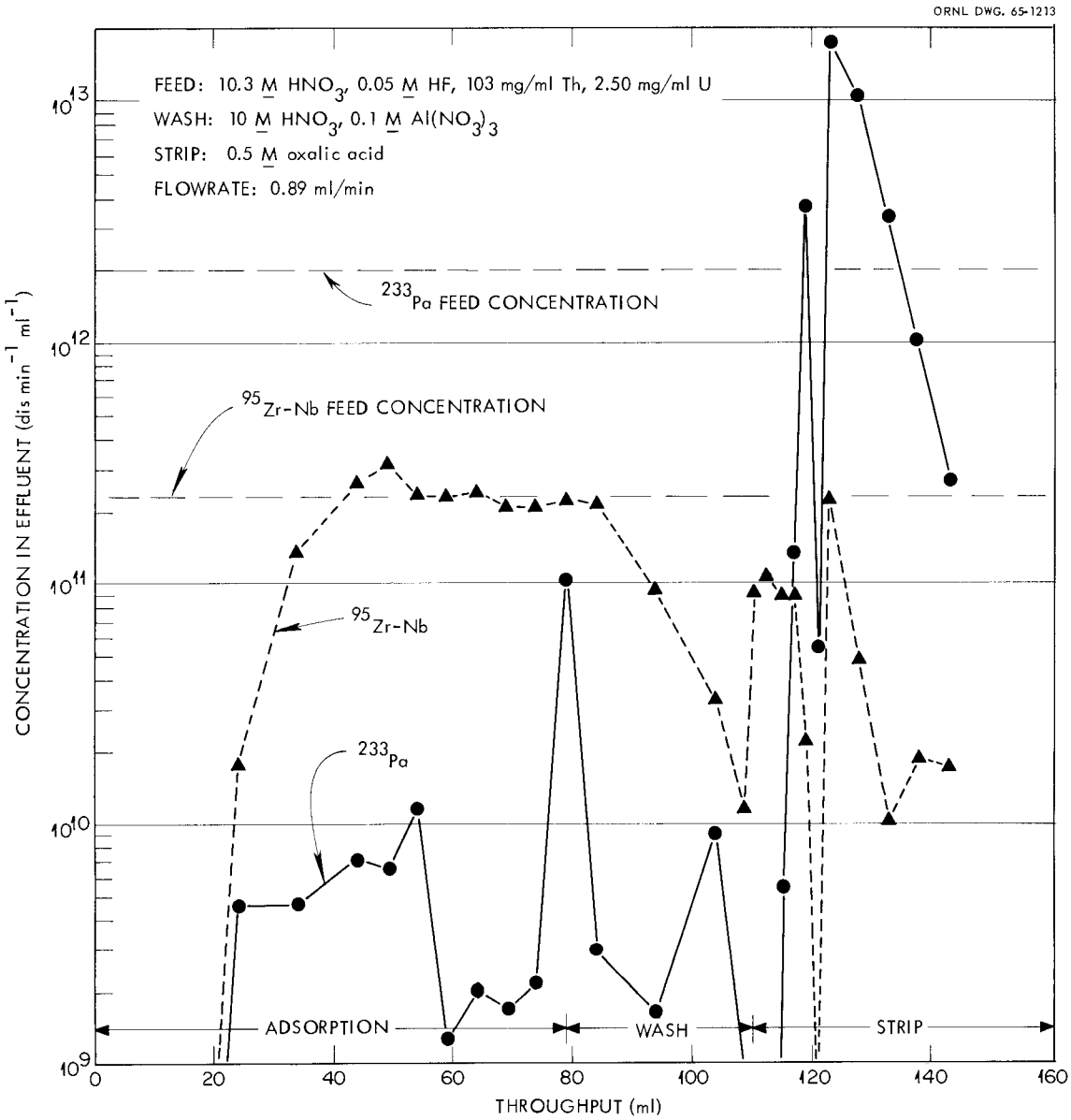

Fig. 4. Concentration of ^{233}Pa and ^{95}Zr-Nb in Column Effluents of Run B.

Figure 5 shows the results of the third and most successful run. As previously mentioned, the material balance in this experiment was excellent. The composite value was within 4% of the feed value for the total protactinium content of the system. The flowrate was the same as for the previous run, about 1 ml/min, but the feed was more dilute and contained sufficient aluminum to complex the fluoride in the feed. This feed contained 69 mg/ml Th, 1.80 mg/ml U, 0.032 mg/ml Pa, 10.1 M HNO_3, 0.05 M HF, 0.1 M $Al(NO_3)_3$, and 1.7×10^{11} counts min^{-1} ml^{-1} gross gamma. According to analytical values of the effluent, 99.6% of the protactinium was adsorbed on the column, about 0.1% of which was removed during the wash cycle. Eluting the column with 0.5 M oxalic acid removed 97.7% of the protactinium. About 92% of this was at a concentration equal to 5.5 times the concentration of the protactinium in the feed. This concentration factor is lower then the values obtained with ^{231}Pa in glove-box experiments,[1] but this was probably due to the low loading in the hot-cell runs. The column was designed on the assumption that sufficient protactinium would be present for loadings of 1.5 to 2 mg of ^{233}Pa per gram of glass, rather than the 0.5 mg actually obtained. Thus, none of the runs gave the desired information on optimum loading and stripping.

Nearly 92% of the protactinium was recovered in this run, with decontamination factors of 9, 6.03×10^3, and 2.87×10^3 from zirconium-niobium, total rare earth beta, and ruthenium, respectively. An additional 5% was recovered by allowing the 0.5 M oxalate solution to remain on the column overnight. A single analysis of this solution indicated that it contained about 100 times more ruthenium than previous aliquots. Unfortunately it was impossible to run a repeat analysis so the value may or may not be real. The high beta and gamma radioactivity, plus the small sample volume, made it difficult to obtain meaningful uranium and thorium analyses. An alpha pulse analysis of the more concentrated protactinium eluate from this run (Fig. 5) showed the presence of only ^{233}U and its daughters. Previous tracer studies had shown decontamination factors of 6×10^3 from thorium, and 1.6×10^4 from uranium.[1]

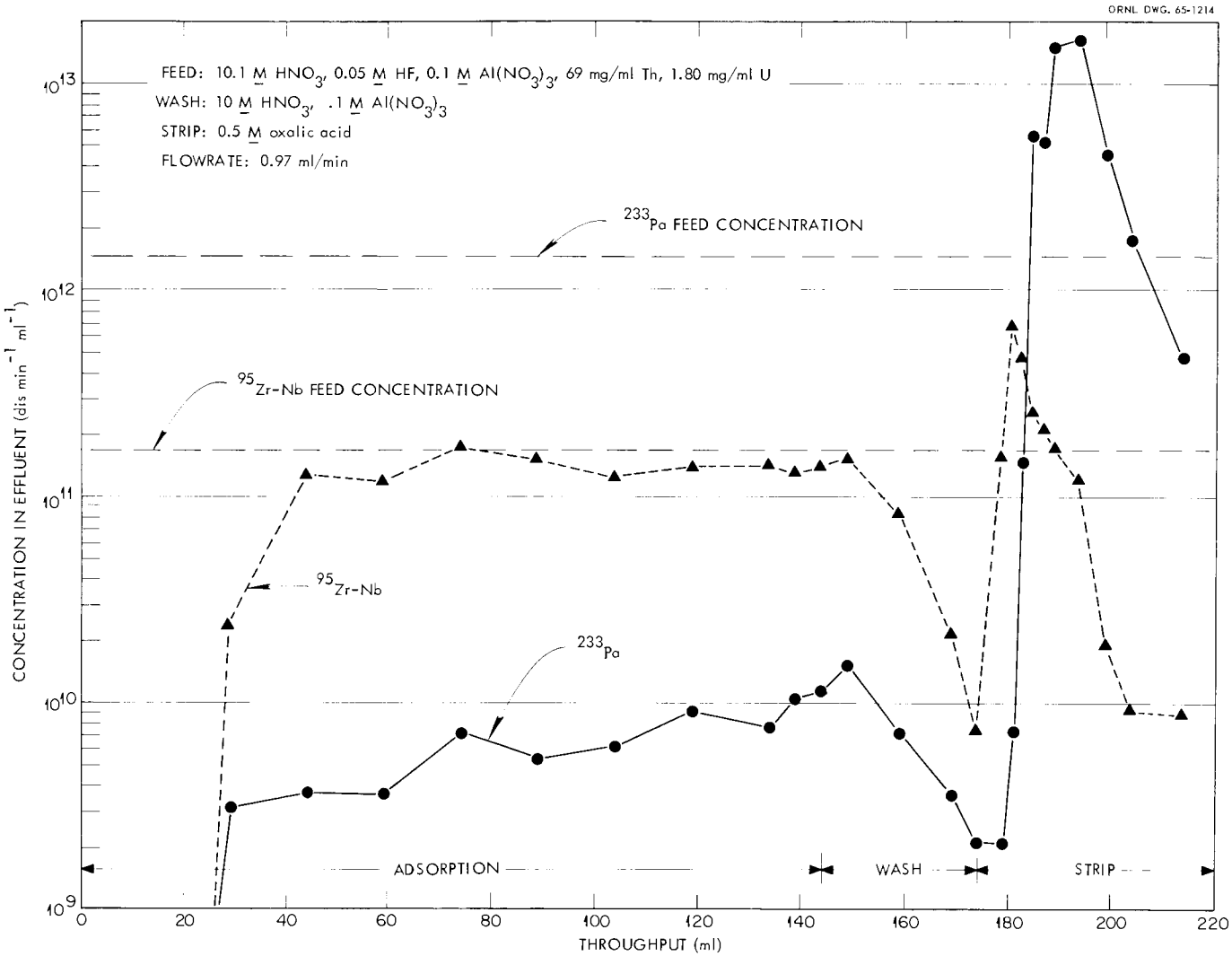

Fig. 5. Concentration of ^{233}Pa and ^{95}Zr-Nb in Column Effluents of Run C.

One of the major questions answered in these initial hot cell studies concerned the effect of large amounts of zirconium-niobium on the behavior of protactinium. In all three runs, about 30% of the zirconium-niobium adsorbed during the adsorption cycle. After the columns were washed, about 10 to 20% of the total zirconium niobium remained on the column. In the third run, 20% of the zirconium-niobium remained on the column, but the majority of this was removed by the first of the eluate before any significant amount of the adsorbed protactinium. Thus 97% of the protactinium was decontaminated from zirconium-niobium by a factor of 8 (Fig. 5).

5. DISCREPANCIES IN ANALYTICAL RESULTS FOR PROTACTINIUM

During the course of these experiments, several discrepancies arose in connection with the determination of the amount of protactinium present in a given system. As pointed out in Sec 3, only about 30 to 40% of the protactinium calculated to be present in the pellets was found by analysis. In addition, the analytical material balance for the first two runs was very poor. Further irregularities appeared when several of the solutions were reanalyzed about three weeks and one month after the runs had been completed. A comparison of the protactinium values from the three different analyses, corrected back to August 3, showed protactinium differences ranging from a few percent to several hundred percent (Table 4). Although previous experience with nitric acid solutions containing up to 100 mg/ml ^{231}Pa had indicated they were quite stable,[1] these analytical differences observed in the hot-cell samples suggest that some change may be occurring in the solution, resulting in either a removal of protactinium from the solutions or interference with the analysis. These irregularities do not decrease our confidence in the general results of the Vycor adsorption tests.

Similar irregular behavior was observed when a single eluate sample and a mixed effluent sample was analyzed for protactinium seven weeks after the runs were completed. The protactinium analysis of the effluent sample, which consisted of a mixture of the effluents and washes from the first experiment, did not show the presence of any protactinium, although

Table 4. Protactinium Analytical Values
All ^{233}Pa calculated back to August 3, 1964
Column 1 - analyses made 1 to 7 days after experiment
Column 2 - analyses made 21 to 22 days after experiment
Column 3 - analyses made 30 days after experiment

Run	Sample No.	1	2	3
A	5 Effluent	5.54×10^{9}	4.33×10^{9}	3.24×10^{9}
B	6 Effluent	1.15×10^{10}	$\leq 5.32 \times 10^{8}$	1.40×10^{9}
C	6 Effluent	5.32×10^{9}	---	6.40×10^{9}
C	9 Effluent	7.62×10^{9}	9.77×10^{9}	8.57×10^{9}
A	4 Wash	1.38×10^{11}	1.35×10^{11}	1.22×10^{11}
B	3 Wash	8.16×10^{9}	$\leq 2.1 \times 10^{8}$	3.50×10^{8}
C	3 Wash	3.64×10^{9}	3.32×10^{8}	3.11×10^{9}
A	3 Strip	5.57×10^{12}	5.09×10^{12}	5.54×10^{12}
B	6 Strip	1.10×10^{13}	4.73×10^{12}	5.44×10^{12}
C	6 Strip	1.53×10^{13}	1.00×10^{13}	8.46×10^{12}

original analyses indicated the solution should have contained about 1×10^{8} counts min^{-1} ml^{-1} of ^{233}Pa in 1×10^{11} counts min^{-1} ml^{-1} of gross gamma emitters, most of which was zirconium-niobium. The eluate analysis was made by removing the residual solution from its original polyethylene bottle and making the eluate 1 M in HF. The original polyethylene bottle was filled with a rinse solution of 11 M HNO_3--1 M HF. After 48 hr, the protactinium content of each solution was determined by gamma spectrometry. The two solutions contained a total of 17% more protactinium than the original analysis indicated, with 90% of the ^{233}Pa in the rinse solution. Similar experiments made with effluent and wash samples showed no such evidence of plating out. However, since the protactinium content of these solutions represented only 0.01 to 0.1% of the gross gamma activity, they may not have been amenable to the analytical procedures (Cf. Sec 2.3).

6. CONCLUSIONS AND RECOMMENDATIONS

These initial hot-cell experiments show the feasibility of recovering protactinium from short-decayed, highly irradiated thorium-uranium fuel by adsorbing protactinium on unfired Vycor glass. Although there were many irregularities in the protactinium analyses, the results were consistent in the three runs and were in excellent agreement with previous work using ^{233}Pa tracer solutions and simulated dissolver solutions containing ^{231}Pa. It is recommended that analytical procedures for protactinium be established and confirmed for solutions similar to the ones which would be encountered in processing highly irradiated, short-decayed thorium uranium fuels. Further, the stability of these solutions should be investigated. Additional hot-cell experiments are planned to determine the capacity of unfired Vycor for protactinium, the maximum concentration factor obtainable with oxalate elution, and the effect of aluminum in 13 M HNO_3--0.05 M HF on the dissolving of thorium-uranium fuels containing protactinium.

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