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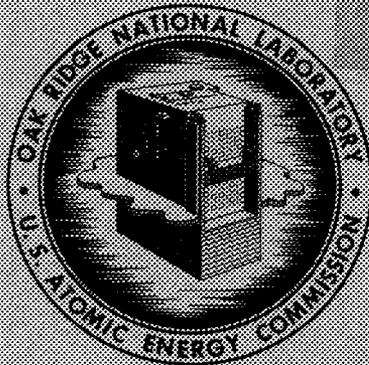
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THE EFFECT OF NITRIC ACID, THORIUM,  
FLUORIDE, AND ALUMINUM ON  
PROTACTINIUM ADSORPTION BY  
UNFIRED VYCOR GLASS

J. G. Moore

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CHEMICAL TECHNOLOGY DIVISION

Chemical Development Section B

THE EFFECT OF NITRIC ACID, THORIUM, FLUORIDE, AND ALUMINUM ON  
PROTACTINIUM ADSORPTION BY UNFIRED VYCOR GLASS

By

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APRIL 1964

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ABSTRACT

The amount of adsorbable protactinium and its distribution coefficient (DC = counts min<sup>-1</sup> g of glass<sup>-1</sup>/counts min<sup>-1</sup> ml<sup>-1</sup> solution) with 60-80 mesh unfired Vycor glass has been determined for Pa<sup>233</sup> tracer solutions containing 4 to 100 g Th/liter, 0.5 to 12 M HNO<sub>3</sub>, 0 to 0.04 M HF, and 0 to 0.4 M Al(NO<sub>3</sub>)<sub>3</sub>. The distribution coefficient (DC) from solutions containing only thorium and nitric acid may be calculated as follows:

$$DC = (378 \pm 72) + (384 \pm 9)x - (1.27 \pm 0.13)xy - (1.13 \pm 1.02)y,$$

where

$$\begin{aligned} x &= \text{M HNO}_3, \\ y &= \text{g Th/liter.} \end{aligned}$$

In solutions containing 100 g Th/liter, the coefficient increased slightly with increasing fluoride when the solution was less than about 3.5 M HNO<sub>3</sub>. At higher nitric acid concentrations, the coefficient decreased with increasing fluoride. The addition of aluminum partially cancelled the effects of fluoride, but the maximum was still only half that of thorium-nitric solution containing no fluoride or aluminum. For example, the coefficient was 3000 for 10 M HNO<sub>3</sub>, 100 g Th/liter, 300 with 0.04 M HF present, and 1500 with 0.04 M HF, 0.4 M Al present. The amount of unadsorbable protactinium depended only on the nitric acid concentration, ranging from a maximum value of about 7% in 0.5 M HNO<sub>3</sub> to less than 2% in solutions containing more than 3 M HNO<sub>3</sub>. Hot-cell experiments are recommended to test the application of this principle for adsorption of protactinium from short-cooled high-burnup thorium.

## 1. INTRODUCTION

Current interest in thorium-breeder reactors in which the fuel is to be irradiated to as much as 100,000 Mwd/metric ton requires that methods for recovering the fissile material from thorium fuels be re-examined. The protactinium-233 and macro quantities of fission products formed in this long-irradiated thorium will produce such a high level of radioactivity that present solvent extraction or organic ion exchange recovery methods will probably not be suitable for fuel processing until the fuel has decayed at least 180 days. This long decay period increases process costs due to charges for inventory and storage. These costs could be reduced by recovering the protactinium from the fuel after a shorter cooling period. By this means, potentially fissionable material would be recovered and a substantial fraction of the activity from the fuel solution removed, thus simplifying the recovery of the remaining thorium and uranium by present methods.

A previous paper presented laboratory results which showed that unfired Vycor glass powder preferentially adsorbs protactinium from nitrate solutions. At a loading of 5 mg of Pa<sup>231</sup> per gram of glass, 95% of the protactinium was removed from a simulated Consolidated Edison dissolver solution containing 0.5 M Th, 11 M HNO<sub>3</sub>, 0.04 M F, 0.1 M Al, and 0.05 g Pa<sup>231</sup>/liter. A portion of the protactinium, about 5%, was found to be unadsorbable by the unfired Vycor. However, when the Pa<sup>231</sup> on the glass was eluted and used to prepare similar feed solutions, the amount of unadsorbable protactinium in these solutions was essentially zero.<sup>1</sup> Thus solutions containing only adsorbable protactinium can be prepared. One of the problems that remained was to determine what other conditions, if any, would decrease the amount of protactinium which is not adsorbed on the glass.

Since the concentration of the major components in the feed solution may be fairly easily adjusted, an investigation was made of the effects of nitric acid, thorium, fluoride, and aluminum concentration on the amount of adsorbable protactinium and its sorption by unfired Vycor. For simplicity in handling and analyses, the experiments were made with Pa<sup>233</sup> tracer. The range of conditions investigated was: 0.5 to 12 M HNO<sub>3</sub>, 4 to 100 g Th/liter, 0.0 to 0.04 M HF, and 0.0 to 0.4 M Al(NO<sub>3</sub>)<sub>3</sub>. There

was considerable scatter in the data for the percent of the protactinium which was unadsorbable, but, in solutions containing more than 1 M or 3 M HNO<sub>3</sub>, the values were less than 5% and 2%, respectively. In addition, sufficient data was collected to allow estimation of the protactinium distribution coefficients over the range of concentrations studied.

The author gratefully acknowledges R. H. Rainey for his helpful advice and critical suggestions, and W. Davis, Jr. for preparing the computer program used in processing the data. R. C. Lovelace assisted in performing the laboratory experiments and Sarah W. Hopkins of the Analytical Chemistry group headed by W. R. Laing, made the vast number of necessary gamma counts.

## 2. REAGENTS AND EXPERIMENTAL TECHNIQUES

### 2.1 Reagents

Protactinium-233 was made by irradiating thorium nitrate crystals, Th(NO<sub>3</sub>)<sub>4</sub>·4H<sub>2</sub>O, 5 hr in the ORNL Graphite Reactor and allowing the resulting product to decay for at least 24 hr. Protactinium solutions were prepared by adding 1 g of irradiated thorium nitrate to 100 ml of aqueous solutions containing all the desired constituents except the Pa<sup>233</sup>. Immediately after adding the irradiated thorium, the Nalgene bottles containing the spiked solutions were placed in boiling water. After 5 min the bottles were closed, the solutions digested 1 hr, then removed and allowed to stand 24 hr at room temperature before contacting with unfired Vycor. The unfired Vycor was obtained from Corning Glass Works, Corning, New York as a powder finer than 60 mesh. The material was screened, and aliquots of the 60-80 mesh fraction used in the adsorption experiments.

### 2.2 Experimental Techniques

A technique similar to the Martin technique<sup>2</sup> was used to determine the distribution coefficients (DC = concentration on the glass (counts min<sup>-1</sup> g<sup>-1</sup>)/concentration in the aqueous phase (counts min<sup>-1</sup> ml<sup>-1</sup>)) for the adsorbable species of protactinium as well as the percentage of unadsorbable protactinium in the solutions. The solutions

were contacted with 60-80 mesh unfired Vycor by shaking 24 hr on a Burrell "wrist-action" shaker. Five to eight separate samples were equilibrated, with the amount of Vycor ranging from 6 to 100 grams per liter of solution. After equilibration, the raffinate was removed from the glass by centrifugation and the activity of the solution determined by gross gamma count. The activity on the glass represented the difference between the initial and final aqueous activity. A linear-coordinate plot was made with the activity in counts per minute per gram of glass as the ordinate and the counts per minute per milliliter of aqueous as the abscissa. For solutions containing two species of protactinium, one of which distributes itself between the adsorbent and the solution, and the other remaining in the solution, a straight line is obtained which may be extrapolated to the abscissa. The intercept is a function of the amount of unadsorbable species, and the slope of the line, the distribution coefficient of the adsorbable species. The method of least squares was used to determine the best straight-line fit for the data.

Examples of data obtained by this method are presented in Fig. 1. The initial aqueous solution was 6.21 M HNO<sub>3</sub> containing 50 g Th/liter and  $9.57 \times 10^5$  counts Pa<sup>233</sup> min<sup>-1</sup> ml<sup>-1</sup>. Eight batch equilibrations were made with the glass-to-solution ratios ranging from 5 to 100.1 g 60-80 mesh unfired Vycor per liter of solution. The equation for the best straight-line fit of the data was:  $y = (2263 \pm 43)x - (2.02 \pm 0.20) \times 10^7$ , indicating a distribution coefficient of  $2263 \pm 43$ , with  $(0.93 \pm 0.09)\%$  of the Pa<sup>233</sup> unadsorbable.

### 3. ADSORPTION OF PROTACTINIUM-233

#### 3.1 Effect of Thorium and Nitric Acid

The distribution of protactinium-233 between unfired Vycor and aqueous solutions containing 4, 50, and 100 g Th/liter and 0.5 to 12 M HNO<sub>3</sub> varies directly with the nitric acid concentration and decreases with increasing thorium concentration (Fig. 2). The distribution coefficient may be calculated from the following empirical equation:

$$Z = (378 \pm 72) + (384 \pm 9)x - (1.27 \pm 0.13)xy - (1.13 \pm 1.02)y,$$

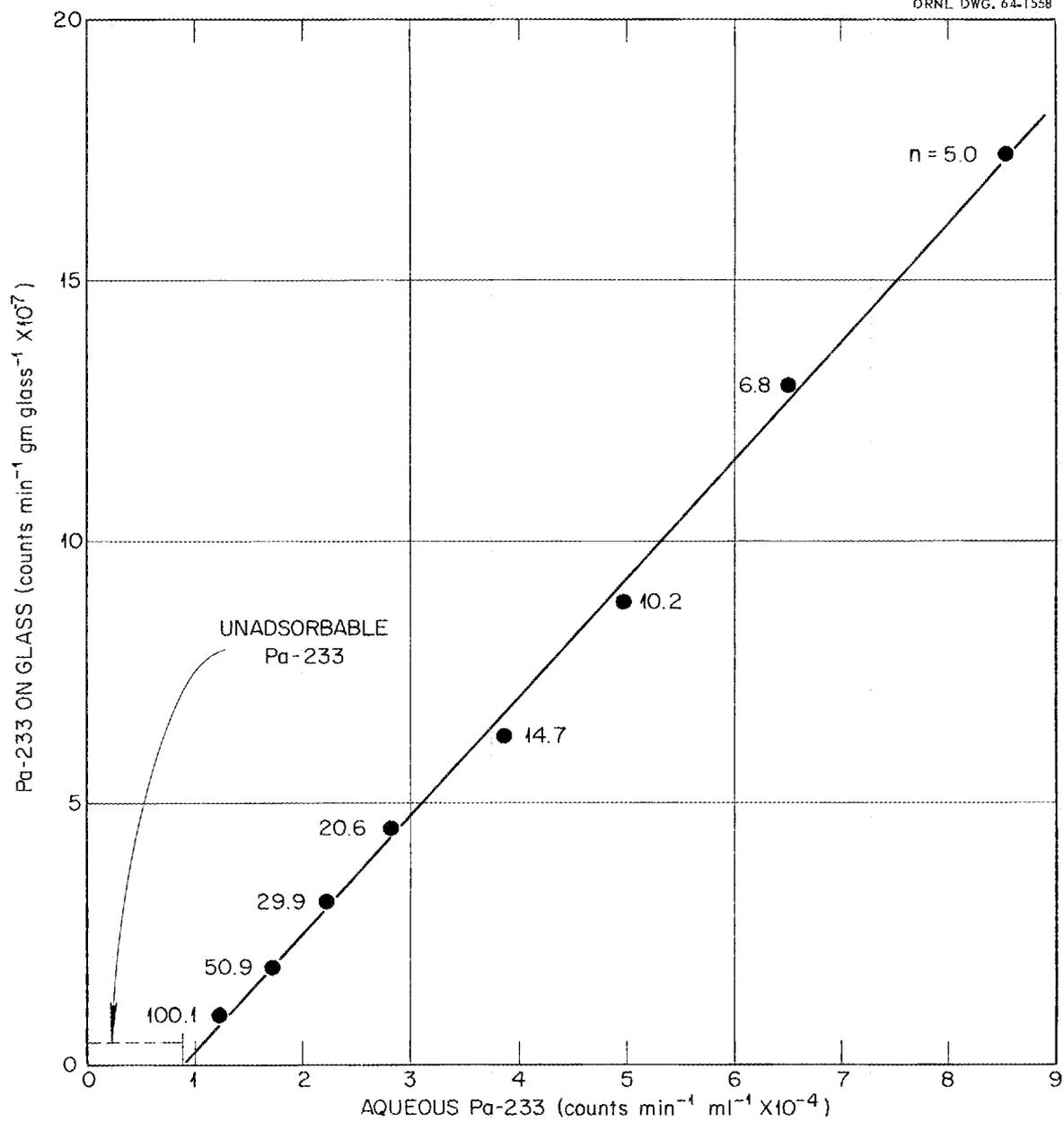


Fig. 1. Distribution of Pa-233 Between 6.21 M  $\text{HNO}_3$ , 50 g Th/liter and 60-80 Mesh Unfired Vycor.  $n = \text{g unfired Vycor/liter solution}$ .

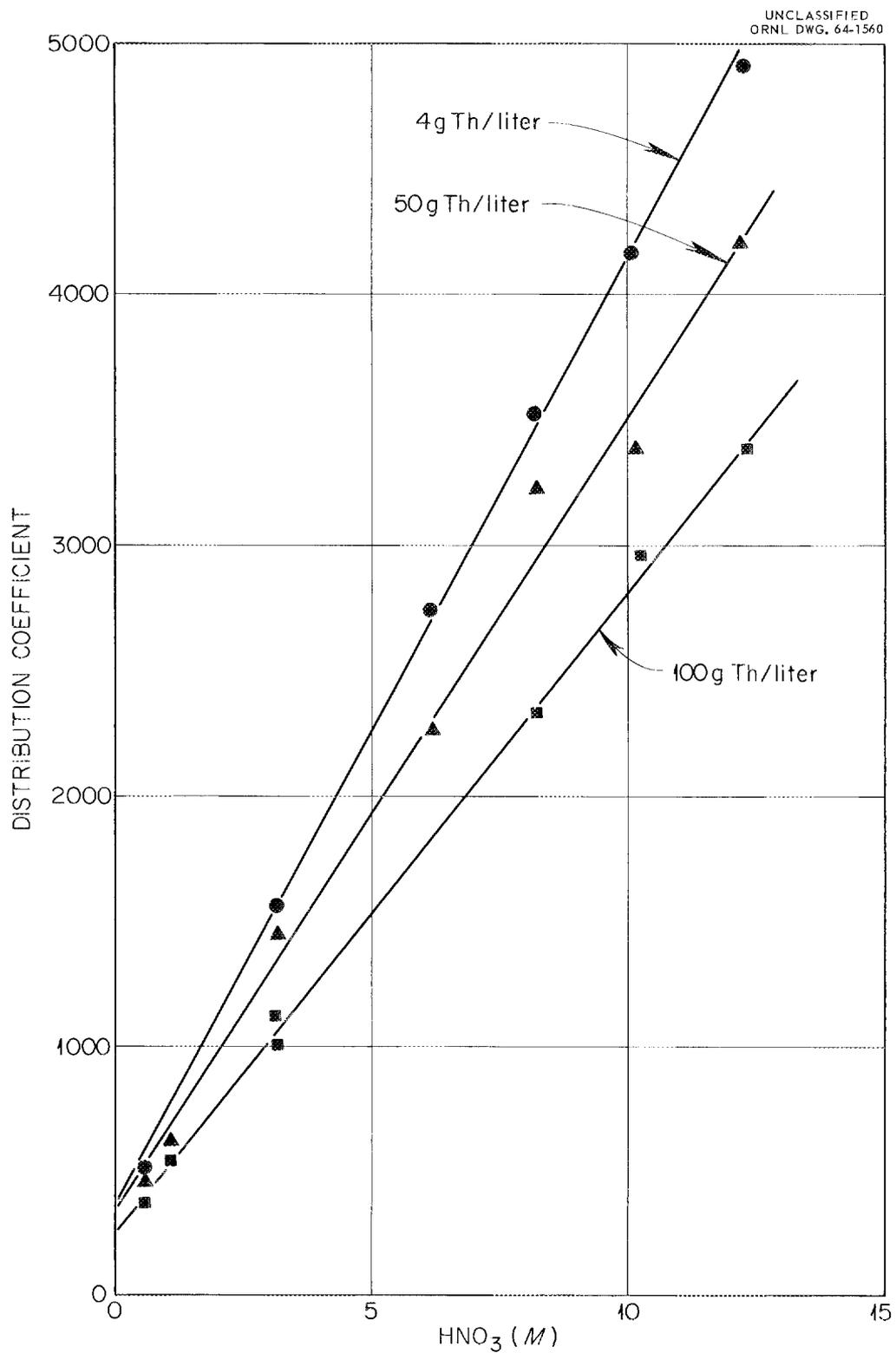


Fig. 2. The Distribution of Pa-233 from Thorium-Nitric Acid Solutions to 60-80 Mesh Unfired Vycor.

where

$$x = \underline{M} \text{ HNO}_3,$$

$$y = \text{g Th/liter},$$

Z = distribution coefficient of the adsorbable protactinium.

The equation is that of a double-distorted plane, as shown in Fig. 3. The distribution coefficients ranged from 380 in 0.5 M HNO<sub>3</sub>, 100 g Th/liter to 4920 in 12 M HNO<sub>3</sub>, 4 g Th/liter. For a typical dissolver solution containing 10 M HNO<sub>3</sub> and 100 g Th/liter, the distribution coefficient according to the empirical equation given above, would be 2840, compared with the value 2960 obtained experimentally.

### 3.2 Effect of Fluoride

The distribution coefficients obtained with 0.5 to 10 M HNO<sub>3</sub> containing 100 g Th/liter and 0 to 0.04 M HF showed no simple relationship as in the thorium-nitric acid solutions containing no fluoride. The distribution coefficient increased slightly with increasing fluoride in solutions containing less than about 3.5 M HNO<sub>3</sub>. At higher nitric acid concentrations, the coefficient decreased with increasing fluoride. The maximum decrease occurred with 10 M HNO<sub>3</sub>, where the distribution dropped from about 3000 with no fluoride present to 300 with 0.04 M HF present. Assuming that the stage heights are similar to those encountered with ion exchange resins, coefficients in the range of 300 would still be ample to assure complete product recovery (Fig. 4).

If we assume that the order of protactinium adsorption is:

nitrate > fluoride > polymer (or hydrolytic species),

then a possible explanation for the effect of fluoride is that in the lower acidities fluoride prevents the formation of protactinium polymers or hydrolytic species thus increasing the distribution coefficient. However, adsorption decreases in the higher acidities because of the competition between the fluoride and the nitrate for the protactinium.

According to the results of a few comparative experiments made with 50 g Th/liter, a decrease in thorium concentration, in thorium-nitric acid solutions containing HF, produces a slight increase in distribution coefficient. Coefficients were

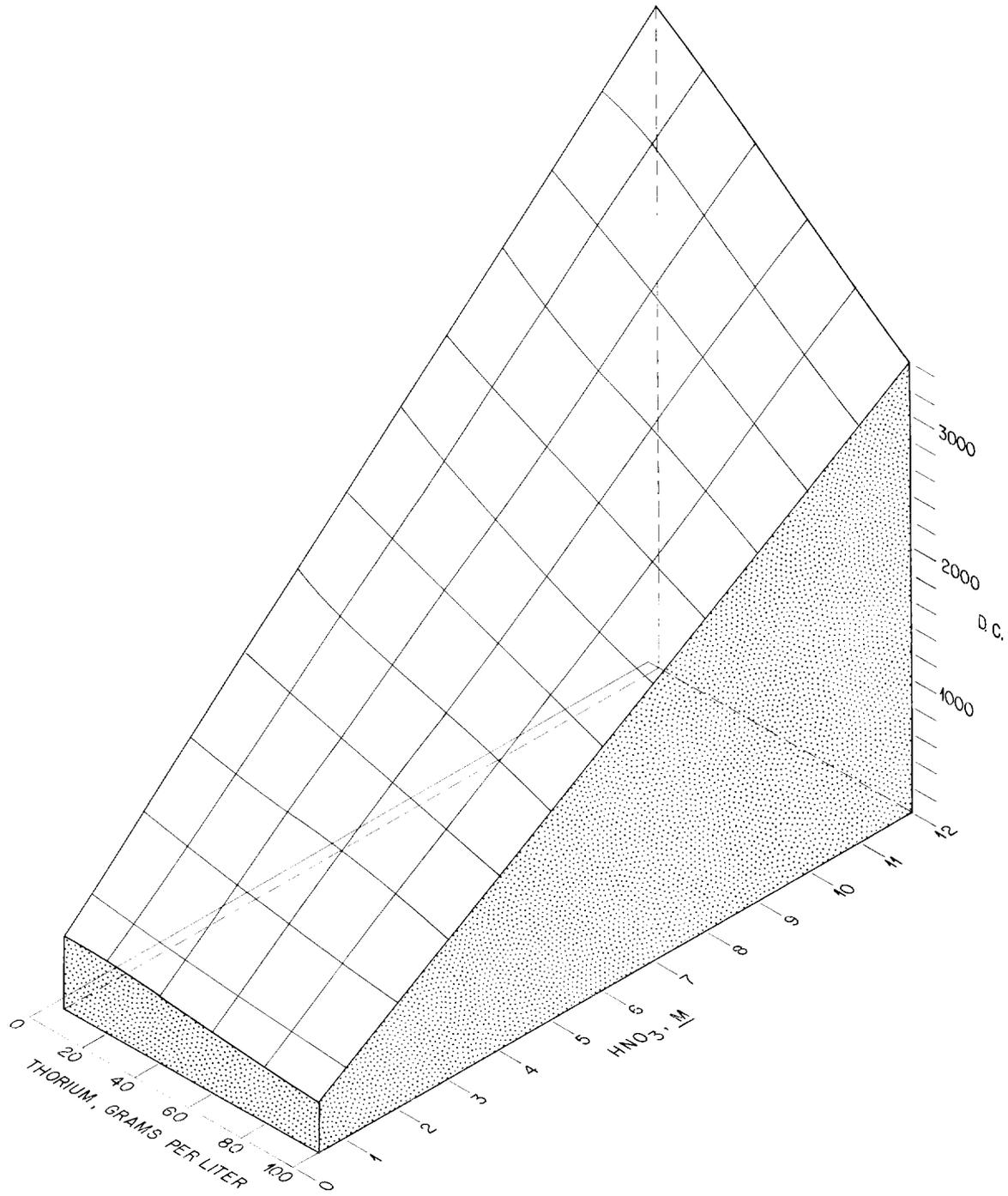


Fig. 3. Adsorption of Pa-233 on Unfired Vycor from Thorium-Nitric Acid Solutions.

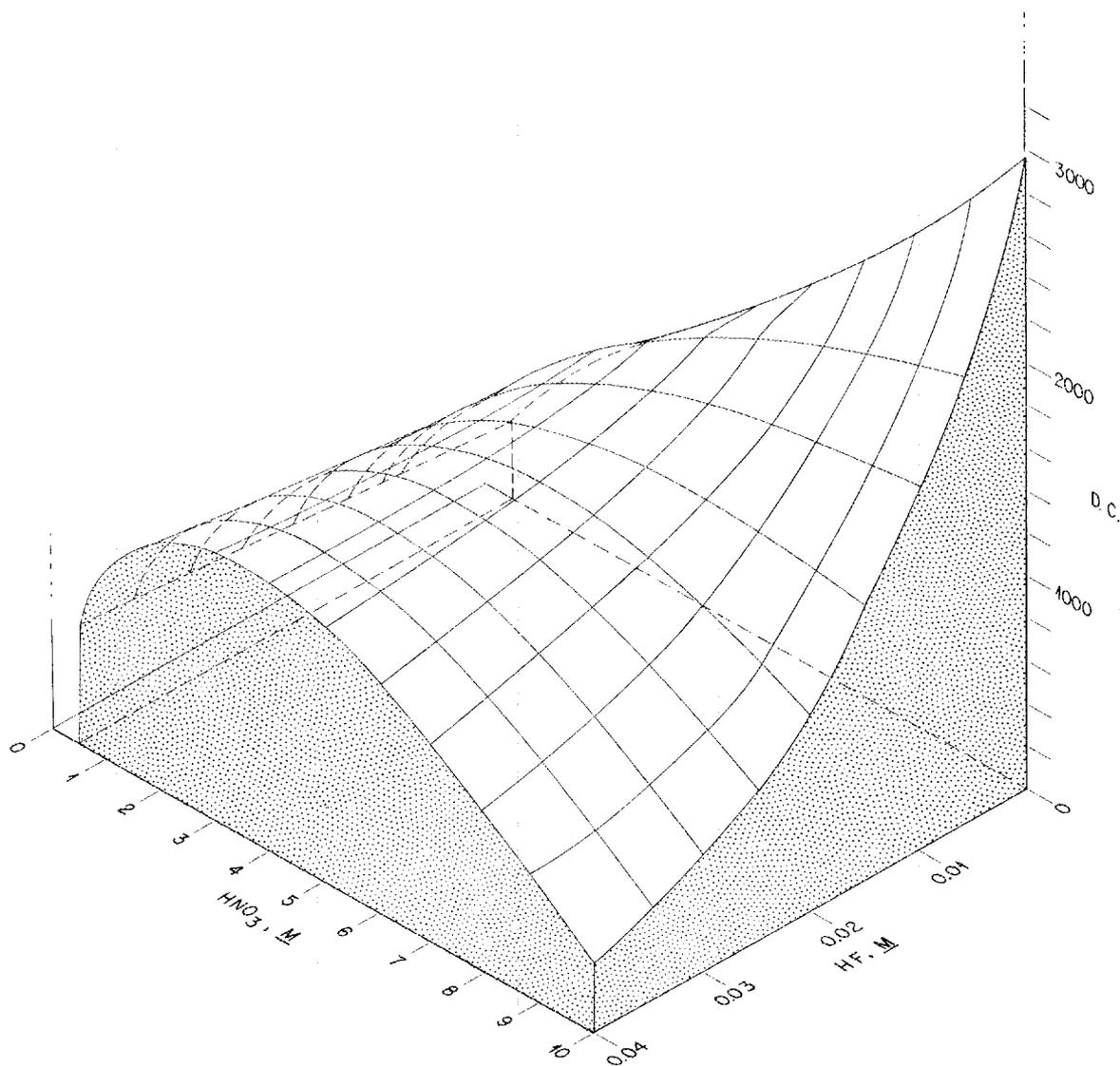


Fig. 4. Distribution of Pa-233 to Unfired Vycor from Nitric Acid Solutions Containing 100 g Th/liter and 0 to 0.04 M HF.

measured with solutions containing 50 g Th/liter, 1 to 10 M HNO<sub>3</sub>, 0.01, and 0.04 M HF. These results suggest that the distribution coefficients of process solutions could be increased by simply diluting the feed to 3 to 6 M HNO<sub>3</sub> (Table 1).

Table 1. The Effect of Thorium on the Distribution of Pa<sup>233</sup> to Unfired Vycor from Nitric Acid - Fluoride Solutions

HNO <sub>3</sub> ( <u>M</u> )	0.01 M HF		0.04 M HF	
	50 g Th/liter	100 g Th/liter	50 g Th/liter	100 g Th/liter
1	780	650	940	905
3	1480	1180	1210	1260
6	1930	1290	1060	940
8	1780	1600	--	760
10	1290	1775	820	320

### 3.3 Effect of Aluminum

The addition of up to 0.4 M Al(NO<sub>3</sub>)<sub>3</sub> to solutions containing 1 to 6 M HNO<sub>3</sub>, 100 g Th/liter, and 0.04 M HF produced a slight increase in protactinium adsorption. The distribution coefficient throughout this range of acidity was about 1100 ± 20% as compared to a value of about 1000 ± 20% for solutions containing no aluminum. In 7 to 10 M HNO<sub>3</sub>, the coefficient increased more markedly with increasing aluminum concentration but the maximum values were still only half that obtained with no aluminum or fluoride present. For example, the coefficient was approximately 3000 in 10 M HNO<sub>3</sub> without fluoride, 300 with 0.04 M HF present, and 1500 with 0.4 M Al(NO<sub>3</sub>)<sub>3</sub>. Thus aluminum should be added to complex all the fluoride in order to decrease corrosion, but decreasing the acidity is a more effective way of increasing the adsorption rather than the addition of more aluminum to the system (Fig. 5).

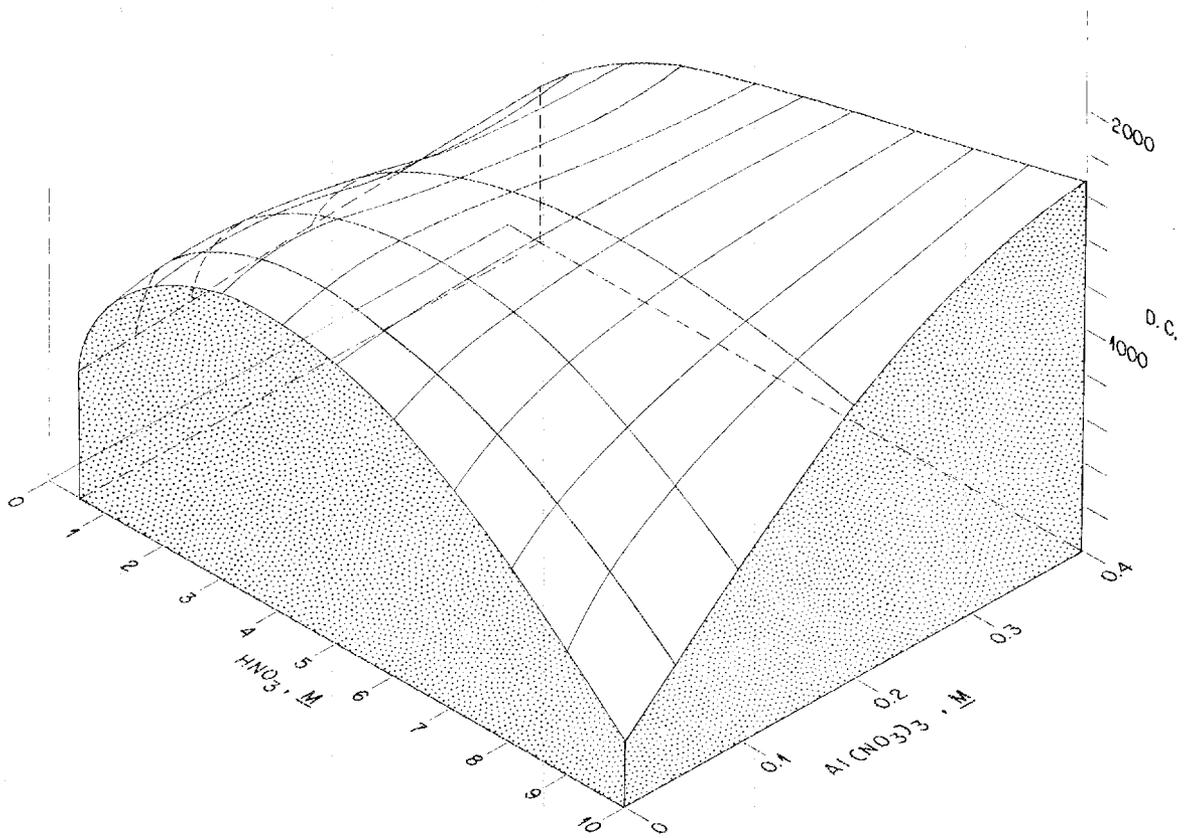
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Fig. 5. Distribution of Pa-233 to Unfired Vycor from Nitric Acid Solutions Containing 100 g Th/liter, 0.04 M HF and 0 to 0.4 M Al(NO<sub>3</sub>)<sub>3</sub>.

### 3.4 Unadsorbable Protactinium

The amount of protactinium that is unadsorbable in nitric acid solutions containing 4 to 100 g Th/liter, 0 to 0.04 M HF, and 0 to 0.4 M Al decreased with increasing nitric acid concentration. The values ranged from a maximum of about 7% unadsorbable in 0.5 M HNO<sub>3</sub> to less than 2% in solutions containing more than 3 M HNO<sub>3</sub>. Although the data were scattered, there was no apparent relationship between the percent that was unadsorbable and the thorium, fluoride, or aluminum concentration. More than 90% of all the data fall within the solid curve shown in Fig. 6.

These loss values are sufficiently low that they would not be a deciding factor in determining the practicability of a protactinium adsorption process using Vycor glass. The fact that about 5% of the protactinium was unadsorbable in a previous experiment,<sup>1</sup> rather than 1 or 2% as suggested by this data, cannot be explained. The difference may be due to a difference in solution preparation, protactinium concentration, or to the specific batch of Pa<sup>231</sup> oxide used in preparing the previous solution. The results do not signify what losses would be encountered in process application since neither experiment represents actual process conditions, and it has been shown possible to prepare solutions containing only adsorbable protactinium.<sup>1</sup>

### 3.5 Reversibility of Protactinium Adsorption

The protactinium distribution coefficients (glass/solution) were 40 to 100% larger when glass containing adsorbed Pa<sup>233</sup> was equilibrated with solutions containing no protactinium (reverse adsorption) than when solutions containing protactinium were contacted with fresh glass (forward adsorption). The coefficients were obtained for Pa<sup>233</sup> solutions containing 0.5 to 12 M HNO<sub>3</sub>, 100 g Th/liter, and 0.4 M Al in the usual manner. After 24 hr of contact, the raffinate was removed from the glass, and identical volumes of similar solutions containing no Pa<sup>233</sup> were contacted with the protactinium-impregnated glass for an additional 24 hr. The distribution coefficients were then calculated using the activity in these solutions minus any activity due to residual raffinate from the first contact. There was less difference between the forward and reverse coefficients in the more concentrated nitric acid solutions, indicating that the adsorption becomes more reversible at the higher acidities (Table 2).

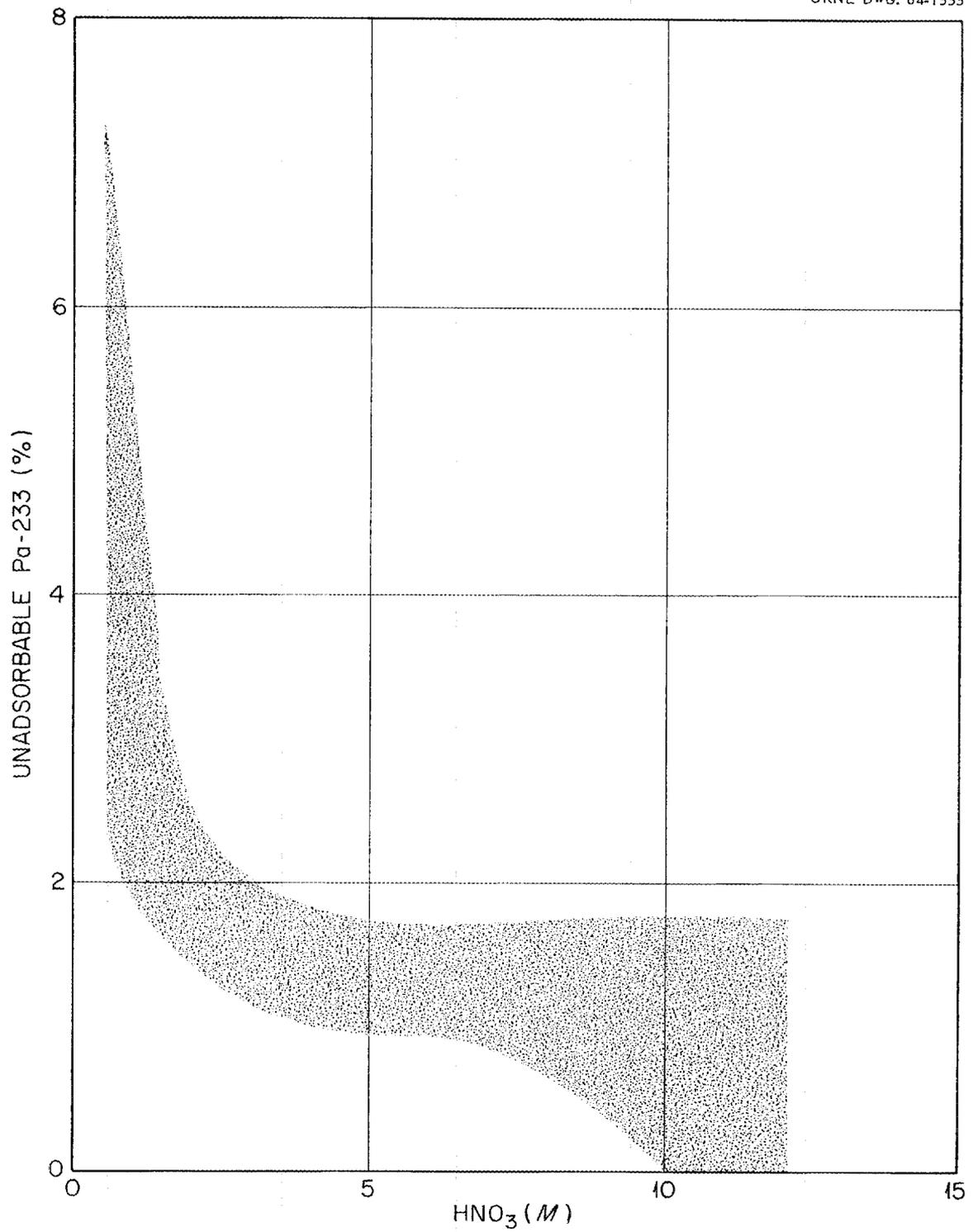


Fig. 6. The Percent Unadsorbable Pa-233 in Nitric Acid Solutions.

Table 2. Distribution of Protactinium-233 from Nitric Acid Containing 100 g Th/l, 0.04 M Al

HNO <sub>3</sub> (M)	Distribution Coefficients	
	Forward	Reverse
0.51	514 ± 33	834 ± 26
1.02	668 ± 43	1340 ± 83
3.07	1080 ± 25	2280 ± 51
4.95	1370 ± 19	2230 ± 107
7.98	2670 ± 81	3760 ± 204
9.60	2740 ± 98	3700 ± 172
11.40	3060 ± 108	4200 ± 163

#### 4. CONCLUSIONS AND RECOMMENDATIONS

These data verify the potentialities of a process for removing protactinium from short-decayed thorium fuels dissolved in nitric acid by adsorption on pulverized unfired Vycor glass. The protactinium distribution coefficients from solutions containing up to 10 M HNO<sub>3</sub>, 100 g Th/liter, 0.04 M F, and about 0.1 M Al are greater than 500 and are sufficient for process application. The coefficient could be increased by decreasing the acidity either by dilution or removal of the acid through an appropriate feed adjustment step. Maintaining a nitric acid concentration above 3 M ensures that less than about 2% of the protactinium will be lost due to its being in an unadsorbable form.

In order to test the feasibility of this process to high-burnup, short-cooled thorium fuels, it is recommended that hot-cell experiments be made using irradiated fuel pins. These experiments would reveal the amount of protactinium that is adsorbable under process conditions as well as the effects of macro concentrations of fission products and high levels of radioactivity on the adsorption. If these runs are successful, then further glove-box experiments using Pa<sup>231</sup> would be warranted to optimize

column design. These studies would include variation in process loss with flow rate, column geometry, and feed preparation procedures.

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