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HOT-CELL STUDIES ON THE SEPARATION OF PROTACTINIUM-233 FROM IRRADIATED THORIA BY COPRECIPITATION WITH MANGANESE DIOXIDE

July, 1965

BATTELLE-NORTHWEST
RICHLAND, WASHINGTON

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By

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by L.L. Humphreys

INTRODUCTION

Recovery of protactinium-233 from irradiated thoria was one segment of the recent Purex Process Test on six tons of irradiated thoria. This test was part of current studies on Hanford's capabilities for producing high isotopic purity uranium-233. The irradiated material was relatively short-cooled (90-120 days) and warranted recovery of the Pa-233 for subsequent decay to isotopically pure U-233. The method proposed for the protactinium recovery was by scavenging (coprecipitation) with manganese dioxide(1) on the head-end of the proposed Thorax flowsheet. Investigations were aimed toward finding optimum conditions for this process and increasing the stability of manganese dioxide in a high radiation field.

SUMMARY

The most important results were that 97% of the protactinium could be recovered by coprecipitation with manganese dioxide (3.5 g/l) at a loading of 10 mg. Pa-233 per gram MnO_2, and that after standing for 20 hours with the feed solution (1 $\underline{M}$ $Th(NO_3)_4$, 1 $\underline{M}$ HNO_3, 0.01 $\underline{M}$ HF, 0.1 $\underline{M}$ NH_2SO_3H, and 35 mg/l Pa-233) 85% of the protactinium was still recovered. This Pa-233 concentration results in 1.33 watts per liter of solution.

The use of either sulfamic acid or urea, to destroy nitrites, gave very good precipitate stability in this high radiation. Attempts to scavenge protactinium from an 0.1 $\underline{M}$ acid deficient 1 $\underline{M}$ $Th(NO_3)_4$ solution using both coformed and preformed MnO_2 and PbO_2 gave low recovery of protactinium and introduced problems with colloid formation. High salt concentration (thorium, aluminum, and sodium nitrates) and fluoride were found to interfere with the scavenging efficiency.

Little effect was observed by increasing the amount of scavenging agent over 0.05 moles of coformed MnO_2 precipitated per liter of feed. At this concentration, precipitate volume was found to be about 9% of solution volume.

PRELIMINARY EXPERIMENTS

Early investigations were directed at the possibility of coprecipitation of protactinium with MnO_2 from an acid deficient system, since the uranium solvent extraction was to be made under these conditions and the free nitric acid could be removed best before the material left the dissolvers. Results are shown as protactinium decontamination factors, or the ratio of initial activity in solution to final activity. This gives a more sensitive measure of protactinium separation when precipitation is nearly complete. For instance, a DF of 2 means 50% recovery, a DF of 10 means 90% recovery, and a DF of 100 means 99% recovery of Pa-233. In the experiments using coformed manganese dioxide, the precipitate was formed as a "reverse strike" (i.e. addition of permanganate to a manganous nitrate solution to avoid strong oxidizing conditions and minimize ruthenium volatilization). The overall chemical reaction is:

$$3\,Mn(NO_3)_2 + 2\,KMnO_4 + 2\,H_2O \rightarrow 5\,MnO_2 + 2\,KNO_3 + 4\,HNO_3.$$

Scavenging of Pa-233 from a 0.1 $\underline{M}$ acid deficient 1.0 $\underline{M}$ $Th(NO_3)_4$ feed with coformed MnO_2 was investigated. Pa-233 DF's were generally low, and severe problems were experienced with colloid formation. When less than 0.1 moles of MnO_2 per liter of feed was used no precipitate would form. At 0.2 moles per liter the DF for Pa-233 was 29, but the precipitate volume was 35% of the initial solution volume. Varying the temperature had essentially no effect on either precipitate volume or Pa-233 DF. Changing the pH had little effect on precipitate volumes, except that above a pH of 2.0 no precipitate would form, and as the pH increased the DF decreased (at a pH of 2, DF = 4). Attempts were made to "break" the colloids, but without success.

To try to alleviate this problem, varying amounts of preformed MnO_2 solid were added to a solution the same as above. Results were very poor, giving a DF of only 2.1 using 0.2 moles of precipitate per liter of feed (compared to a DF of 29 for coformed material). Both coformed and preformed lead dioxide were also tried(2). These also resulted in low protactinium recovery from the acid deficient system.

Because of these difficulties, attempts to recover protactinium from acid deficient systems by coprecipitation were abandoned. The proposed separations flowsheet was changed so that nitric acid was removed in the dissolvers to the desired acidity for the MnO_2 scavenge, and the supernate was then neutralized with sodium hydroxide to the desired acid deficiency for the solvent extraction.

LABORATORY TRACER EXPERIMENTS

Experiments designed to determine optimum process conditions are summarized in Tables I, II, and III, and in Figures I and II. Figure I, showing the effects of nitric acid and thorium concentrations on protactinium removal, show that 1 $\underline{M}$ HNO_3 is optimum, and also show a fairly large break in the effects of thorium between 1.0 $\underline{M}$ and 1.5 $\underline{M}$ (a DF of 100 versus 50 at 1 $\underline{M}$ nitric acid), and for this reason the feed composition chosen was 1 $\underline{M}$ HNO_3, 1.0 $\underline{M}$ $Th(NO_3)_4$.

The experiment reported in Table I, showing the effect of fluoride on protactinium recovery, shows an 8% reduction in Pa-233 DF with 0.01 $\underline{M}$ HF. However, when 0.1 $\underline{M}$ aluminum was added to the feed solution, to complex the fluoride, the DF for protactinium was decreased by 30% at 0.01 $\underline{M}$ HF. At an HF concentration of 0.04 $\underline{M}$, the reduction in Pa-233 DF is about 25% both with and without the presence of aluminum. At higher fluoride concentrations, the solution containing 0.1 $\underline{M}$ aluminum gave better DF's for protactinium. The precipitations were made from a 1 $\underline{M}$ $Th(NO_3)_4$, 1 $\underline{M}$ HNO_3 solution, with 30 minute contact and 0.1 moles coformed per liter. Solution A was without any aluminum, and solution B was with 0.1 M aluminum.

TABLE I - EFFECT OF FLUORIDE ON Pa-233 DF

Fluoride molarity	0	0.01	0.03	0.05	0.07	0.10
Pa-233 DF (soln. A)	73	67	58	52	46	36
Pa-233 DF (soln. B)	51	52	53	56	51	45

The effect of temperature, shown in Table II, indicates relatively small changes in scavenging efficiency with moderate temperature changes. 0.1 mole of MnO_2 was precipitated per liter 1 M $Th(NO_3)_4$, 0.5 M HNO_3, with a 30 minute contact time.

TABLE II - EFFECT OF TEMPERATURE ON Pa-233 DF

Temp. °C	10	20	30	40	50	60
Pa-233 DF	52	64	48	63	68	75

Moore and Goodall(3) found the protactinium DF to be roughly linear in amount of MnO_2 precipitated between 0.005 and 0.075 moles per liter. This is shown in Table III between 0.01 and 0.05 moles per liter, but above that the changes become increasingly smaller.

TABLE III - EFFECT OF AMOUNT OF COFORMED SCAVENGING AGENT ON Pa-233 DF

Moles/liter	0.01	0.05	0.10	0.50	1.00
Pa-233 DF	13	54	69	51	81

These precipitates were coformed in a 1.0 M $Th(NO_3)_4$, 0.5 M HNO_3 solution, with a 30 minute contact time.

The effect of sodium nitrate on protactinium DF was investigated to see if it would be possible to recover Pa-233 from plant wastes (about 4.5 M $NaNO_3$) by coprecipitation. Figure II shows high interference, with a Pa-233 DF of 2.6 at 4 M $NaNO_3$, 1 M HNO_3. If this solution was diluted by a factor of two

(2 M $NaNO_3$, 0.5 M HNO_3) the protactinium DF was found to be 204, using 0.04 moles of coformed MnO_2 per liter. The interferences displayed by thorium, aluminum, and sodium nitrates are apparently not a function of ionic strength alone, but rather of both the nature of the salt and its concentration, indicating specific chemical interference.

RADIATION STABILITY STUDIES

On the basis of the above results, conditions adopted for testing the scavenging technique on irradiated thorium solutions in the hot-cell were 1.0 M $Th(NO_3)_4$, 1 M HNO_3, 0.015 M HF, with 0.04 moles of MnO_2 precipitated per liter of solution (a restriction imposed by the size of the centrifuge in the plant), ambient cell temperature (about 30° C), and at least 30 minutes digestion time.

Experiments conducted at a protactinium concentration of 10 mg. Pa-233 per liter (or a loading of 3 mg/g MnO_2) indicated that the precipitate had redissolved within 30 minutes. The effects of reprecipitating(2,3) and of inhibiting radiation degradation by both sulfamic acid and urea(2) are given in Figure III. In experiments with less protactinium (1 mg/g MnO_2), the presence of the inhibitors caused lower initial DF's than where these were absent, but gave increased precipitate life.

These inhibitors were also used in a solution which was 35 mg. per liter Pa-233 (10 mg/g MnO_2 or 1.33 watts per liter), to see if this method could be used to concentrate and further purify the material from the test at the Purex Plant. Results are shown in Figure IV. A DF of 6.4 (84.4% recovery) was obtained, even after nine hours, using sulfamic acid. Time cycles expected in the plant operation would run four to eight hours. The success and similarity of these traditional "nitrite-getters" in providing enhanced precipitate stability indicates that nitrites are primarily responsible for MnO_2 dissolution in high radiation fields. Laboratory tests showed that sodium nitrite will dissolve MnO_2.

The conditions recommended for protactinium recovery at Purex (for the six ton test) were 0.04 moles MnO_2 coformed (reverse strike) per liter of 1 $\underline{M}$ $Th(NO_3)_4$, 1 $\underline{M}$ HNO_3, 0.01 $\underline{M}$ HF, 0.1 $\underline{M}$ sulfamic acid, and no more than 0.1 $\underline{M}$ $Al(NO_3)_3$. The MnO_2 would then be centrifuged, slurried out of the centrifuge into a tank, heated to 70° C, and sucrose added to dissolve the precipitate(4). At this point, the Pa-233 would only be concentrated by a factor of three, and contain some thorium and uranium, about 10-15% of the cerium, and most of the barium (as a sulfate precipitate from the sulfamic acid inhibitor). As a concentration step, and for further purification, the sugar treated solution would then be recentrifuged (to remove the sulfate precipitates) and treated with potassium permanganate to reform MnO_2. This gives added decontamination from thorium and uranium, and also serves as a concentration step. The precipitate is centrifuged out, dissolved in 0.05 $\underline{M}$ H_2SO_4 with sucrose, and allowed to stand (to allow decay to U-233). The uranium may then be recovered by anion exchange (to be reported in a subsequent document).

This procedure was performed in the plant in January, 1965. Initial scavenging removed 90% of the Pa-233 from the feed solution, and the remainder of the procedure worked as expected, except for the loss of some of the material due to equipment malfunction.

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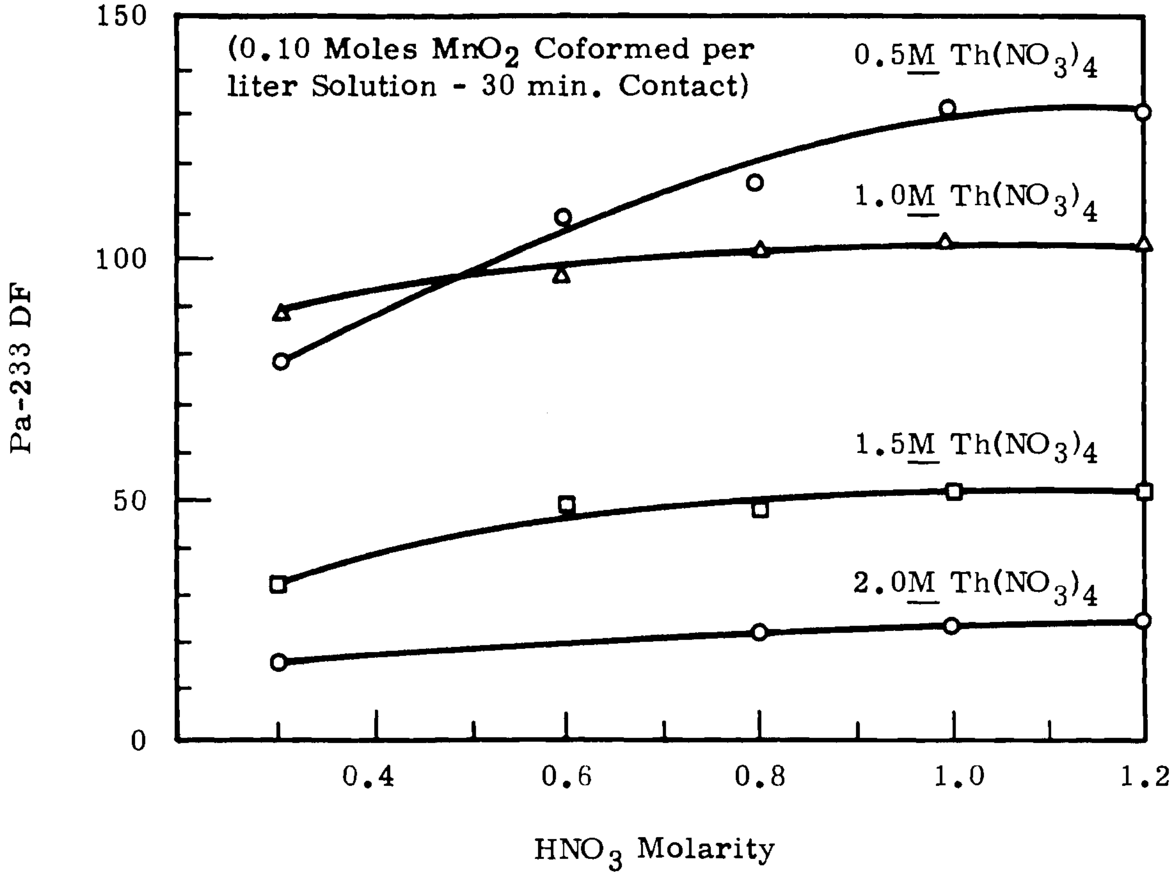


FIGURE 1

Effects of Acid and Thorium Nitrate on Pa-233 DF

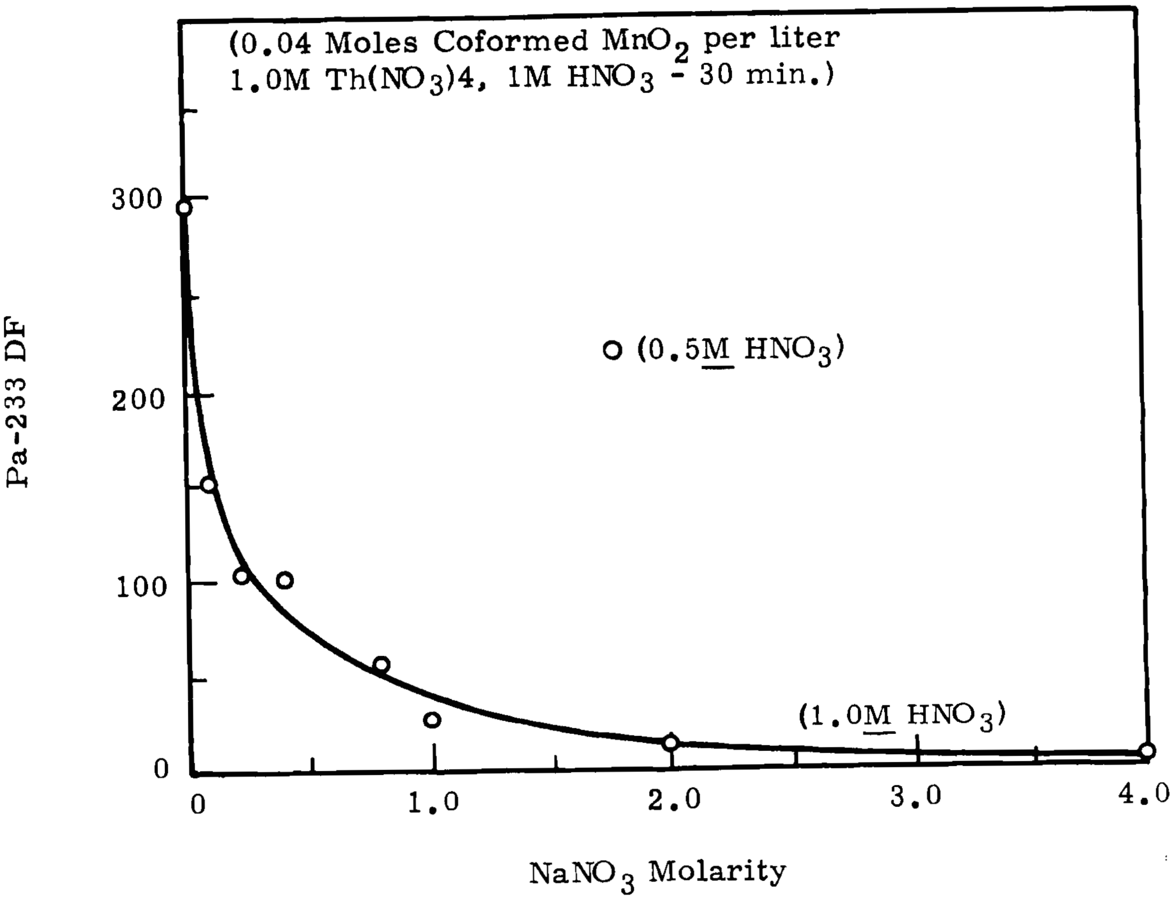
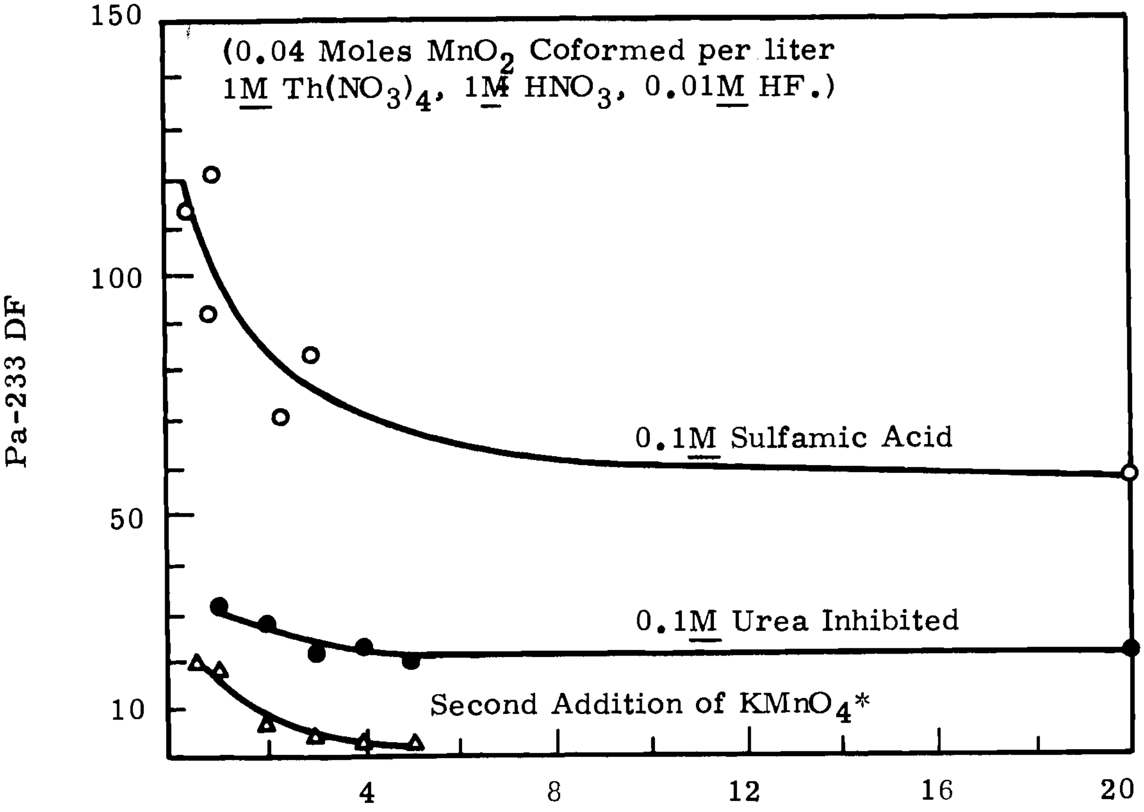


FIGURE 2

Effect of Sodium Nitrate on Pa-233 DF



*In the first addition of $KMnO_4$, no precipitate was formed which would last 30 minutes (10 mg. Pa-233 per liter)

FIGURE 3

Protactinum-233 Recovery versus Time

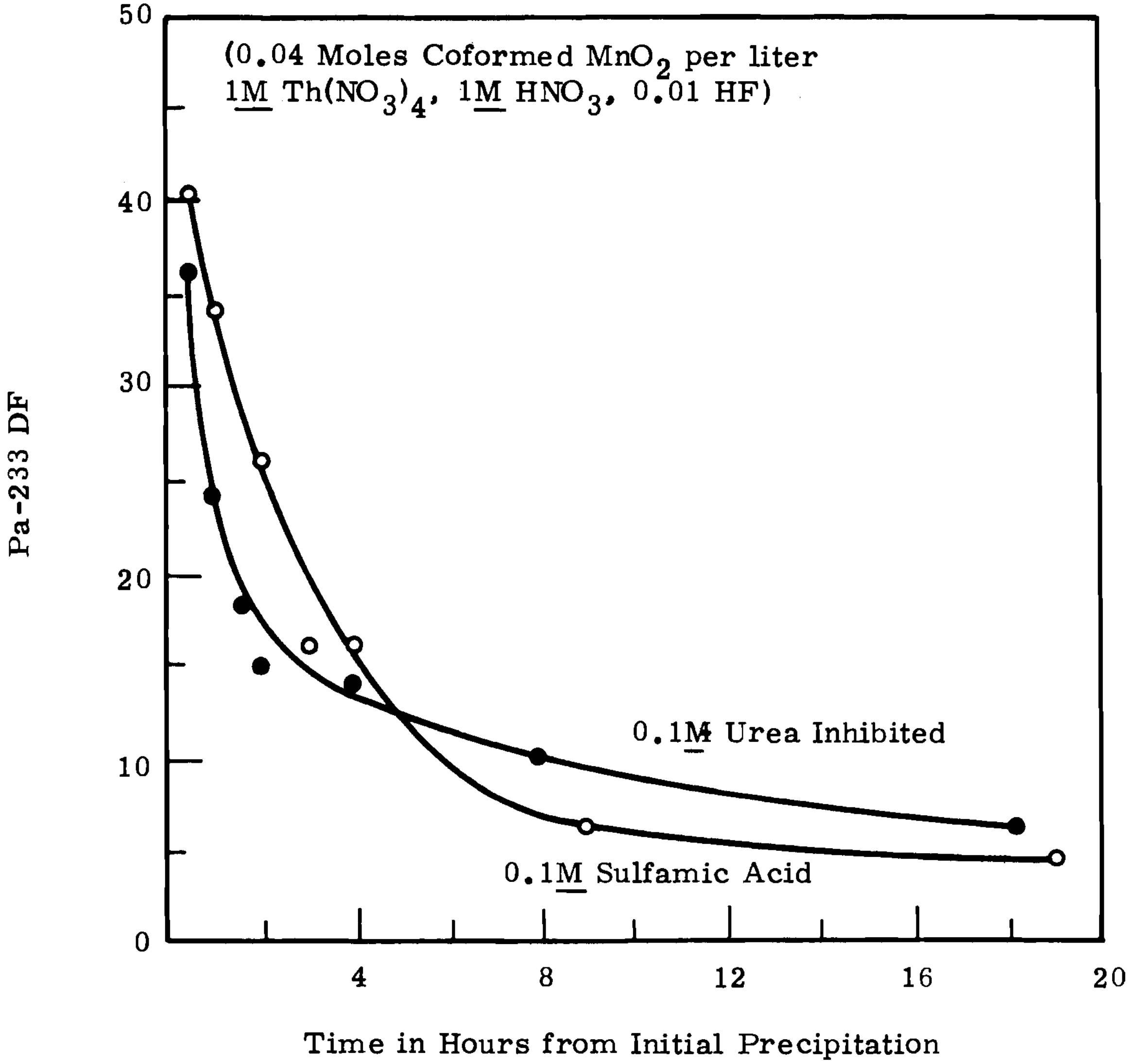


FIGURE 4

Protactinium Recovery versus Time from a Solution Containing
35 mg./1. Pa-233

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