[redacted]

DECLASSIFIED

HW-45700

AEC RESEARCH AND DEVELOPMENT REPORT

TECHNOLOGY - PLUTONIUM

[redacted]

CONTINUOUS PLUTONIUM(IV) OXALATE PRECIPITATION, FILTRATION, AND CALCINATION PROCESS

BY

R. L. BEEDE

CHEMICAL PROCESSING DEPARTMENT

SEPTEMBER 27, 1956

ROUTE TO			SIGNATURE AND DATE
R.H. Hart BNW	67696	NOV 19 1971	

[redacted]

HANFORD ATOMIC PRODUCTS OPERATION

RICHLAND, WASHINGTON

GENERAL ELECTRIC

~~Classification Cancelled (Change to~~
~~CONFIDENTIAL)~~
~~By Authority of Classification Coordinator, Battelle-Northwest~~
By Date 3/21/73

[redacted]

AEC - GE. - RICHLAND WASH

DECLASSIFIED

[redacted]

[redacted]

DECLASSIFIED

T[redacted] docume[redacted] class[redacted]ed by
[redacted]. H[redacted]opkins

HW-45700

Technology - Plutonium
(M-3679, 18th Ed.)

This document consists
of 40 pages. [redacted]

CONTINUOUS PLUTONIUM(IV) OXALATE PRECIPITATION, FILTRATION, AND CALCINATION PROCESS

By

R. L. Beede

234-5 Development Operation
Research and Engineering Operation

September 27, 1956

Classification Cancelled (Change to
DECLASSIFIED
UNCLASSIFIED
By Authority of printout
dated 11-14-74
By L. Pope 9/19/75
J E Savely 6-15-98

~~Classification Cancelled (Change to CONFIDENTIAL)~~
~~By Authority of Classification Coordinator Battelle-Northwest.~~
~~By Date 3/22/73~~

HANFORD ATOMIC PRODUCTS OPERATION
RICHLAND, WASHINGTON

Work performed under Contract No. W-31-109-Eng-52 between the Atomic Energy Commission and General Electric Company

[redacted]

[redacted]is docum[redacted] contains R[redacted]cted Data[redacted]defined i[redacted] Atomic
[redacted] Act [redacted]
tents [redacted]er to [redacted]uthorized p[redacted]on is pr[redacted]hibited.

Route To:	P. R. No.	Location	Files Route Date	Signature and Date
~~H N Mobley~~	~~200-EXT 68~~	~~2704Z~~	~~1-30-57~~	~~2/5~~
REFERENCE COPY	670	234-5	9-7-57	4/22/58

Printed in USA. Charge 40 cents. Available from the U. S. Atomic Energy Commission, Technical Information Extension, P.O. Box 1001, Oak Ridge, Tennessee. Please direct to the same address inquiries covering the procurement of other classified AEC reports.

[redacted]

DECLASSIFIED

[redacted]

EXCLUDED FROM AU[redacted]
[redacted] DECLASSIFICATION

[redacted] [redacted]

[redacted]

Technology - Plutonium
(M-3679, 18th Ed.)

INTERNAL DISTRIBUTION

Copy Number	
1	C. J. Berglund
2	H. W. Crocker
3	K. M. Harmon
4	H. H. Hopkins, Jr.
5	W. N. Mobley
6	W. H. Reas
7	R. B. Richards
8	R. E. Smith
9 - 14	Extra
15	300 Files
16	Record Center

EXTERNAL DISTRIBUTION

Copy Number	
17 - 20	Argonne National Laboratory
21	Armed Forces Special Weapons Project, Sandia
22	Armed Forces Special Weapons Project, Washington
23 - 25	Atomic Energy Commission, Washington
26	Battelle Memorial Institute
27	Chicago Operations Office
28	Chicago Patent Group
29	Dow Chemical Company (Rocky Flats)
30 - 33	duPont Company, Aiken
34	duPont Company, Wilmington
35	Hanford Operations Office
36	Iowa State College
37 - 39	Knolls Atomic Power Laboratory
40 - 41	Los Alamos Scientific Laboratory
42	New York Operations Office
43	Patent Branch, Washington
44 - 46	Union Carbide Nuclear Company (ORNL)
47	University of California Radiation Laboratory, Livermore
48	Vitro Engineering Division
49 - 113	Technical Information Service Extension

[redacted]

[redacted]

[redacted] [redacted]

[redacted]

TABLE OF CONTENTS

[redacted]

[redacted]

[redacted] [redacted]

DECLASSIFIED

[redacted]

LIST OF FIGURES AND TABLES

DECLASSIFIED

[redacted]

[redacted]

agitated by a reciprocating rake. Plutonium (IV) oxalate was continuously filtered, washed with water, and air-dried on the drum. The cake was removed from the drum by a scraper and dropped into a screw-type drier-calciner. The plutonium (IV) oxalate was calcined to plutonium dioxide. The plutonium dioxide could be readily hydrofluorinated in the prototype continuous Task II hydrofluroinator.(4, 5, 6) Continuous decomposition of the oxalate in synthetic plutonium (IV) oxalate filtrates containing plutonium (IV) oxalate solids was demonstrated using co-current flow in a U-shaped reactor.

Feeds containing from 10 to 100 g/l Pu, as plutonium (IV) nitrate, and 1.0 to 6.5 M HNO_3 respectively, can be processed. One molar oxalic acid is used as the precipitant. Filtrate losses ranged from one to five per cent plutonium using Dynel SD-9 as the filter medium on the prototype. Temperatures of 20 to 35 C for the precipitation and filtration are satisfactory. Hold-up times as low as ten minutes for the precipitation process have been demonstrated. Plutonium (IV) oxalate can be calcined at 300 to 400 C in a screw-type drier-calciner to plutonium dioxide and hydrofluorinated at 450 to 550 C. Plutonium dioxide exceeding purity requirements has been produced in the prototype equipment. The oxalate in filtrates can be decomposed continuously with four per cent potassium permanganate using co-current flow with a residence time of fifteen minutes at 45 C.

Advantages of continuous precipitation and filtration are: uniform plutonium (IV) oxalate, improved filtration characteristics, elimination of heating and cooling facilities, and higher capacities through a single unit. Advantages of the screw-type drier-calciner are the continuous production of an oxide satisfactory for feed for the proposed plant vibrating tube hydrofluorinator, and ease of coupling continuous precipitation and filtration to this proposed hydrofluorinator.(7) Continuous decomposition of oxalate in filtrates offers advantages in decreasing filtrate storage requirements when coupled to a filtrate concentrator.

III. DISCUSSION

A. Continuous Plutonium (IV) Oxalate Precipitation and Filtration

1. Laboratory Scale Runs

a. Equipment

The continuous precipitation and filtration process consists of the concurrent addition of a plutonium (IV) nitrate-nitric acid stream and an oxalic acid stream to a vessel with agitation, while slurry is continuously removed and filtered.

The equipment consisted of a glass reactor with a 1600 rpm stirrer, burettes for metering feeds, and sintered Pyrex filter funnels.

b. Process Description

The initial continuous precipitation and filtration run was made by precipitating plutonium(IV) oxalate batchwise at 55 C in an agitated glass vessel by the standard procedure for a 70 to 90 g/1 Pu (IV) feed.(1, 2, 3) Sufficient 1.0 M $H_2C_2O_4$ was added to precipitate plutonium(IV) oxalate and have the resulting slurry contain 0.1 M $H_2C_2O_4$. The slurry was cooled to 20 C. For continuous operation, plutonium and oxalic acid streams were then metered concurrently into the agitated slurry. Slurry was removed simultaneously and filtered. Improvements in plutonium (IV) oxalate settling rate and filterability were immediately apparent after the first throughput, indicating that plutonium (IV) oxalate of larger particle size was formed in the continuous operation. Three throughputs were made: after two throughputs, filtration rates no longer improved.

c. Temperature

The next investigation tested whether the initial batch precipitation with a 90 g/1 Pu feed could be performed at room temperature and produce a slurry with satisfactory filtration characteristics during continuous operation. (The filtration properties of plutonium (IV) oxalate from a batch precipitation at room temperature from 90 g/l Pu are very poor).(3) After three throughputs, the filterability was much improved and equal to the filterability after one throughput in the first run. These room temperature precipitations demonstrated that a continuous precipitation and filtration process does not require heating and cooling facilities.

d. Residence Time

The first two runs were made with residence times of two hours in the reactor. The residence time can be defined as the weight in grams of plutonium holdup divided by grams of plutonium per minute added in the feed. A holdup is the grams plutonium in the unit at any given time.

For a single precipitation and filtration unit to handle plant production, this residence time represented a large plutonium holdup and would result in a design problem for a critically safe operation. The next runs were made to evaluate reduced residence time and to determine the effects upon filterability. Runs were made with 30, 20, 15, and 10 minute residence times with 90g/l Pu (IV) feeds, and no differences in filterability or settling characteristics were apparent.

e. Startup Procedures

The next investigation was the development of a procedure whereby the first portion of slurry to be filtered would have good filtration characteristics. The most satisfactory method of startup consisted of precipitating 15 per cent of the plutonium operating holdup by metering 1.0 $\underline{M}$ $H_2C_2O_4$ into a plutonium (IV) nitrate solution at room temperature with agitation. The plutonium (IV) nitrate and oxalic acid streams were then metered concurrently until the operating level (100 per cent) was reached and a readily filterable slurry was produced.

Another possible method of startup investigated consisted of charging the precipitation vessel with filtrate from a previous run and metering the plutonium (IV) nitrate and oxalic acid streams concurrently with filtration beginning simultaneously. This method is unsatisfactory because a slurry with very poor filtration characteristics was obtained.

f. Valence Adjustment

Since plant plutonium solutions do not contain 100 per cent plutonium (IV), a valence adjustment step is required. Plutonium nitrate solutions containing 30 g/l Pu (IV) - 65 g/l Pu (VI) and 4.0 to 6.0 M HNO_3 were prereduced to 100 per cent plutonium (IV) by the addition of 50 per cent hydrogen peroxide. This reaction is rapid (about five minutes) with 70 to 90 g/l Pu and 4.0 to 6.0 M HNO_3 solutions. Feeds of 10 g/l Pu (IV) and 1 M HNO_3 were prepared from 90 g/l Pu (IV) and 5 M HNO_3 by dilution and the addition of nitric acid. To prereduce plutonium (VI) nitrate feeds at 10 g/l Pu and 1.0 M HNO_3 heat and control of the quantity of hydrogen peroxide are needed to prevent precipitation of plutonium peroxide.

Continuous plutonium (IV) oxalate precipitation with a feed containing 30 g/l Pu (IV) - 65 g/l Pu (VI) and 5.0 M HNO_3, with an hour residence time at 15 C and a mixed hydrogen peroxide -oxalic acid stream(3) was unsatisfactory. Oxalate cake filtration improved with operating time, but soluble plutonium in the filtrate produced filtrate losses of 16 per cent. From this run, it was concluded the plutonium (VI) was not reduced, and this method of combining reduction and precipitation was discontinued.

g. Continuous Prereduction

Small scale tests were made in which plutonium (VI) feed containing 40,000 ppm iron was continuously prereduced at room temperature. The startup procedure for continuous prereduction consisted of the addition of hydrogen peroxide to an agitated plutonium solution over a five-minute period

[redacted] [redacted]

[redacted]

more difficult it becomes to produce a filterable plutonium (IV) oxalate slurry. To aid particle growth, slower oxalic acid addition times and longer digestion of the slurry are required.(3, 9) Large amounts of metallic impurities effect the startup of the continuous precipitation process; however, a slurry as filterable as one from a pure feed is produced during the continuous operation. For a feed of 95 per cent purity, a 15 per cent batch startup will produce a slurry of optimum filtration properties. Per cent purity is the per cent of plutonium considered with respect to all metallic ions present. The 15 per cent batch startup for feeds of 95 to 84 per cent purity produces slurries of optimum filtration characteristics after one-half to one throughput.

k. Filtrate Losses

Filtrations made with "M" sintered Pyrex (10 to 15 micron nominal pore size) produced soluble filtrate losses of 1.0 to 0.04 g/l Pu. Dynel SD-9, a filter cloth marketed by T. Shriner and Son, retains plutonium (IV) oxalate from the continuous precipitation process but it passes fines of plutonium (IV) oxalate prepared by the standard batch precipitation process. Filtrate losses for the Dynel SD-9 were 1.7 to 0.04 g/l Pu. Sintered stainless steel frits, micrometallic "F" and "E" were tested for oxalate particle retention from the continuous process. Micrometallic "F" (nominal pore size 20 microns) would retain, and micrometallic "E" (nominal pore size 35 microns) would not retain this oxalate.

l. Purity Data

Purity data for continuous plutonium(IV) oxalate precipitation and batch precipitation processes from 90 g/l Pu feed were determined as a function of wash type and wash volume. The data are recorded in Table I. A continuous precipitation run with the same feed adjusted to 10 g/l Pu and 1.0 M HNO_3 was made and the purity data are recorded in Table II.

[redacted]

[redacted]

These data show the continuous process to be equivalent to the batch process for metallic impurity removal, with no significant differences for impurity removal evident for precipitation from 10 or 90 g/1 Pu feed.

The data in Table I and Table II indicate little change in plutonium (IV) oxalate cake impurity as a function of wash volume. This is believed to result from the low solution holdup on the readily filterable continuously prepared oxalate.

2. Prototype Runs

a. Equipment

The equipment used in the prototype runs consisted of a modified Eimco rotary drum filter with accessory tankage, pumps, and drive apparatus (Figure 2). The 18 inch diameter by 12 inch wide Eimco drum filter was modified to reduce the pan volume from 22 to 14 liters. The filter area was reduced to a maximum of 1.2 square feet (18 inch diameter by 3 inch wide band). The voids in the drum were filled with paraffin wax to increase the minimum critical mass. A reciprocating rake in the filter pan used for agitation consisted of five one-half inch angle irons on two-inch centers, thirteen inches wide with a four-inch travel. The drum filter and pan were constructed of 316 and 304 stainless steels and a Dynel SD-9 filter cloth was used for the filtering medium. The plutonium and oxalic acid streams were pumped by air-vacuum operated pumps into the filter pan where plutonium (IV) oxalate was precipitated. The plutonium (IV) oxalate was picked up by the revolving drum and washed at the top of the drum. Air-dried oxalate cake was removed from the drum by a scraper and the cake dropped into the screw-type drier-calciner shown in Figure 2.

b. Operation

In this prototype equipment, 15 per cent of the operating level plutonium holdup was metered in while an air blowback was maintained on the drum to keep plutonium solution from entering the drum. Then 15 per cent of the operating level holdup of oxalic acid was metered in, with the air blowback maintained on the drum and with the agitator operating. After the 15 per cent startup batch strike was made, the feeds were added concurrently and when the operating level (or 100 per cent holdup) was reached, the air blowback on the drum was stopped and the vacuum turned on. From this point, the continuous operation began. Prototype run data are summarized in Table IV.

c. Critical Mass Control

A one kilogram plutonium batch limit was used in each run for critical mass safety since the minimum critical mass was established as 1.2 kilograms.(10) The kilogram batch limited the plutonium feed volume to 11.1 liters for 90 g/l feed.

d. Feed Source and Prereduction

Feeds processed in the prototype equipment were concentrated CCP and dissolved plutonium metal solutions diluted to about 90 g/l. Feed plutonium purities ranged from 84 to 96 per cent for the concentrated Recuplex CCP and 90 to 96 per cent for the dissolved metal solutions. Typical compositions of these feeds are given in Tables I, II, and III. The Recuplex CCP was used for the first five runs. Fifty thousand parts per million each of aluminum and iron were added in run No. 3; 25,000 ppm of aluminum was added in run No. 4, and 20,000 ppm each of aluminum and iron were added in run No. 5 for performance studies. The last four runs (No. 6, 7, 8 and 9) were made with dissolved plutonium metal solutions to which aluminum had been added. Plutonium concentrations in the feeds ranged from 70 to 95 grams per liter and nitric acid concentrations ranged from 4.0 to 6.5 molar.

Feeds for the nine prototype runs were prereduced to the plutonium (IV) batchwise by the addition of 50 milliliters of 50 per cent hydrogen peroxide per mole of plutonium at room temperature. A temperature rise of about 5 C was obtained.

e. Plutonium (IV) Oxalate Cake

The thickness of the plutonium (IV) oxalate cake on the drum filter ranged from one-quarter to one-half inch under optimum operating conditions. Under startup conditions when the cake was of poor quality, less cake was picked up. After the feed addition was completed, the slurry was removed from the pan by continued operation of the rotary filter. A marked increase in cake thickness occurred at this point in the first seven runs, and oxalate cake up to 1.5 inches thick was picked up. A slurry concentration resulted from inadequate agitation throughout the run and was corrected in the last two runs by increasing the agitator frequency.

The plutonium (IV) oxalate on the filter drum was a light color at the beginning of some runs and did not dry readily; but during continuous operation, the dark "olive drab" color was produced and the oxalate was dry (free of absorbed liquid) before reaching the scraper.

f. Agitation

The agitator frequency in the first seven runs was about 90 cycles per minute. The last two runs were made with an agitator frequency of 140 cycles per minute, and improved slurry pick-up on the drum was observed. This resulted from adequate suspension of the large plutonium (IV) oxalate particles that are produced by the continuous precititation.

g. Drum Speed

The filter drum speeds ranged from six to eighteen revolutions per hour. No differences in washing efficiency or dryness of the cake as a function of drum speed were observed when optimum slurry properties were present.

The faster drum speed was tried to aid in controlling the liquid level in the pan. This method of maintaining liquid level was not satisfactory since nearly the same quantity of filtrate was obtained per unit time even though more plutonium (IV) oxalate was removed from the pan.

The only satisfactory method of controlling liquid level, other than changing feed rates, was adjustment of the vacuum differential across the drum.

h. Washing

Plutonium (IV) oxalate from the first three runs was washed with 2 M HNO_3 - 0.05 M $H_2C_2O_4$. The wash flow rate was 50 per cent of the plutonium feed rate. A water wash was used in the last six runs. The water wash flow rate was 30 to 50 per cent of the plutonium feed rate. The water wash gave no evidence of "peptizing" the cake, as had been observed previously with batch precipitated plutonium(IV) oxalate.

The water wash was tested to see if the nitric acid vapors produced in the calciner from residual liquid in the cake could be reduced or eliminated. The water eliminated the nitric acid vapors in the calciner and also reduced plutonium dioxide dusting. (See Section B, below.)

i. Temperature

The continuous precipitation and filtration in the unit were carried out at 28 to 35 C. The plutonium and oxalic acid feed streams were at room temperature. The temperature obtained in the filter pan was partially the result of the heat of formation of plutonium (IV) oxalate. A larger contributor to the temperature increase was the heating of the pan and filter by the drier-calciner heating units.

j. Residence Time

The first three runs were made with a ten liter holdup and one-half hour residence time. Initially, it was thought that controlling the liquid level below ten liters would be difficult, but since very little data could be collected with the imposed one-kilogram plutonium batch limit, the holdup volume was changed to five liters in the next five runs. The five-liter holdup made possible a run with three throughputs instead of one throughput, and more operating experience could be obtained. Five runs were made with residence times of 30, 30, 20, 20, and 15 minutes, respectively. The last run made in this equipment and reported here was made with a holdup of 1.5 to 4 liters or residence times of four to ten minutes. Difficulty in maintaining a low liquid level arose because less filter drum area was exposed to the slurry, and because a zero per cent startup had to be used. The zero per cent startup in this equipment is unsatisfactory, since little agitation is produced when the pan contains less than one liter. The poor agitation, with the resulting poor cake characteristics, produced poor oxalate cake pickup and filtration throughout the first portion of this run.

k. Filter Cloth Performance

Filtration rates up to 0.4 liter per minute were obtained with the Dynel SD-9 filter area of 0.8 square feet (54 inches in circumference by 2 inches wide) with a vacuum differential of six inches of mercury and an operating level of five liters.

The filter cloth is stable in 5 M HNO_3 -1 M $H_2C_2O_4$, dilute hydrogen peroxide and acidified potassium permanganate solutions. Hot neutral potassium permanganate causes the Dynel SD-9 to disintegrate. On the sixth prototype run, trouble was encountered in getting the filter cloth to to filter. A pressure differential of 13 inches of mercury could be maintained across the drum, and little filtering was evident. The feed for this run was dissolved metal solution and contained some undissolved plutonium dioxide which may have caused the blinding. The filter cloth was replaced. During the removal of the cloth, it was evident the cloth had lost some plysical strength, which may also have contributed to the blinding.

Additional tests were then made with samples of Dynel SD-9 immersed in 5 M HNO_3 - 0.1 M $H_2C_2O_4$ and in 5 M HNO_3 -0.1 M $H_2C_2O_4$ - 80 g/l Pu (as plutonium(IV) oxalate slurry) at room temperature. After seven weeks, a loss in physical strength was evident for the Dynel SD-9 immersed in the plutonium bearing test solution. Radiation -induced degradation is suggested as causing the loss of physical strength.

A test to check the blinding of Dynel SD-9 had been performed by W. S. Figg and reported in HW-41702H.(11) A plutonium (IV) oxalate slurry was prepared, and filtered and recycled through Dynel SD-9 cloth for two days. After and equivalent of 500 hours of filter drum operation no blinding was evident.

The Dynel SD-9 cloth is expected to last at least three weeks in continuous operation; however, investigations for better filter media will continue.

1. Filtrate Losses

Filtrate losses ranged from one to five per cent plutonium in the prototype runs, except in run No. 3.

The higher filtrate losses from the prototype operation were due to leakage of slurry by the filter media mounting system, and to fines which were present at the beginning of the filtration. Also, the method of startup could have contributed to the over-all filtrate content because plutonium solution may have leaked through the cloth or around the cloth, even though an air blowback was used. Expected soluble plutonium losses from continuous precipitations are 0.04 to 1.0 g/l, or as many as 50 times lower than the filtrate losses obtained in the prototype.

Run No. 3 had a plutonium filtrate loss of 16 per cent. Small scale continuous oxalate precipitations and batch oxalate precipitations with the same feed confirmed that the continuous process and the prototype equipment were not the cause of the high plutonium concentrations in the filtrate. The metallic impurities in the feed were not the cause of the high plutonium concentrations in the filtrate. This was demonstrated by making batch precipitations with slurries containing 0.8, 0.14, and 0.30 molar excess oxalic acid. It is believed that organic contaminants in this concentrated Recuplex CCP feed formed a stable plutonium complex.

m. Plutonium (IV) Oxalate Purity

The purity of the plutonium (IV) oxalate produced in the first four runs was unsatisfactory in the prototype equipment because of external contamination. After the fourth run, the materials of construction producing this contamination were cleaned and painted with Tygon in an attempt to produce plutonium (IV) oxalate of satisfactory purity. Data were collected across the prototype oxalate precipitation process and across the drier-calciner. The data on the prototype oxalate precipitation are recorded in Table III. The data across the drier-calciner are discussed in a later section and are reported in Table IV. The data in Table III indicate satisfactory performance of the prototype precipitation and filtration unit.

The data in Table III show that feeds containing 50,000 ppm aluminum and 44,000 ppm iron can be processed and will produce plutonium (IV) oxalate of satisfactory purity for subsequent calcination, hydrofluorination, and reduction to metal of the necessary purity.

B. Prototype Screw Drier-Calciner

1. Equipment

Continuous calcination has been demonstrated and reported with the prototype Task II hydrofluorination equipment.(4) Much difficulty was encountered feeding plutonium (IV) oxalate into this unit. In planning the precipitation and filtration equipment for the present work, a screw-type drier-calciner was also included to determine if it would calcine plutonium(IV) oxalate satisfactorily and produce a satisfactory plutonium dioxide for feeding this continuous Task II hydrofluorinator.(5)

[redacted]

[redacted]

The drier-calciner consists of a 304L stainless steel trough and screw. The trough is round-bottomed, three inches wide and three and one-third feet long. The screw conveyor is three inches in diameter, has a one and one-half inch shaft and a three-inch pitch. The screw is driven by a variable speed motor with a shaft through the hood panel. Speeds can be adjusted from 0.6 to 1.2 revolutions per minute. The trough is heated by three twelve-inch independently controllable 1650 watt furnaces.

2. Operation

Plutonium (IV) oxalate was fed into the trough via the scraper attached to the drum filter. Plutonium dioxide dropped out of the other end into a four-inch diameter stainless steel receiver.

The trough was open at the feed and exit ends and was covered with a thirty-inch long Transite cover.

A schematic diagram of the drier-calciner is included in Figure 2.

3. Feeds and Processing Rates

Feeds processed in the drier-calciner were plutonium(IV) oxalate from the nine runs processed in the prototype drum filter. Additional runs were made using plutonium (IV) oxalate from the present 234-5 Building batch Task I process.

Feed rates up to two kilograms per hour were processed. It was determined that the furnaces would handle one kilogram per hour. Higher feed rates produced significant temperature drops in the drier-calciner.

A Screw speed of one revolution per minute was used, which gave a contact time of eleven minutes per pass. Runs were made with plutonium(IV)

[redacted]

[redacted] ~~UNCLASSIFIED~~ DECLASSIFIED

[redacted]

oxalate feed rates of one kilogram plutonium per hour at 300 C and 400 C, and two passes through the unit were required to obtain complete conversion to plutonium dioxide.

4. Temperature of Operation

The plutonium dioxide produced from the drier-calciner was used as feed for the Task II prototype continuous hydrofluorinator.

Temperatures greater than 400 C were not readily obtainable in this drier-calciner unit because of heat losses into the hood and the accompanying equipment. Calcination temperatures greater than 480 C decrease the reactivity of the oxide in subsequent hydrofluorination, and should not be used.

No permanent sticking of the plutonium (IV) oxalate or the decomposition products was observed. Particle sizes up to one-quarter inch were present after one pass, and after the second pass, a few particles of one-sixteenth inch were present.

5. Per Cent Calcination

Two passes of the oxalate through the unit at one kilogram per hour at 300 or 400 C were necessary to effect conversion to plutonium dioxide. Samples of powder taken after two passes were determined to be 98.4 to 99.6 per cent calcined. The per cent calcination was determined by exposing weighed samples of product in air at 500 C, reweighing, and calculating the per cent conversion to plutonium dioxide.

Plutonium(IV) oxalate calcined at 300 or 400 C has been successfully hydrofluorinated at 450 and 500 C in the prototype vibrating tube hydrofluorinator and reduced to metal.

DECLASSIFIED

[redacted]

[redacted]

6. Purity

Purity data on plutonium dioxide and plutonium (IV) oxalate feeds are recorded in Table V. These data indicate 304L stainless steel to be a satisfactory construction material for the drier-calciner.

Plutonium metal produced from runs Nos. 5, 6, 7, and 8 contained less than 50 ppm aluminum, 200 ppm chromium, 200 ppm iron, and 200 ppm nickel.. These data indicate that for feeds similar to those processed, approximately 2500 ppm of metallic impurities will be present in the oxides and less than 800 ppm of aluminum, chromium, iron, and nickel will be present in the metal.

Purex, Redox, and Recuplex plutonium product solutions will be satisfactory feeds for the described continuous process (and materials of construction) for the production of plutonium metal of the necessary purity.

C. Plutonium (IV) Oxalate Filtrate Treatment

Filtrates from batch and continuous plutonium (IV) oxalate precipitations contain plutonium which can be recovered in Recuplex of Redox. The soluble oxalate and insoluble fines in the filtrates must be decomposed with four per cent potassium permanganate solution before the filtrate can be processed.

The decomposition of batch and continuously produced plutonium (IV) oxalate filtrates with four per cent potassium permanganate solution was investigated to determine the optimum kill conditions.(12)

1. Laboratory Scale Kills

a. Batch

DECLASSIFIED

(1) Equipment

The equipment consisted of an agitated glass vessel for mixing the potassium permanganate and oxalate bearing filtrates. The vessel was heated on a hot plate.

[redacted]

[redacted]

DECLASSIFIED

[redacted]

(2) Process Description

Runs were made by metering four per cent potassium permanganate solution into filtrates, by metering filtrates into the permanganate, and by simultaneous mixing of the two streams. The oxalate-permanganate reaction was stopped by the addition of 50 per cent hydrogen peroxide, which reacted with the permanganate and converted manganese dioxide to soluble manganous ion. The rate of kill was not determined, but rather the time and temperature necessary to produce solutions free of oxalate solids after standing a minimum of twenty-four hours at room temperature.

(3) Filtrate Preparation

The filtrates used for the "kill" studies were prepared by adding 100 ml of one molar oxalic acid rapidly to a plutonium (IV) nitrate and nitric acid solution at room temperature to produce one liter of simulated filtrate containing oxalate solids. The filtrates contained 0.7 g/l Pu and 5 g/l Pu, 3 $\underline{M}$ HNO_3 and 0.1 $\underline{M}$ $H_2C_2O_4$.

The plutonium(IV) oxalate solids produced in the 0.7 g/l and 5.0 g/l Pu bearing solutions were retained by "M" sintered Pyrex filters but were passed by "C" sintered Pyrex filters. An oxalate particle growth occurred with aging, and after the filtrates were aged twenty-four hours at room temperature the solids were retained by "C" sintered Pyrex filters. Runs were also made with fresh and aged plutonium (IV) oxalate filtrates prepared by adding one molar oxalic acid at 55 C during a 20-minute period to aid particle growth. The oxalate was retained by "C" sintered pyrex. These particle size ranges and plutonium concentrations represent the upper limits of particle size and plutonium concentration encountered in a plant batch or continuous oxalate precipitation and filtration process.

DECLASSIFIED

[redacted]

[redacted]

(4) Mixing Filtrate and Permanganate

No significant differences in the time required for a kill were obtained for the three methods of mixing the filtrate and potassium permanganate. The time necessary for a kill is the time required to decompose the oxalate after the addition of permanganate to filtrate (or filtrate to permanganate). Simultaneous mixing of the two streams on a large scale is not recommended because of the rapid carbon dioxide evolution rate.

(5) Excess of Permanganate

Excesses of permanganate, up to 80 per cent over the quantity necessary to oxidize Pu (IV) to Pu (VI) and the oxalate to carbon dioxide (with manganous ion as a product), has no discernible effect upon the time and temperature relationship. Temperature was found to be more important, probably because of the dependence of the reaction upon the rate of solution of solid plutonium(IV) oxalate.

(6) Results

The data from the laboratory runs are summarized in Table VI. A flow diagram is shown in Figure IV.

To assure a complete kill of filtrates, a temperature of 45 C with agitation for five minutes is required after mixing the reactants.(12)

b. Continuous Kills---Co-current Flow

(1) Equipment

The permanganate oxalate kill column used in these experiments was a one-inch diameter vertical glass pipe which was operated with a 15-inch column of solution.

(2) Process Description

Permanganate and filtrate were added co-currently at the top of the column and the effluent was removed at the bottom. No agitation is used in

[redacted] [redacted]

[redacted]

the column, since vertical mixing is not desirable. The effluent was treated continuously with hydrogen peroxide to stop the permanganate-oxalate reaction.

The solution was heated with an immersion heater at the inlet and the temperature was measured with a thermometer on the effluent end.

Downflow and upflow were both tested; however, most of the runs were made with downflow to minimize the back-mixing caused by the carbon dioxide. Most of the carbon dioxide is produced near the inlet of the column and if upflow were used, the carbon dioxide would travel through the column and produce mixing.

(3) Filtrate Preparation

The synthetic filtrates used in these tests have the same properties as those described under batch kills.

(4) Excess Permanganate

Continuous runs with 80 per cent excess permanganate were made, but excess permanganate produced no increase in reaction rate. Five to ten per cent more than the stoichiometric amount of permanganate should be used, since some manganese dioxide is formed.

(5) Results

The fresh 0.7 g/l and 5.0 g/l Pu bearing filtrates were killed with a 15 minute residence time at 45 C.

The plutonium (IV) oxalates from these freshly-prepared filtrates and plutonium concentration have larger particle sizes and higher plutonium concentrations than those expected from a continuous oxalate precipitation and filtration process. Filtrates aged for 24 hours and those prepared by

[redacted]

[redacted]

controlled oxalic addition at 55 C were killed with a residence time of 30 minutes at 45 C. The 30-minute residence for these filtrates is borderline; and if this much time is required, the temperature should be raised to increase the rate of solution of the solid oxalate.

The data for the laboratory scale co-current flow "kills" are summarized in Table VII.

c. Continuous Kills - Homogeneous Agitated Reactor

(1) Equipment and Process Description

The permanganate and filtrate streams were metered into an agitated reactor which overflowed into another reactor containing hydrogen peroxide. The process consisted of metering four per cent potassium premanganate into the agitated reactor containing the filtrate at the desired temperature until a batch kill was made. The permanganate and filtrate were then metered concurrently into the agitated solution and the contents were withdrawn continuously. Hydrogen peroxide was added to the oxidized filtrate to destroy the excess permanganate.

(2) Filtrate Preparation

The filtrates were prepared in the same manner as described previously.

(3) Results

Two runs were made with fresh simulated 5.0 g/1 Pu filtrate, with residence times of 15 and 30 minutes at 45 C. Solid oxalate was evident in the effluent of both runs, but to a much lesser extent with the longer residence time. This type reactor for killing oxalate filtrates is not satisfactory, since a finite quantity of solids can be expected in the effluent even with long residence times.

2. Prototype Kills --- Co-Current Flow

a. Equipment

A U-shaped prototype reactor was installed in the Task I prototype hood to study the effects of backmixing and to make a continuous kill in large-scale equipment. The U-shaped reactor had a four-inch diameter glass pipe oxalate-permanganate reaction arm and a one-inch glass pipe peroxide-permanganate reaction arm. These arms were joined at the bottom by a curved one-inch glass pipe. The solutions were heated at the top, or inlet, of the four-inch column by two immersion heaters.

b. Process Description

The runs perviously discussed were all made in a one-inch column. This column had a height to area ratio of 18, whereas an expected plant unit might be six feet high by six inches diameter, or have a height to area ratio of 2.6.(13) A height to area ratio of 2.6 was used in the oxalate-permanganate reaction arm in this prototype unit.

c. Filtrate Preparation

Four per cent potassium permanganate and the simulated filtrate were mixed in a common line before entering the reactor. Ten per cent hydrogen peroxide was added by gravity through a 3/8 inch diameter tube to the one inch diameter reaction arm.

The filtrate composition was 1.5 g/l Pu (as oxalate aged 18 hours) 0.1 $\underline{M}$ $H_2C_2O_4$, 2 $\underline{M}$ HNO_3, and 3.3 g/l Fe^{+3}.

d. Results

A residence time of 15 minutes at 45 C produced a complete oxalate kill. No back mixing was observed in the oxalate permanganate reaction arm.

A flow diagram for continuous kills with co-current flow is shown in Figure 5. A co-current flow hydrogen preoxide-permanganate reaction

[redacted]

[redacted]

arm is shown. A residence time of five minutes in this arm is suggested; however, any method of mixing the hydrogen peroxide stream with the permanganate-oxalate arm effluent would be satisfactory, since this reaction is extremely rapid.

The prototype investigation showed that the peroxide kill arm should be larger than one inch diameter. This was evident from the change in head produced by the sporadic addition and decomposition of the hydrogen peroxide in this arm, which produced a liquid level control problem in the oxalate-permanganate reaction arm. Initially, the ten per cent hydrogen peroxide was added 24 inches from the surface of the solution. When the hydrogen peroxide was added 12 inches from the surface, the head control problem in the four-inch arm was greatly reduced, but not eliminated. Fifty per cent hydrogen peroxide is unsatisfactory, since impurities can become trapped in the addition line. A run in which permanganate was allowed to enter the hydrogen peroxide addition line was made and the fifty per cent hydrogen peroxide decomposed, heated, and blew back out the addition line. This difficulty was not evident, nor could it be produced with ten per cent hydrogen peroxide.

Some manganese dioxide collected at the bottom of the vessel; however, periodic recycling of the peroxide kill effluent through the bottom should keep this line open. This will be investigated in a new laboratory continuous processing unit.

R. L. Beede / HH Hopkins Jr.
R. L. Beede

[redacted]

[redacted]

[redacted] [redacted] DECLASSIFIED

[redacted]

IV. BIBLIOGRAPHY

1. Harmon, K. M. and J. F. Facer, Jr., The Precipitation of Plutonium (IV) Oxalate in Task I. HW-27563, March 3, 1953 (Secret).

2. Harmon, K. M. and J. F. Facer, Jr., The Precipitation of Plutonium (IV) Oxalate in Task I: Nitric Acid Tolerances; Reactor Dimensions. HW-28168, May 26, 1953 (Secret).

3. Facer, J. F., and K. M. Harmon, Precipitation of Plutonium(IV) Oxalate. HW-31186, March 30, 1954 (Secret).

4. Figg, W. S., Progress Report: Continuous Task II Program, Plutonium (IV) Oxalate Calcination and Hydrofluorination Studies. HW-36173, April 12, 1955 (Secret).

5. Figg, W. S. and H. H. Hopkins, Jr., Technical Specification Letter No. 2 - Continuous Task II - Calcination Reactor Substitution. HW-41635, February 23, 1956 (Secret).

6. Figg, W. S. and H. H. Hopkins, Jr., Technical Specification Letter No. 1 - Continuous Task I. HW-41708, February 28, 1956 (Secret).

7. Hopkins, H. H., Jr., Recommendations for Inclusion of Continuous Task I In Scoping of Continuous Task II. HW-41100, February 22, 1956 (Secret).

8. Attanas, J. G., Improved Task I and II Project Meeting Minutes of May 14, 1956.

9. Beede, R. L., Recuplex Product Coupling to Task I and 231 Building Products. HW-41275, December 5, 1955 (Secret).

10. Ketzlach, N., Critical Mass Considerations For Continuous Filter, 234-5 Development Laboratory. HW-40274, December 2, 1955 (Secret).

DECLASSIFIED

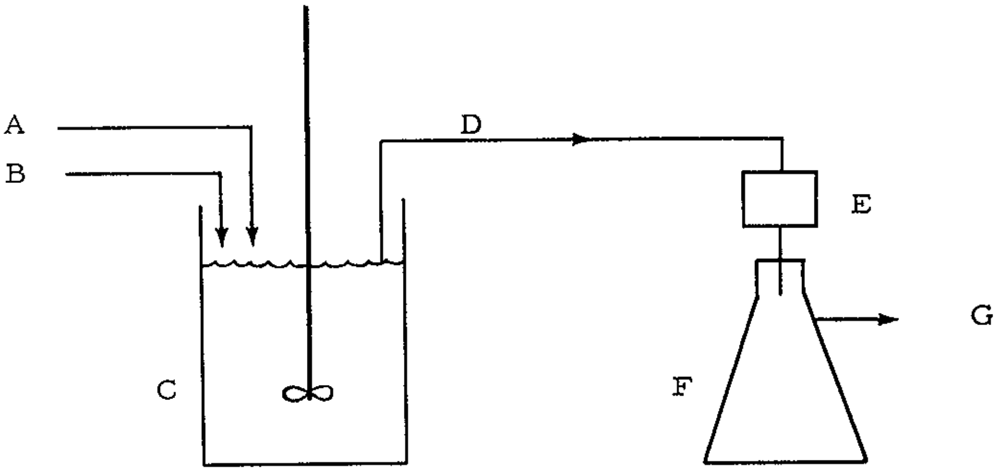
[redacted]

[redacted]

11. Richards, R. B., Separations Technology Section - Monthly Report - February, 1956. HW-41702H, March 12, 1956 (Secret).

12. Beede, R. L. and H. H. Hopkins, Jr., Technical Specification Letter No. 2 - Continuous Task I. HW-44258, July 11, 1956 (Secret).

13. Fritz, J. R., Yoenger, C. F., and J. L. Weeks, Improvements to Task I and II 234-5 Building. HW-44105, July 9, 1956 (Secret).



A, B. Plutonium and oxalic acid feed streams.
C. Agitated precipitation vessel.
D. Vacuum slurry transfer line.
E. Filter funnel.
F. Filtrate receiver.
G. Vacuum

FIGURE 1

LABORATORY SCALE CONTINUOUS PRECIPITATION

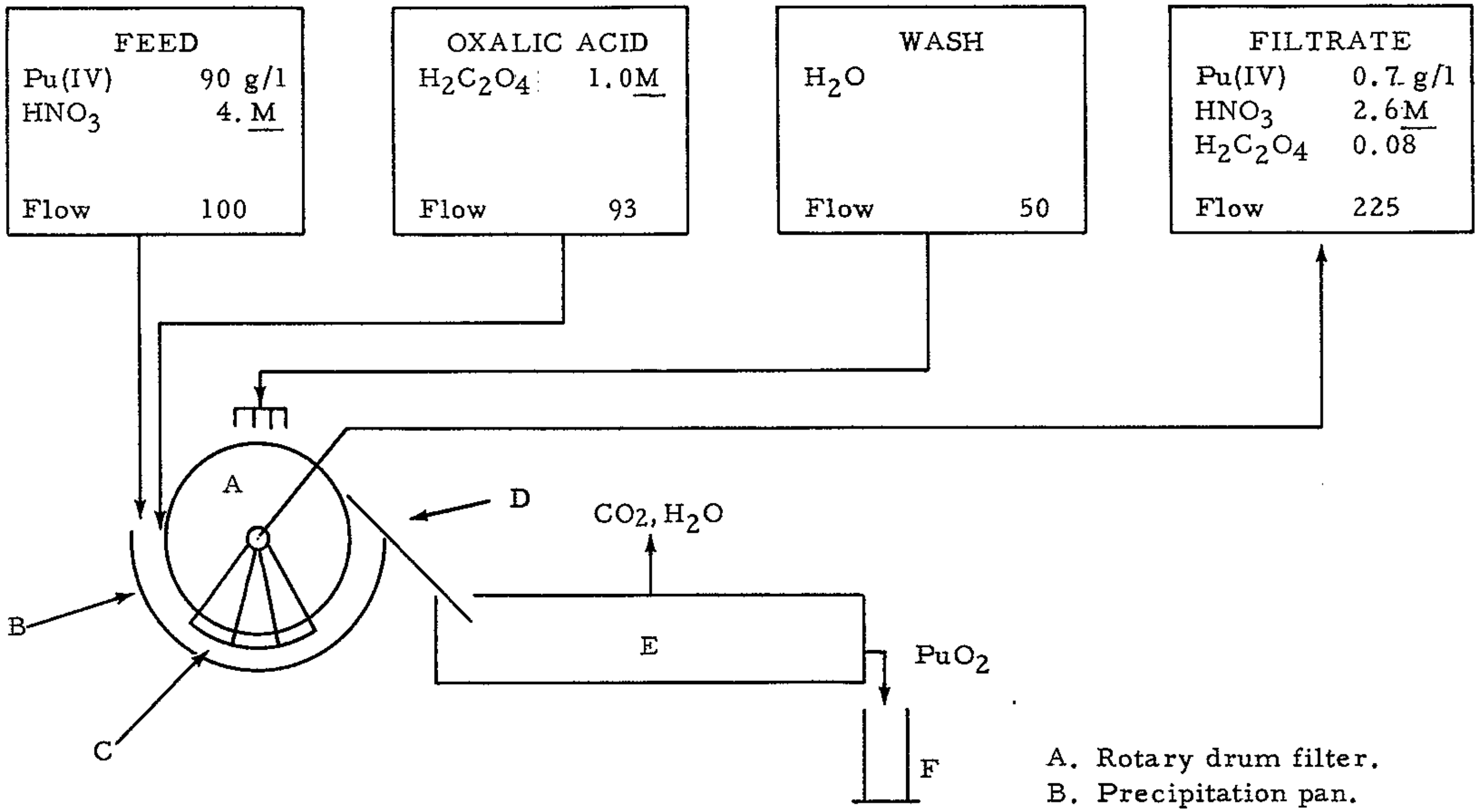
AND FILTRATION EQUIPMENT

[redacted]

[redacted]

~~UNCLASSIFIED~~

DECLASSIFIED



A. Rotary drum filter.
B. Precipitation pan.
C. Agitator.
D. Scraper.
E. Continuous calciner.
F. Oxide receiver.

FIGURE 2

FLOW DIAGRAM FOR CONTINUOUS PLUTONIUM(IV) OXALATE PRECIPITATION, FILTRATION AND CALCINATION

DECLASSIFIED

[redacted]

[redacted]

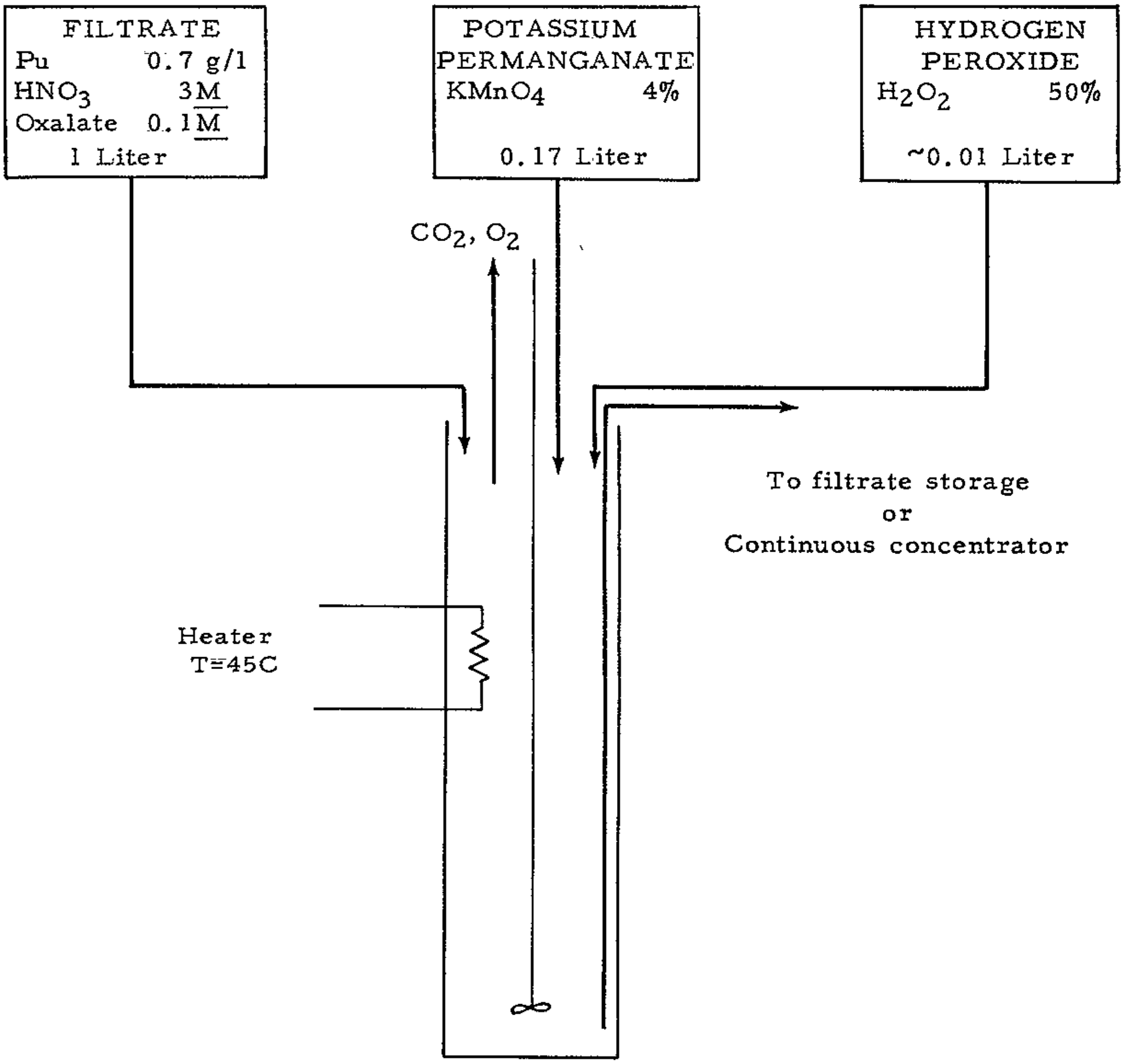


FIGURE 3

FLOW DIAGRAM FOR OXALATE FILTRATE KILL (BATCH)

DECLASSIFIED

[redacted]

[redacted]

[redacted]

[redacted]

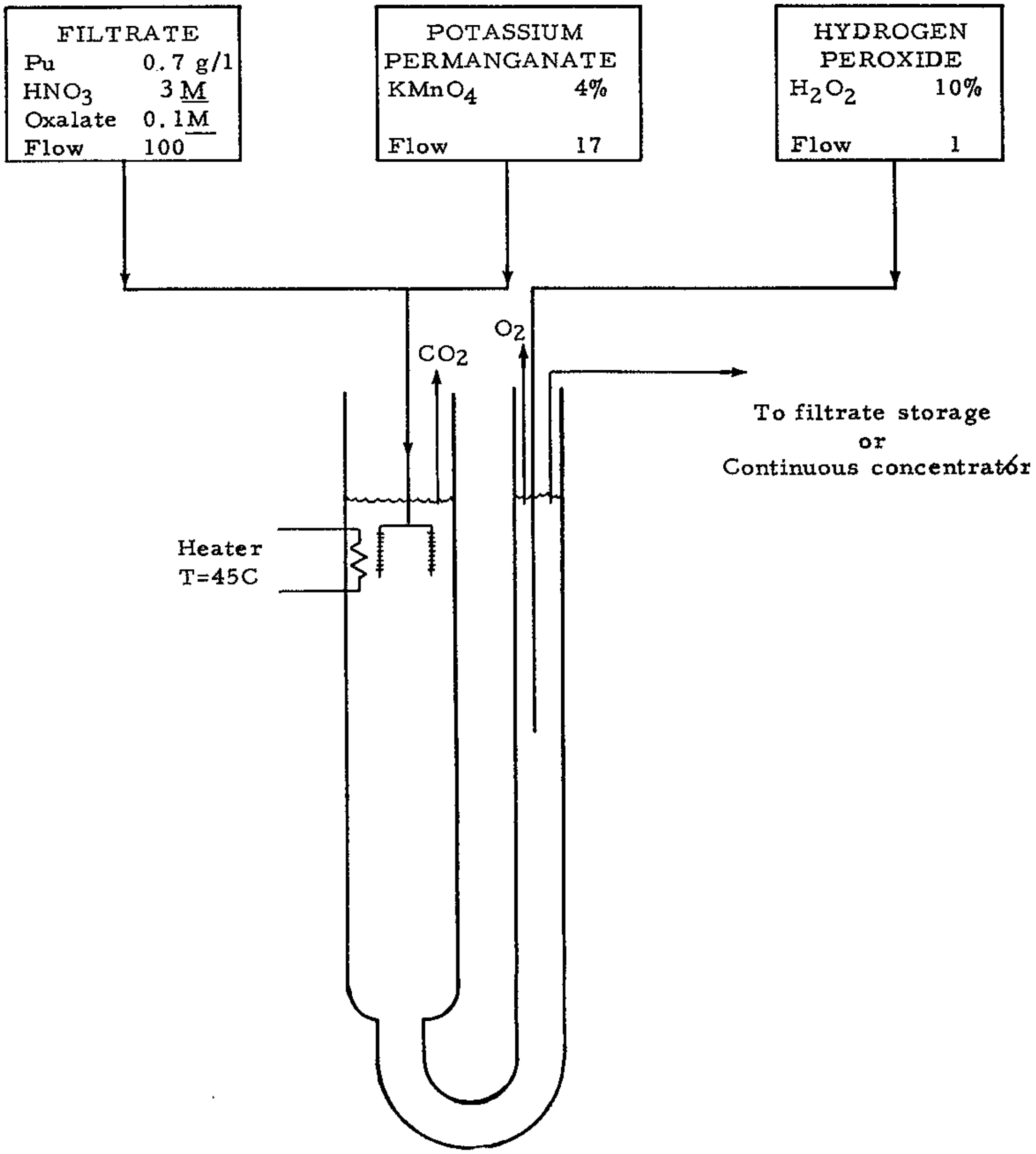


FIGURE 4

FLOW DIAGRAM FOR OXALATE FILTRATE KILL (CONTINUOUS CO-CURRENT FLOW)

[redacted]

[redacted]

[redacted]

[redacted]

[redacted]

DECLASSIFIED

TABLE I

PURITY OF PLUTONIUM(IV) OXALATE FROM 90 g/1 Pu - 4 M HNO_3 FEED

		Batch Precipitated Oxalate					Continuously Precipitated Oxalate			
Element	Feed[(1)]	Not Washed	Equal Volume Water Wash(3)	10X Volume Water Wash(4)	Equal Volume 205 Wash(3,5)	10X Volume 205 Wash(4,5)	No Wash	Equal Volume Water Wash(3)	10X Volume Water Wash(4)	Equal Volume 205 Wash(3,5)
Al	50,000(2)	640	<100	500	500	500				
B	20	30	30	30	50	50	20	20	20	30
Cr	2,000	100	150	300	100	300	150	150	100	100
Cu	600	500	100	700	500	500	100	100	100	100
Fe	44,000	350	650	160	200	200	320	160	130	<100
K	600	--	50	--	100	100	100	50	100	100
Mg	500	200	100	200	200	200	100	105	150	100
Mn	600	<100	100	<100	<100	200	100	100	100	100
Na		200	1000	700	600	600	1000	1000	1000	1000
Ni	1,000	1000	600	200	100	600	150	100	100	100
Pb	200	200	200	200	200	200	200	200	200	200
Si	50	50	100	50	50	50	100	100	100	100
Others(6)										

(1) Feed: Concentrated Recuplex CCP, diluted and spiked with aluminum and iron.
(2) All numbers are parts per million impurity per million parts plutonium, and average of duplicate samples.
(3) Plutonium(IV) oxalate cake volume and wash volume equal.
(4) Plutonium(IV) oxalate cake washed with ten volumes of wash.
(5) 205 solution is 2 M HNO_3 - 0.05 M $H_2C_2O_4$.
(6) Ag, As, Be, Bi, Cd, Ge, La, Li, Mo, P, Sn, V, and Zn not detected.

DECLASSIFIED

[redacted]

TABLE II

PURITY OF PLUTONIUM(IV) OXALATE PRECIPITATED CONTINUOUSLY FROM 10 g/l Pu - 1 M HNO_3

Element	Feed(1)	Plutonium(IV) Oxalate (Not Washed)
Al	50,000(2)	
B	20	
Cr	2,000	< 200
Cu	600	100
Fe	44,000	200
K	600	---
Mg	500	500
Mn	600	< 200
Na		200
Ni	1,000	200
Pb	200	100
Si	50	---
Others(3)		

(1) Feed: This is the same feed used in the runs reported in Table I except it was diluted and spiked with nitric acid.

(2) All numbers are parts impurity per million parts plutonium and the average of duplicate samples.

(3) Ag, As, Be, Bi, Cd, Ge, La, Li, Mo, P, Sn, V, and Zn not detected.

DECLASSIFIED

[redacted]

[redacted]

TABLE III

PURITY OF PLUTONIUM(IV) OXALATE PRECIPITATED CONTINUOUSLY IN PROTOTYPE EQUIPMENT

Element	Run No. 5(1) Feed	Run No. 5(1) Oxalate Not Washed	Run No. 5(1) Oxalate Water(3) Washed	Run No. 6 Feed	Run No. 6 Oxalate Water Washed(3)	Run No. 8 Feed	Run No. 8 Oxalate Water Washed(3)	Run No. 9 Feed	Run No. 9 Oxalate Water Washed(3)
Al	50,000(2)	80	80						
B	20	20	20	40	2	40	2	40	20
Cr	2,000	100	100	2000	30	4000	1000	10000	400
Cu	600	100	100	2000	10		<20	400	<20
Fe	44,000	390	370	4200	<50	10600	490	17000	560
K	600	150	150	200	200		700		1000
Mg	500	200	200	400	20	400	300	2000	100
Mn	600	100	100	400	30	2000	200	2000	400
Na		1000	1000	2000	500	20000	2000	20000	2000
Ni	1,000	100	100	1000	200	1000	200	2000	100
Pb	200	100	100	400	100	400	200	1000	1000
Si	50	100	100	200	50	100	100	100	100
Others(4)									

(1) Feed: Same as feeds used in runs reported in Table I and Table II.

(2) All numbers are parts impurity per million parts plutonium, and the average of duplicate samples.

(3) Water wash rates 30 to 50 per cent of plutonium solution feed rate.

(4) Ag, As, Be, Bi, Cd, Ge, La, Li, Mo, P, Sn, V, and Zn not detected.

[redacted]

[redacted]

TABLE VI

BATCH KILLS OF SYNTHETIC PLUTONIUM(IV) OXALATE FILTRATES WITH POTASSIUM PERMANGANATE

Run No.	Filtrate Composition	Excess Permanganate %	Temperature C	Agitation Time Minutes	Results
1	5 g/l Pu(1) 3 $\underline{M}$ HNO_3 0.1 $\underline{M}$ $H_2C_2O_4$	66	25	5	Pu oxalate solids evident immediately after kill.
2	Same(1)	66	25	10	Pu oxalate solids evident immediately after kill.
3	Same(1)	66	25	20	Pu oxalate solids evident immediately after kill.
4	Same(2)	30	40	5	Borderline.
5	Same(2)	30	45	5	Oxalate killed. No solids formed upon standing 24 hours.
6	Same(1)	5	45	10	Oxalate killed. No solids formed upon standing 60 hours.
7	Same(1)	0	45	10	Oxalate killed. No solids formed upon standing 24 hours.
8	Same(3)	25	45	20	Oxalate killed. No solids formed upon standing 60 hours.
9	Same(3)	25	45	10	Oxalate killed. No solids formed upon standing 60 hours.
10	Same(3)	25	45	5	Oxalate killed. No solids formed upon standing 60 hours.
11	Same(3)	0	45	5	Oxalate killed. No solids formed upon standing 60 hours.
12	Same(4)	25	45	30	Oxalate killed. No solids formed upon standing 60 hours.
13	Same(4)	25	45	10	Oxalate killed. No solids formed upon standing 60 hours.
14	0.7 g/l Pu(1) 3 $\underline{M}$ HNO_3 0.1 $\underline{M}$ $H_2C_2O_4$	30	30	5	Oxalate killed. No solids formed upon standing 24 hours.
15	Same(2)	30	28	5	Pu oxalate solids evident immediately after kill.
16	Same(2)	30	28	15	Pu oxalate solids evident immediately after kill.
17	Same(2)	30	25	30	Oxalate killed. No solids formed upon standing 60 hours.

(1) Filtrate prepared 0.5 hour before kill by adding 1.0 $\underline{M}$ $H_2C_2O_4$ rapidly to a plutonium solution. The plutonium(IV) oxalate solids were retained by "M" but passed by "C" sintered Pyrex filters.

(2) Filtrate prepared as in (1) but aged 24 hours before kill. Plutonium(IV) oxalate retained by "C" sintered Pyrex filters.

(3) Filtrate prepared by adding 1.0 $\underline{M}$ $H_2C_2O_4$ slowly at 55 C to facilitate particle growth. Plutonium(IV) oxalate retained by "C" sintered Pyrex filters.

(4) Filtrate prepared as in (3) but aged 24 hours.

[redacted]

[redacted]

[redacted]

[redacted]

~~UNCLASSIFIED~~ DECLASSIFIED

TABLE V

PURITY OF OXIDE AFTER CALCINATION IN THE PROTOTYPE DRIER-CALCINER

Element	Run No. 5		Run No. 8		Run No. 9		Run A[2]		Run B[2]	
	Oxalate Feed	Oxide Product	Oxalate Feed	Oxide Product	Oxalate Feed	Oxide Product	Oxalate Feed	Oxide Product	Oxalate Feed	Oxide Product
Cr	100[1]	150	1000	300	400	400	<200	<200	<200	<200
Fe	350	620	490	440	560	500	<1000	<1000	<1000	<1000
Mn	100	100	<200	<200	400	300	<200	<200	<200	<200
Ni	100	150	200	200	1000	600	<200	<200	<200	<200

(1) All numbers in parts impurity per million parts plutonium.

(2) Run A and Run B were 234-5 Building batch Task I Plutonium(IV) oxalates.

DECLASSIFIED

[redacted]

[redacted]

[redacted]

[redacted]

TABLE VII

CONTINUOUS KILLS OF SYNTHETIC PLUTONIUM(IV) OXALATE FILTRATES WITH POTASSIUM PERMANGANATE - CO-CURRENT FLOW

Run No.	Filtrate Composition	Excess Permanganate %	Temperature C	Residence Time Minutes	Results
1	5 g/l Pu(1) 3 M HNO_3 0.1 M $H_2C_2O_4$	66	25	30	Pu oxalate solids evident immediately after kill.
2	Same(1)	80	25	60	Pu oxalate solids evident immediately after kill.
3	Same (1)	60	45	30	Oxalate killed. No solids formed upon standing 48 hours.
4	Same(1)	30	45	15	Oxalate killed. No solids formed upon standing 48 hours.
5	Same(1)	30	35	15	Pu oxalate solids evident immediately after kill.
6	Same(1)	30	40	15	Trace of Pu oxalate solids immediately after kill.
7	Same(1)	<5	45	15	Oxalate killed. No solids formed upon standing 24 hours.
8	Same(2)	80	45	15	Pu oxalate solids evident immediately after kill.
9	Same(2)	80	45	30	Trace of Pu oxalate evident immediately after kill.
10	Same(3)	5	45	15	Pu oxalate solids evident immediately after kill.
11	Same(3)	5	55	15	Oxalate killed. No solids evident upon standing 24 hours.
12	Same(3)	5	45	30	Trace of Pu oxalate solid evident immediately.
13	0.7 g/l Pu(1) 3 M HNO_3 0.1 M $H_2C_2O_4$	35	30	15	Pu oxalate solids evident immediately after kill.
14	Same(1)	80	30	15	Pu oxalate solids evident immediately after kill.
15	Same(1)	30	30	30	Pu oxalate solids evident immediately after kill.
16	Same(1)	5	40	15	Oxalate killed. No solids formed after standing 60 hours.

(1) Filtrate prepared 0.5 hour before kill by adding 1.0 M $H_2C_2O_4$ rapidly to a plutonium solution. The plutonium(IV) oxalate solids were retained by "M" but passed by "C" sintered Pyrex filters.

(2) Filtrate prepared as in (1) but aged 24 hours before kill. Plutonium(IV) oxalate retained by "C" sintered Pyrex filters.

(3) Filtrate prepared by adding 1.0 M $H_2C_2O_4$ slowly at 55 C to facilitate particle growth. Plutonium(IV) oxalate retained by "C" sintered Pyrex filters.

[redacted]

[redacted]

[redacted]

DECLASSIFIED

BEST AVAILABLE COPY

TABLE IV

PROTOTYPE PRECIPITATION AND FILTRATION RUN DATA

Run No.	Pu Feed[(1)] Conc. g/l	Pu Feed Purity %	Pu Feed HNO_3 $\underline{M}$	Pu Feed Rate ml/min.	Oxalic Acid Rate ml/min.	Excess Oxalic $\underline{M}$	Residence Time Minutes	Through-puts No.	Pu in Filtrate[(6)] %	Remarks
1	90	96.3	5.0	170	170	0.10	30	1	3.9	Difficult to filter. Filter drum did not pick up slurry well.
2	90	96.3	5.0	170	160	0.10	30	1	3.0	Same as above.
3	90	84[(2)]	5.0	170	170	0.14	30	1	16	Bridge blocks were installed in drum. Vacuum transfer line size changed from 3/8 to 1/2 in. tubing. Filtration much improved.
4	90	90[(3)]	5.2	85	85	0.14	30	3	2.5	Decreased hold-up volume to five liters. Decreased filter area from 1.2 to 0.39 sq. ft. Filtration good. Six inches mercury across drum.[(5)]
5	90	90[(4)]	4.0	85	85	0.14	30	3	4.9	Filtration good. Oxalate cake good throughout the run. No improvement with processing time.
6	90	93	6.5	125	125	0.14	20	3	1.1	Filtration good. Oxalate cake good throughout the run. No improvement with processing time.
7	90 75	93 90	6.5 4.4	120 180	120 144	0.14 0.14	20	3	2.8	Made startup with the 90 g/l feed. The continuous operation made with the 75 g/l feed. Dynel filter cloth plugged.
8	92	96	4.1	180 to 200	180 to 200	0.14	<15	3	4.6	Replaced filter cloth. Filtration at startup excellent. Filter area now 0.8 sq. ft. Agitation increased from 90 to 140 cycles per minute.
9	88	92	4.3	200	200	0.14			4.0	Zero per cent startup. Goal of five minute residence and two liter holdup. Goal not obtained because of poor oxalate characteristics initially and less drum filter area exposed with low liquid level.

(1) Feeds for Runs Nos. 1, 2, 3, 4, and 5 from concentrated Recuplex CCP. Feeds for Runs Nos. 6, 7, 8, and 9 were dissolved plutonium metal solutions.

(2) Per cent purity after the addition of 50,000 ppm of Al and 50,000 ppm of Fe.

(3) Per cent purity after the addition of 25,000 ppm of Al.

(4) Per cent purity after the addition of 20,000 ppm of Al and 20,000 ppm of Fe.

(5) Oxalate in first three runs washed with 2 $\underline{M}$ HNO_3 - 0.05 $\underline{M}$ $H_2C_2O_4$. Oxalate in the last six runs washed with H_2O.

(6) Pu in filtrate for the run, including startup.

[redacted]

DECLASSIFIED

[redacted]