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For S.E. Gydesen 4/20/76

By L Pope 5/5/76

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## THE PRECIPITATION OF PLUTONIUM(IV) OXALATE IN TASK I

### Introduction

A revised Task I is being designed for the precipitation of plutonium as Pu(IV) oxalate, following reduction of Pu(VI) to Pu(IV) with hydrogen peroxide, in the RM line of the 234-5 Building. Feed solutions for Task I will be Redox, Purex, and Recuplex product solutions which will contain 50-75 grams of plutonium per liter (ca. 90% Pu(VI), 10% Pu(IV)), not more than five to six molar nitric acid, and varying amounts of aluminum (currently, Redox PR solution contains 5000 to 100,000 parts aluminum per million parts plutonium), iron, chromium, uranium, and fission products.

Laboratory work has shown that the process is adaptable to Task I. Although no precipitations using Task I feeds have been made in the plant, plant experience with Pu(IV) oxalate has confirmed laboratory observations that:

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1) Precipitation from solutions containing 50 to 100 grams of plutonium per liter (diluted AT solution) gives satisfactory results. This process was used in the 234 building RG line from January, 1952, until the wet chemistry hoods were shut down in July, 1952.

2) Precipitation from Redox PR solution (3BP concentrated by evaporation) gives, at 10-20 grams of plutonium per liter, sufficient separation of plutonium from the bulk and fission product impurities now found in 3BP.

## Objectives

This memorandum has been written to summarize the laboratory experience which has demonstrated the feasibility of precipitation of Pu(IV) oxalate in Task I. Where possible, a comparison between the laboratory results with two solution concentrations - 10 g/l Pu and 50 g/l Pu - has been given to provide a basis for the prediction of Task I performance from 231 Building process data.

Complete data from laboratory studies are available in monthly progress reports issued since October, 1951, by V. R. Cooper for Separations Technology - Process. A final report (1) on Production Test 234-5 has been issued.

## Summary and Conclusions

1. Readily filterable plutonium(IV) oxalate with a filter cake density of 0.6 to 0.7 grams of plutonium per cubic centimeter of cake has been precipitated from Redox PR solutions containing from 10 to 200 grams of plutonium per liter and from two to six molar nitric acid. Variations in purity of feed solution have resulted in marked variations in precipitate characteristics.

2. Ease of filtration was found to increase with strike temperature over the range of 35 to 60°C; temperature higher than 60°C caused the formation of gummy precipitates. To prevent post-precipitation from the filtrate, especially when processing solutions at the high end of the acidity range, it has proved necessary to cool the slurry to a temperature of less than 10°C.

3. In order to produce easily filtered precipitates as the process has been scaled up, it has been necessary to decrease the rate of oxalic acid addition as the reactor size has increased. This was probably caused by less effective agitation in the larger reactors.

4. With Redox PR solution containing 60 grams plutonium per liter (prepared by evaporation to remove excess nitric acid, followed by dilution to the desired concentration), the use of optimum precipitation and washing techniques has given results which indicate:

(a) Anticipated process times of 1.5 to 3 hours for pre-reduction (reduction of Pu(VI) to Pu(IV)), precipitation and digestion and one to three hours for filtration and washing;

(b) Separations factors of 80, 40, 20 and 12 for Al, Cr, Fe and U, respectively;

(c) Decontamination factors of 1.2, 12 and 3 for Am, Ru and Zr-Nb, respectively, (compared with factors of 1.0, 12 and 6 for precipitation from Redox PR solution containing 10 to 20 grams of plutonium per liter).

## Recommendations

From experience in the Development Laboratory, we recommend:

1) That Task I equipment be designed:

   (a) To permit variation of solution and slurry temperatures through the range of five to sixty degrees Centigrade.

   (b) With provisions for vigorous agitation.

2) That attempts be made to lower and standardize the aluminum nitrate content of Redox PR solution to assure plutonium(IV) oxalate of uniform precipitate characteristics and to permit the concentration of PR solution to greater than 200 grams of plutonium per liter without supersaturation with respect to aluminum nitrate.

3) That consideration be given to designing for a possible 1200 gram batch (vide (2)) by either increasing the working volume of Task I reactors to 18 liters or providing a jacketed storage tank and lines to permit the use of two to three molar oxalic acid.

## Experimental

Laboratory work was done on scales of 0.5 to 25 grams of plutonium, using pyrex glass cylindrical reactors (2" O.D. x 6", 3" O.D. x 8", 6" O.D. x 6"). 1750 r.p.m. stainless steel stirrers were used for agitation. Precipitates were either settled in the reactor and washed by decantation or they were filtered through a Corning M (15 micron) sintered glass funnel or a Micrometallic F to G (20 to 10 micron) sintered stainless steel funnel. Filter cakes were washed on the funnels.

## Results and Discussion

A listing of optimum precipitation conditions for Redox PR solution, possible range of variations in these conditions, and typical results obtained under optimum conditions is compiled in Tables I and II. The discussion which follows is based upon laboratory experience with a variety of feed solutions and, unless otherwise stated, is generally applicable. Plutonium(IV) oxalate has been precipitated from solutions containing 1 to 550 grams of plutonium per liter. Since the plutonium concentration in filtrates and washes does not vary appreciably with the plutonium concentration of the starting solution, the lowest plutonium recycle will result from using the maximum plutonium concentration in the starting solutions. The upper limit seems to be the highest concentration at which the solution is stable at room temperature with respect to crystallization of any of its constituents. With current 3BP, which frequently contains as much as 100,000 parts of aluminum per million parts of plutonium, the upper limit appears to be less than 200 grams of plutonium per liter. The results of laboratory studies of solids in concentrated 3BP are discussed in another memorandum (3).

Using one molar oxalic acid and 3BP concentrated to 200 grams of plutonium per liter, it can be seen from figure 1 that the largest batch which can be processed in the proposed Task I reactor (14 liter working volume) is 900 grams of plutonium. To attain the 1200 gram batch which has been considered in another memorandum (2), it would be necessary: to use a reactor with an 18 liter working volume (see figure 2); to use 1.5 molar oxalic acid (see figure 1), which would require heating of storage vessel and lines to prevent crystallization; or to reduce the aluminum content of Redox PR solution to less than 10,000 parts per million parts of plutonium and to use concentrated 3BP containing approximately 500 grams of plutonium per liter (figure 1).

Plutonium(IV) oxalate may be precipitated from any solution containing more than 1.5 molar nitric acid, as long as the final slurry is 1.5 to 4.5 molar in nitric acid. At lower acidities, the co-precipitation of impurities is favored, plutonium recycle is high, and filtration times are long. At slurry acidities higher than 4.5 molar, pre-reduction becomes slow, plutonium recycle is high, and filtration times are very long. A final slurry concentration of 2.5 to 3.5 molar nitric acid was found to be optimum.

Pre-reduction, as far as is known, is best accomplished by addition of one-half to one per cent by weight of hydrogen peroxide and digestion of the resulting solutions. Lower concentrations of hydrogen peroxide give slow or incomplete reduction, and at higher concentrations, plutonium peroxide sometimes precipitates. In general, the reduction rate increases with increasing plutonium concentration and decreases with increasing hydrogen ion concentration. The required digestion time also varies with temperature (for current 3BP, 30 minutes at 25°C or 15 minutes at 50°C suffices) and solution purity. The optimum temperature for plutonium(IV) oxalate precipitation lies between 35 and 60°C. At strike temperatures below 20°C, the plutonium(IV) oxalate which is formed is so finely divided that it cannot be filtered or settled within reasonable time periods. If the strike temperature is too high, a gum is formed which cannot be processed.

Increasing the strike temperature from 20°C to 60°C decreases filtration times, but the laboratory fluorides obtained by direct hydrofluorination of the oxalate precipitated at a temperature of 50°C or above have not been completely free-flowing. No difficulties have been experienced in plant handling of the fluorides prepared from plutonium(IV) oxalate, precipitated at 50°C from current Redox PR solution.

The amount of oxalic acid used for a plutonium(IV) oxalate precipitation may be varied to give the slurry an oxalic acid concentration between 0.04 and 0.16 $\underline{M}$ with little change in the plutonium recycle (See Table II). Lowest recycle (0.02 to 0.05 gms Pu per liter) is obtained with 0.1 $\underline{M}$ $H_2C_2O_4$ in the slurry. With lower oxalic acid concentrations (0.05 M) in the slurry, plutonium recycle has been found to be increased ten to fifty fold by the presence of usual amounts of iron, aluminum and chromium.

One molar oxalic acid is the highest concentration that can be handled without some crystallization at room temperature. Concentrations of oxalic acid from 0.6 to 1.7 molar have been used for laboratory strikes, and higher concentrations should be equally satisfactory. Laboratory attempts to precipitate plutonium(IV) oxalate by adding solid oxalic acid to plutonium solutions have been unsuccessful. The oxalic acid particles became occluded by plutonium(IV) oxalate and any further reaction was too slow for process use.

In the laboratory, plutonium(IV) oxalate filtration times have been found to increase hyperbolically with decreasing oxalic acid addition times. On a five gram scale, minimum process times were achieved by a five minute oxalic acid addition. The optimum oxalic acid addition time for 231 and 234 Building operations is between 30 and 90 minutes. The difference between optimum oxalic acid addition times for laboratory and plant operations may be due to using more vigorous agitation for laboratory processing than is used for plant processing.

If plutonium(IV) oxalate slurries are not chilled before filtration or decantation, the precipitate will continue to form in the recycle solution. No such post-precipitation has been observed in the laboratory when the slurry has been chilled to less than 10°C before separating the supernatant or filtrate from the precipitate.

No process improvement has as yet been demonstrated for any of the following: digestion at 35°C after the oxalic acid addition; variation in the time required to chill the slurry from 35° to below 10°C; or digestion at below 10°C.

If the plutonium(IV) oxalate is washed by decantation in the reactor, minimum turbidity of supernatants is obtained by using a 2 $\underline{M}$ $HNO_3$ - 0.05 $\underline{M}$ $H_2C_2O_4$ wash solution. If the plutonium(IV) oxalate cake is washed on a filter, water or 2 to 4 $\underline{M}$ $HNO_3$ - 0.05 $\underline{M}$ $H_2C_2O_4$ may be used for washing with little variation (0.03 to 0.06 gms. Pu per liter) in plutonium recycle to washes. It is thought that 2 $\underline{M}$ $HNO_3$ - 0.05 $\underline{M}$ $H_2C_2O_4$ will give best washing, but that a final water wash may give a cake best suited for Task II use.

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The separation of plutonium from fission products in 3BP solution, by plutonium(IV) oxalate precipitations from solutions containing 1 to 60 grams of plutonium per liter, is shown in Table IV for laboratory runs. Little difference in results at 10 and at 60 g Pu/1 can be shown for ruthenium. The decontamination from Zr-Nb may be twice as good at 10 g/1 as at 60 g/1 Pu.

In addition to a high concentration of aluminum nitrate, current 3BP contains alumina and silica (3). This material cannot be removed by filtration of Redox 3BP solution, but upon evaporation of the 3BP solution to 100 to 300 grams of plutonium per liter, a gelatinous precipitate is formed. In one case, separating this precipitate by filtration removed (Table IV) about 70% of the zirconium-niobium gamma activity in the 3BP.

Plutonium(IV) oxalate as currently precipitated is retained completely by sintered filters of less than 25 microns average pore opening. Sintered materials must be carefully checked for largest pore openings, and material having pores larger than 40 microns should be rejected for plant use.

References

| | | |
|---|---|---|
| (1) | HW-26450 | Final Report Production Test 234-5, Plant Process Evaluation Precipitation of Plutonium(IV) Oxalate, W. B. Kerr. December 3, 1952 |
| (2) | HW-26488 | Consideration of the Plutonium Purification and Fabrication Process with Respect to Replacement of Part I of the RG Line, R. W. Benoliel. December 5, 1952. |
| (3) | HW-27562 | Laboratory, Batch Evaporation of Redox PR Solution, K. M. Harmon by R. L. Beede, J. F. Facer, and R. A. Pugh. April 3, 1953. |

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Table I - Plutonium (IV) Oxalate Precipitation from Redox Product Solution

| | Range | Optimum 10 g/l Pu | Optimum 60 g/l Pu |
|---|---|---|---|
| Starting Solution: | | | |
| g/l Pu | 1 - 200 | --- | --- |
| g/l $H^+$: 10-75 g/l Pu | 1.5 - 6 | 4.0 | 5.0 |
| 200 g/l Pu | 1.5 - 12 | | |
| Pre-reduction: | | | |
| Wt.% $H_2O_2$ | 0.5 - 1.0 | | |
| Temp, °C | 20 - 50 | 50 | 50 |
| Precipitation: | | | |
| Reagent, M $H_2C_2O_4$ | 0.6 - 1.7 | 1.0 | 1.0 |
| Temp, °C | 25-60 | 50 | 50 |
| Slurry: | | | |
| mole/l. $H_2C_2O_4$ | 0.04 - 0.16 | 0.1 | 0.1 |
| g/l $H^+$ | 1.5 - 4.5 | 3.2 | 3.2 |
| Final Temp, °C | 5 - 30 | L 10 | L 10 |
| Precipitate: | | Typical Values | |
| Settled Density, g/cc Pu | 0.15 - 0.35 | 0.3 | 0.3 |
| Filtered Density, g/cc Pu | 0.35 - 0.7 | 0.6 | 0.6 |
| Munsell Color | 2.5 $Y^{8/4}$ - 7/10 | 2.5 $Y^{7/6}$ | 2.5 $Y^{7/6}$ |
| Filtrate: | | | |
| Solubility, g/l Pu | 0.02 - 2 | 0.05 | 0.05 |
| Washes: | | | |
| Solubility, g/l Pu | 0.015 - 0.3 | 0.03 | 0.03 |

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Table II - Variation in Solubility with Oxalic Acid Concentration in Slurry

| Feed Solution: | | | | | | |
|---|---|---|---|---|---|---|
| g/l Pu | 10-20 | | | 50-75 | | |
| g/l $H^+$ | 2 | 4 | 8 | 2 | 3 | 4 |
| Filtrate: | | | | | | |
| g/l Pu at 0.04 $\underline{M}$ $H_2C_2O_4$ | 0.015 | -- | 0.9 | 0.05 | 0.06 | 0.09 |
| g/l Pu at 0.07 $\underline{M}$ $H_2C_2O_4$ | 0.017 | -- | 0.9 | 0.02 | 0.04 | 0.04 |
| g/l Pu at 0.10 $\underline{M}$ $H_2C_2O_4$ | -- | 0.05 | --- | 0.016 | 0.012 | 0.016 |
| g/l Pu at 0.13 $\underline{M}$ $H_2C_2O_4$ | 0.020 | 0.03 | 1.0 | 0.03 | -- | -- |
| g/l Pu at 0.16 $\underline{M}$ $H_2C_2O_4$ | -- | 0.02 | --- | 0.04 | -- | -- |

All slurries chilled to less than 10°C before filtration.

### Table III - Separation of Plutonium from Aluminum, Chromium, Iron and Uranium

| Element | Run No. | Solution | Metal Content ppm (1) | | |
|---|---|---|---|---|---|
| | | | Feed Solution | $Pu(C_2O_4)_2$ Cake | Button |
| Al | 192 | Spiked 3BP 60 g/l Pu | 300,000 | 1750 | 40 |
| | 193 | Spiked 3BP 60 g/l Pu | 300,000 | 1550 | 20 |
| | 163 | AT 60 g/l Pu | | 800 | 20 |
| | 191 | 3BP 10 g/l Pu | 50,000 | 50 | 1 |
| | 99 | Spiked stock 223 g/l Pu | 10,000 | 640 | -- |
| Cr | 192 | Spiked 3BP 60 g/l Pu | 200,000 | 200 (2) | 40 |
| | 193 | Spiked 3BP 60 g/l Pu | 200,000 | 200 (2) | 4 |
| | 174 | Syn. 3BP 60 g/l Pu | 100,000 | 800 | 10 |
| | 191 | 3BP 10 g/l Pu | 2,000 | 20 | 2 |
| Fe | 99 | Spiked stock 223 g/l Pu | 10,000 | 950 | -- |
| | 100 | Spiked stock 150 g/l Pu | 10,000 | 180 | -- |
| | 191 | 3BP 10 g/l Pu | 5,000 | 350 | 135 |
| | 192 | Spiked 3BP 60 g/l Pu | 5,000 | --- | 230 |
| | 193 | Spiked 3BP 60 g/l Pu | 5,000 | --- | 200 |
| U | 28, 32 | Spiked stock 60 g/l Pu | 100,000 | 1000-2400 | -- |
| | 27, 29, 31 | Spiked stock 60 g/l Pu | 10,000 | 150-570 | -- |
| | 30, 33 | Spiked stock 60 g/l Pu | 1,000 | 70 | |

**(1) Parts of impurity element per million parts of plutonium**

**(2) These values are one fifth as large as would be expected on the basis of dilutions occurring during filtration and washing.**

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Table IV - Fission Product Separation Obtained by One Plutonium (IV) Oxalate Precipitation(1) from 3-BP Solution

| Fission Product<br>Strike Conditions |  |  | Pu | Ru |  | Zr - Nb |  | Am |  |
|---|---|---|---|---|---|---|---|---|---|
| Run | M $HNO_3$ | g.Pu/l. | c/min./sample(5) | DF | c/min./sample | DF | c/min./sample | DF | c/min./sample |
| 162 | 2.0 | 1 | $6.45x10^5$ | 15 | (4) | 6.2 | $0.28x10^5$ | 0.7 | $8.42x10^5$ |
| 160 | 5.0 | 1 | $4.93x10^5$ | 2.3 | $3.14x10^5$ | 1.8 | $0.74x10^5$ | 1.0 | $4.52x10^5$ |
| 163 | 2.0 | 10 | $3.80x10^5$ | 10.6 | $0.52x10^5$ | 6 | (4) | 0.8 | $4.44x10^5$ |
| 164 | 5.0 | 10 | $4.14x10^5$ | 15 | (4) | 6 | (4) | 1.1 | $3.74x10^5$ |
| 161 | 2.0 | 60 | $5.57x10^5$ | 15 | $0.52x10^5$ | 3.8 | $0.39x10^5$ | 1.2 | $4.37x10^5$ |
| 159 | 4.9 | 53 | $4.78x10^5$ | 10.2 | $0.64x10^5$ | 2.4 | $0.57x10^5$ | 1.2 | $3.98x10^5$ |
| 3-BP | (2) |  | $4.50x10^5$ | --- | $6.87x10^5$ | --- | $3.66x10^5$ | --- | $4.52x10^5$ |
| 3-BP | (3) |  | $5.22x10^5$ | 1.0 | $7.72x10^5$ | 2.8 | $1.52x10^5$ | 1.0 | $5.08x10^5$ |
| 158 | 5.0 | 115 | $5.52x10^5$ | 9.4 | $0.92x10^5$ | 5.9 | $0.81x10^5$ | 1.0 | $5.46x10^5$ |

(1) Strike at 35°C, by addition of mixed $H_2O_2$ - $H_2C_2O_4$; no pre-reduction.

(2) Solution as received in PR can from Redox.
Starting Solution for run 158.

(3) 3-BP evaporated to 300 g. Pu/l, diluted to 60 g Pu/l, and filtered.
Starting solution for runs 159 - 162 inclusive.

(4) Not detectable.

(5) Each sample contained 3 ml of solution containing 10 grams of plutonium per liter.

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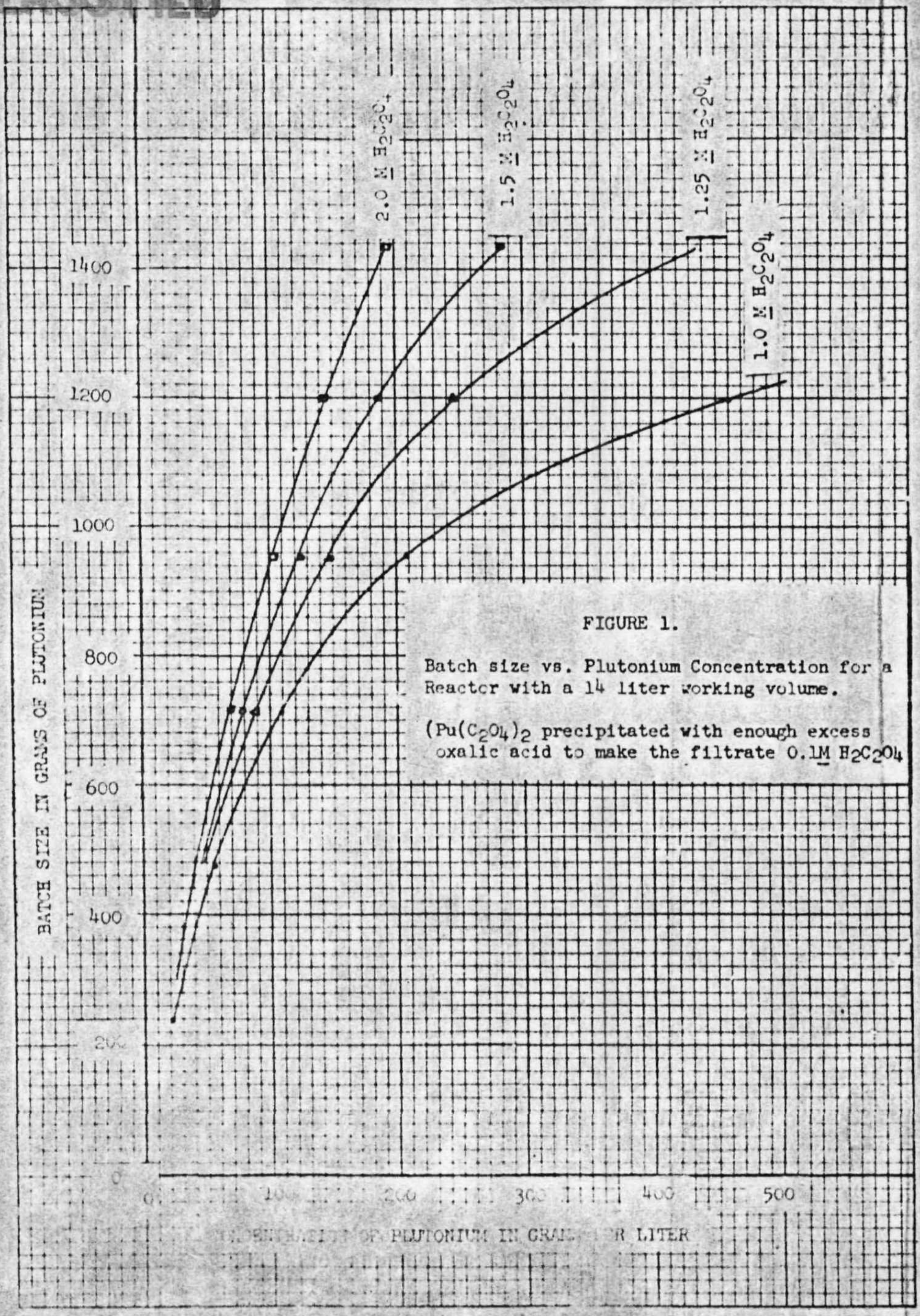

FIGURE 1.

Batch size vs. Plutonium Concentration for a Reactor with a 14 liter working volume.

$(Pu(C_2O_4)_2$ precipitated with enough excess oxalic acid to make the filtrate 0.1M $H_2C_2O_4$

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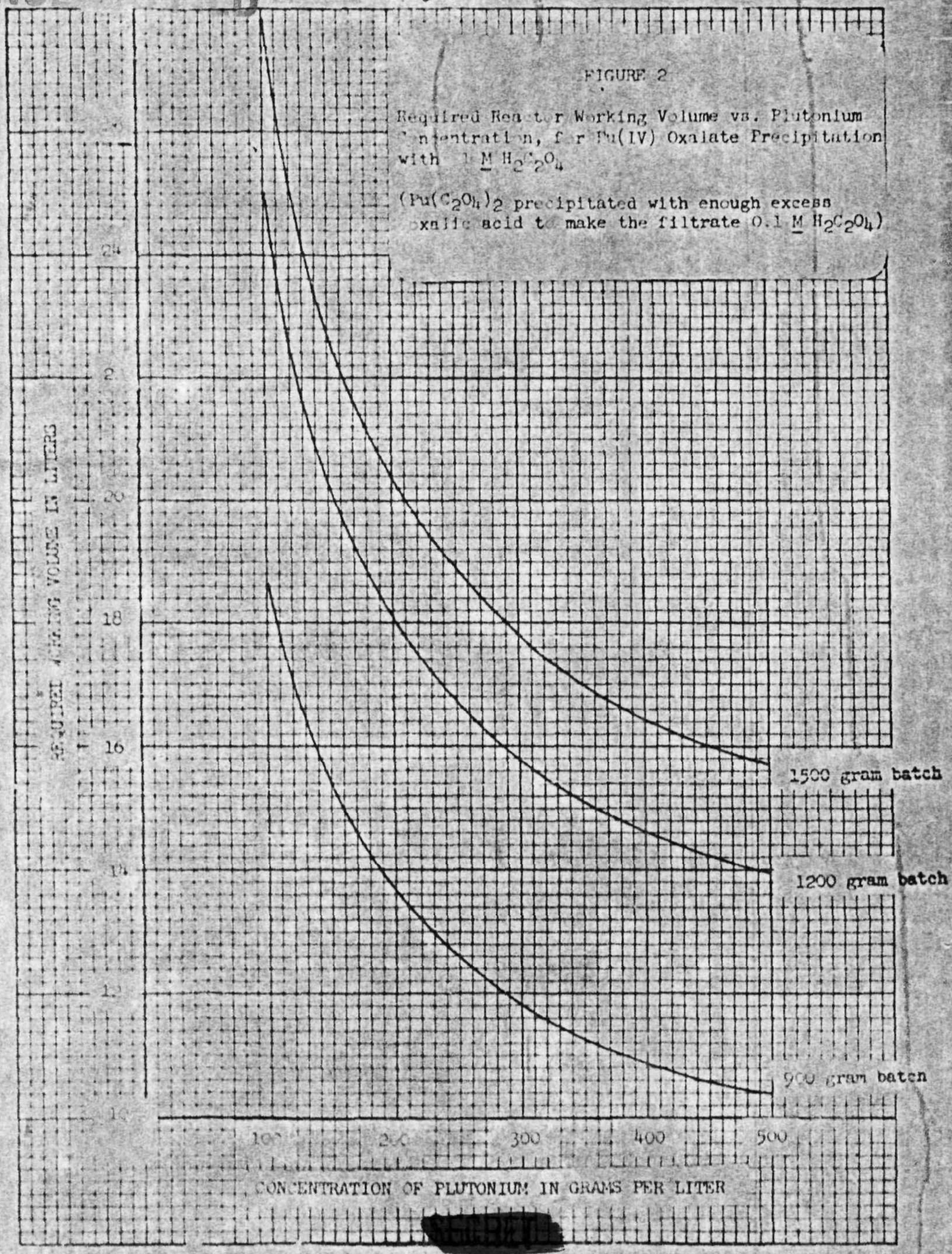

FIGURE 2

Required Reactor Working Volume vs. Plutonium Concentration, for Pu(IV) Oxalate Precipitation with 1 M $H_2C_2O_4$

($Pu(C_2O_4)_2$ precipitated with enough excess oxalic acid to make the filtrate 0.1 M $H_2C_2O_4$)

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