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PRECIPITATION OF PLUTONIUM(IV) OXALATE

By

J. F. Facer, Jr. and K. M. Harmon

Plant Processes Unit
Separations Technology Sub-Section

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INTRODUCTION

The plutonium(III) oxalate precipitation process was developed at Los Alamos for the final plutonium purification step prior to the dry chemistry and metal reduction operations. As originated the process employed hydriodic acid for the reduction of plutonium(IV-VI) to the plutonium(III) state. However, the corrosiveness and cost of the hydriodic acid made its replacement desirable, and experimental programs pointed toward the development of alternate procedures were carried out at Los Alamos and at Hanford.

The precipitation of plutonium peroxide was substituted for the plutonium(III) oxalate process at Los Alamos(1) and was tested at Hanford.(2, 3) When it was found that either an alcohol wash or a slow, drying step was needed to prepare the peroxide for hydrofluorination, attention at Hanford was turned to the precipitation of plutonium(IV) oxalate. Work on the latter compound had been done by Brown and Reas,(4) who showed that hydrogen peroxide could be used for the plutonium valence adjustment. The subsequent work in the 234-5 Development Laboratory is described in this report. It was done to find the best conditions for the precipitation of plutonium(IV) oxalate and to prove that the process could be used as the final step in the purification of plutonium.

SUMMARY AND CONCLUSIONS

Conditions were set for the precipitation of plutonium(IV) oxalate, $Pu(C_2O_4)_2 \cdot 6\ H_2O$, from plutonium nitrate solutions which contain 10 to 550 grams of plutonium per liter and from two to six molar nitric acid.

Thus, the plutonium(IV) oxalate process has proven adaptable to use with the following feed solutions: a) product from the Redox and Purex plants; b) product from the plutonium peroxide process in the Isolation Building; and c) product from Recuplex.

The procedure requires the use of 0.5 to 1.0 weight per cent hydrogen peroxide (for plutonium valence adjustment) and of enough oxalic acid solution to provide 0.1 molar oxalic acid in the supernatant after all of the plutonium is precipitated. Studies of procedural variations gave these results:

a) Raising the strike temperature from 15 to 60 C increased the filterability of the precipitate. Strike temperatures of 70 to 75 degrees or higher gave gummy precipitates.

b) With pure stock solutions, plutonium(IV) oxalate solubility was smallest when the excess oxalic acid concentration in the slurry was between 0.04 and 0.16 molar. With as little as 10,000 parts of aluminum, iron, or chromium per million parts of plutonium in the feed solution, 0.10 molar excess oxalic acid was needed for low solubility.

c) As the process was scaled up, it was necessary to increase the time required for oxalic acid addition in order to produce easily filtered precipitates.

d) Any increase in the nitric acid concentration of the slurry above three molar increased the plutonium loss to recycle.

e) Small changes in the filterability of the precipitate resulted from changes in agitator speed during the precipitation.

f) The slurry had to be cooled to less than 10 C to prevent post-precipitation.

Recommended procedures for precipitation of plutonium(IV) oxalate are described in <u>DISCUSSION OF RESULTS</u>, below.

[redacted]

EXPERIMENTAL

Solution Compositions

The following reagents and plutonium solutions were used in this investigation:

Valence Adjustment:	5 or 50 per cent H_2O_2 (Becco, stabilized with one milligram of sodium pyrophosphate per liter of 50 per cent H_2O_2).
Precipitation:	0.67 - 1.7 molar H_2C_2O4, 1 molar preferred; solid $H_2C_2O_4 \cdot 2\ H_2O$ (Baker and Adamson, Reagent grade).
Wash Solutions:	0.05 molar $H_2C_2O_4$, 1 - 8 molar HNO_3 (2 molar HNO_3 preferred); water
AT Solution:	300 - 400 g/l plutonium, 10 molar HNO_3 (prepared by evaporation of nitric acid solution of plutonium peroxide).
Redox PR Solution:	10 - 20 g/l plutonium, 2 - 7 molar HNO_3 (plutonium solution from the Redox product evaporator).
Stock Solutions:	1 - 550 g/l plutonium, 1 - 12 molar HNO_3

The impurities found in these plutonium solutions are listed in Tables I and XXV.

Equipment and Procedures

The equipment and procedures used for precipitation in this investigation were similar to those described in another publication.(5)

The precipitations were made in cylindrical, pyrex glass vessels which varied in size from 100 to 2500 cubic centimeters. The contents of the precipitation vessels were stirred with electrically driven, 1750 rpm, stainless steel impellers and were heated or cooled by a water bath.

Reagents were added from separatory funnels. Supernatant liquids or slurries were transferred from the precipitation vessel to a filter or to a platinum boat, as desired, by way of a separatory funnel which served as a vacuum head tank.

The plutonium(IV) oxalate precipitates were separated from their supernatants either by decantation or by filtration through a medium (15 micron average pore opening), sintered, pyrex glass filter or a ten to twenty micron (average pore opening), sintered, stainless steel filter. After washing, the precipitate was transferred, either as a thick slurry or as a damp filter cake, to a platinum boat for dry chemistry operations.

The plutonium(IV) oxalate was dried or converted to plutonium dioxide by pulling air across the platinum boat in a tube furnace held at 130 to 300 C.

Analytical Work

Most of the analytical work for this investigation was done by the Isolation and Fabrication Laboratories, Analytical Control. Special analyses were made by the Analytical Laboratories, Separations Technology Sub-Section; by the Redox Laboratories, Analytical Control; and by the Methods Improvement Laboratory.

DISCUSSION OF RESULTS

The following procedures have been recommended for process use at HAPO:

	For Redox PR Solution (10-20 g/l Pu)	For Redox, Purex or Recuplex Product (60-100 g/l Pu)
Adjust acidity to	2 - 5 $\underline{M}$ HNO_3	3.5 - 7.0 $\underline{M}$ HNO_3
Add 50 per cent H_2O_2 to give	0.5 weight per cent H_2O_2	
Heat to	50 C	
Add 1 $\underline{M}$ $H_2C_2O_4$ to give	0.1 $\underline{M}$ excess $H_2C_2O_4$	
$H_2C_2O_4$ addition time	45 - 60 minutes	45 - 90 minutes
Chill slurry to	5 C	
Filter		
Wash cake with	20 g/g Pu of 2 $\underline{M}$ HNO_3 - 0.05 $\underline{M}$ $H_2C_2O_4$	

The effects of variations in these procedures are discussed in the sections below. [redacted]

Plutonium Solution Compositions

Interest in the precipitation of plutonium(IV) oxalate from solutions which varied widely in composition was caused by the need to adapt the process to a variety of plant solutions and to plant equipment which varied in size. The first plant plutonium(IV) oxalate was precipitated as a direct replacement of plutonium(III) oxalate in the rubber glove line equipment of the Hanford 234-5 Building. This precipitation was made from diluted AT solution, containing 40 to 75 grams of plutonium per liter, in glass vessels of eight liter working capacity. Subsequently, plutonium(IV) oxalate was precipitated directly from P-2 cake solution (20 to 40 grams of plutonium per liter) and from Redox PR Solution (10 to 20 grams of plutonium per liter) in the Isolation Building, in sixty-liter, stainless steel vessels which were originally designed for the precipitation of plutonium peroxide. It is planned to use the plutonium(IV) oxalate process in the new wet chemistry operation (Task I) of the remote mechanical line of the 234-5 Building, with concentrated product solutions (60 to 80 grams of plutonium per liter) from the Redox and Purex Plants. Thought was also given to increasing Task I batch sizes by using, as feed, solutions containing 200 to 400 grams of plutonium per liter.

Plutonium Concentrations

In the laboratory, plutonium(IV) oxalate was precipitated from solutions containing from one to 550 grams of plutonium per liter. The maximum concentration is set by the stability of the solution at room temperature with respect to crystallization of any of the solution constituents. Ions which have caused crystallization from Hanford process solutions are sulfate in AT solution(6, 7) and aluminum in Redox PR solution.(8) With Redox product solutions, the upper limit of plutonium concentration is 200 to 300 grams of plutonium per liter, since formation of solid aluminum nitrate occurs at these concentrations. When plutonium(IV)

[redacted]

oxalate was precipitated from plutonium solutions containing suspended aluminum nitrate, the resulting slurry became too thick for proper agitation, plutonium losses were ten to 100 times greater than normal, aluminum separation was very poor, and the precipitate was thixotropic, slow-filtering, difficult to wash, and slow-drying.

Nitric Acid Concentrations

It was found that plutonium(IV) oxalate could be precipitated from any plutonium solution containing more than 1.5 molar nitric acid, as long as the final slurry was 1.5 to 4.5 molar in nitric acid. At acidities lower than 1.5 molar, the co-precipitation of impurities was favored, plutonium recycle was high, and filtration times were long. At slurry acidities higher than 4.5 molar, plutonium recycle was high and filtration times were very long (Table II). A final slurry concentration of 2.5 to 3.5 molar nitric acid was found to be optimum.

Anionic Impurities

In a brief study of the effect which anionic impurities might exert upon the precipitation, it was observed that certain anions markedly affect precipitate quality. Normal plutonium(IV) oxalate was obtained from feed solutions containing 0.055 $\underline{M}$ H_2SO_4 or 0.055 $\underline{M}$ isobutyric acid, but milky plutonium(IV) oxalate was obtained from feed solutions containing 0.055 $\underline{M}$ oxalic acid, 0.055 $\underline{M}$ tartaric acid, or 0.3 $\underline{M}$ sulfamic acid.

Plutonium Valence Adjustment

Since plutonium in feeds to the purification process is generally present at least partly in the hexavalent state, use of a reducing agent is necessary.* Although either plutonium(III) or plutonium(IV) oxalate, or

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*Attempts to make an oxalate precipitation from solutions containing some hexavalent plutonium have given high losses, since plutonium(VI) oxalate is relatively soluble. It has also been found that plutonium(VI) oxalate decomposes too vigorously upon heating for its use in dry chemistry operations.

a mixture of both, can be used as a starting material for the dry chemistry operation, the optimum precipitation conditions for the two compounds are sufficiently different that appreciably better yields are obtained if one or the other valence state is established completely and the precipitation made under the appropriate conditions.

Hydrogen peroxide was found to be the most satisfactory reducing agent of those studied, for process use in the preparation of plutonium(IV) solutions.* It is noncorrosive, acts rapidly, introduces no foreign ions, can be used with plutonium nitrate solutions of any acidity, and is inexpensive.

The reaction of hydrogen peroxide with plutonium ions occurs stepwise, with the successive appearance of the brown and red peroxy complexes,(10) blue plutonium(III), and finally the desired plutonium(IV). In general, the reaction rates decrease with decreasing temperature (Table III), and can be so low that 24 hour digestion will leave predominantly plutonium(III). In the Hanford process, the valence adjustment occurs rapidly both because of the impurity content and because of the strike temperature (50 - 55 C). The rates appear to be increased by the presence of impurities which catalyze the decomposition of hydrogen peroxide (e.g., iron salts). Reas and Brown(11) have found that sulfamic acid may be used to stabilize plutonium(III) solutions which have been prepared by reduction with hydrogen peroxide. Other impurities may exert a similar inhibiting action upon the plutonium(III) to (IV) conversion.

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*Other reducing agents which were considered included: a) oxalic acid, which acts too slowly for process use as well as giving milky precipitates; b) ammonium sulfite, which would introduce the objectionable sulfate ion into the solution; c) hydroxylamine, the common salts of which would introduce either chloride or sulfate; and d) HI, which is corrosive and which is unstable in solutions containing $>3\ \underline{M}\ HNO_3$.

[redacted]

Three procedures for plutonium valence adjustment in the feed solutions to the plutonium(IV) oxalate purification process were investigated, using temperatures of 35 and 50 C, and solutions containing 10 to 75 grams of plutonium per liter, two to seven molar nitric acid and up to 100,000 parts of aluminum and 3000 parts of iron per million parts of plutonium.

Procedure 1 a: The hydrogen peroxide is added to the plutonium solution at the strike temperature, and the mixture is agitated until the blue color disappears (with Redox PR solution, this requires thirty minutes at 35 C and ten minutes at 50 C), before addition of the oxalic acid is begun.

Procedure 1 b: Addition of the oxalic acid is commenced immediately after the hydrogen peroxide addition.

Procedure 2: The hydrogen peroxide and oxalic acid are added slowly and simultaneously. In the laboratory experiments, the two were mixed. The same results should come from use of separate streams of the two reagents.

Procedure 1 a has been used extensively in the plant and has proven generally satisfactory when carried out at 50 C. In the laboratory, with solutions containing 1.5 to 4.5 M HNO_3, 10 to 75 g/l plutonium, and up to 100,000 ppm aluminum, this method gave low plutonium solubilities and low filtration times at temperatures of 25 to 50 C (Table II, IV, V). When the feed solution contained more than 4.5 M HNO_3, the method proved unsatisfactory at temperatures less than 50 C. The plutonium solubility was high and the precipitate was thixotropic.

At 50 C, procedure 1 b gave the lowest plutonium solubilities which were measured, and as short filtration times as any procedure which was tried (Tables IV, VI); however, it was demonstrated that with procedure 1 b at strike temperatures below 50 C, thixotropic plutonium(IV) oxalate precipitates were obtained from most Redox PR solution (Table II, VI) and from plutonium stock solutions spiked with 100,000 ppm of aluminum (Table V).

[redacted]

Neither procedure 1 a nor 1 b was satisfactory for the valence adjustment, at 50 C, of Redox PR solution which had been concentrated to 60 g/l plutonium. The hydrogen peroxide decomposed rapidly and caused excessive foaming. No such difficulty was experienced with Redox PR solutions containing only 10 g/l plutonium.

At 50 C, procedure 2 gave the best plutonium(IV) oxalate strikes from solutions containing 30 to 550 grams of plutonium per liter and an acidity such that the slurry contained 1.5 to 4.5 molar nitric acid.

With Redox PR solution at strike temperatures below 50 C, procedure 2 gave "non-equilibrium" precipitations when used with the standard laboratory process times.* Whether the apparent solubility was higher or lower than the true solubility depended upon the acidity. When the feed solutions were 4.5 to 6 molar in nitric acid, the filtration rates were high and the plutonium content of the filtrates was low (Table VII). When the feed solution contained less than four molar nitric acid, the apparent solubility was high. Digestion of the plutonium(IV) oxalate slurry at the strike temperature brought the system closer to equilibrium. The apparent solubility was reduced to a satisfactory value in the low acid slurries and increased greatly in the high acid slurries (Table VII).

Oxalic Acid Addition

Reagent Concentration

Reagent oxalic acid concentrations ranging from 0.6 to 1.7 molar have been used for laboratory strikes. The only limitation found was the solubility of the oxalic acid: a one molar solution is almost saturated at room temperature, and heat is necessary to maintain a solution which is much more concentrated.

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*15 minute oxalic acid addition time followed by immediate chilling to 5 C.

[redacted]

Laboratory attempts to precipitate plutonium(IV) oxalate by adding solid oxalic acid to plutonium solutions were unsuccessful. The oxalic acid particles became occluded by plutonium(IV) oxalate, and any further reaction was too slow for process use.

Slurry Concentration

Because of the complexing effect of oxalate upon plutonium(IV),(22) narrow limits have had to be set upon the excess oxalic acid to be added for a precipitation. The lowest plutonium solubilities (0.02 to 0.05 g/l plutonium) were found with 0.1 molar oxalic acid in the slurry. With pure plutonium solutions, little variation resulted over the range of oxalic acid concentrations from 0.04 to 0.16 molar (See Tables VIII, IX). The presence of iron, chromium, or aluminum, in concentrations often found in Hanford process solutions, was found to result in increased plutonium solubilities when the excess oxalic acid concentration was only 0.05 $\underline{M}$ (Tables X, XI). The effect, caused by the complexing action of the metal ions on oxalate, was overcome by using 0.1 $\underline{M}$ excess oxalic acid.

Addition Rates

Proper control of the rate of addition of oxalic acid proved to be quite important to the formation of an easily handled precipitate. Too rapid addition produced small precipitate particles which were difficult to filter. The required addition times were found to depend upon the strike temperature and upon the composition of the feed solution.(12) The best times, in the plant, were between 30 and 90 minutes.

One might expect the shortest process times to result from the proper combination of reagent addition and filtration rates. In the laboratory, filtration times were found to decrease hyperbolically with increased oxalic acid addition times (Tables XII, XIII). On a five gram scale, the shortest process times were achieved by addition over a five minute period. The difference between laboratory and plant results may be due to more vigorous agitation in the laboratory equipment.

[redacted]

The apparent plutonium solubility was found to increase slightly with increasing oxalic acid addition rate (Tables XII, XIII).

Temperature Relationships

Strike Temperature

Plutonium(IV) oxalate strikes were made at temperatures from 15 to 90 C. These precipitates prepared at temperatures below 20 C were very finely divided and slow to filter. The precipitates prepared at temperatures above 75 C were too gummy to handle easily. The best precipitates, judging from filtration rates and waste losses, were obtained at approximately 50 C(13) (Table III). In the laboratory, it was observed that when plutonium tetrafluoride was prepared from plutonium(IV) oxalate precipitated at 60 C, it was less free-flowing than when prepared from material precipitated at 25 C (Table XIV). No caking problem has been encountered in the plant with plutonium tetrafluorides prepared from plutonium(IV) oxalate precipitated at 50 to 60 C.

Chilling the Slurry

The solubility of plutonium(IV) oxalate increases with the temperature (Tables XV, XXV). Also, the final stages of the precipitation are slow, giving rise to possible post-precipitation. In order to achieve minimum solubility routinely and to prevent post-precipitation after the slurry is filtered, it proved necessary to cool the slurry to less than 10 C. A 20 minute cooling period was required in the laboratory work. Neither slower chilling nor digestion at the low temperature proved helpful.

Agitation

Agitation rate was not found to be of great importance, provided the slurry was well mixed. Oxalates were precipitated with stirrer speeds of 300 and 1700 rpm. Comparison of their properties showed that precipitates made with the higher stirrer speed were finer and required 20 to 50 per cent greater filtration times (Table XVI).

[redacted]

Decantation and Filtration

Both decantation and filtration have been used with success, in the laboratory and in the plant,(14) for separating plutonium(IV) oxalate from its supernatant solution.

Microscopic examination of plutonium(IV) oxalate particles showed that the diameters of 95 per cent of them fall within the range of five to seven microns. In filtration experiments, the oxalate was retained completely by the following filter media:

a) 100 x 950, twilled Dutch weave metal cloth;(9)
b) medium filter papers (Whatman No. 40 and No. 42);
c) one-eighth inch thick, medium, sintered glass filters (Corning M, 15 micron average pore opening); and
d) selected, one-eighth inch thick, sintered stainless steel filters having average pore openings of less than 25 microns and maximum pore openings of 40 microns.

Appreciable amounts of plutonium(IV) oxalate were passed by such media as:

a) 100 x 250, twilled Dutch weave metal cloth;(9)
b) Whatman No. 41 or Reeve Angel No. 802 filter papers;
c) Corning C (35 micron average pore opening) sintered Pyrex filters; and
d) sintered stainless steel filters having a larger than twenty-five micron average pore opening.

In the Isolation Building process, an average time of two hours is required to filter and wash a batch of oxalate under these conditions: sintered platinum filter surface, one-quarter inch thick and with an average pore opening of 15 microns; a pressure drop across the filter of 15 to 20 inches of mercury; twenty grams of plutonium, in two liters of slurry, per square inch of filter surface; and twenty grams of wash solution per gram of plutonium.

[redacted]

Plutonium(IV) oxalate settles at about one-fourth to one-half the settling rate of plutonium(III) oxalate. Fines account for ten to sixty per cent of the plutonium wastes in a decantation process.

Washing

Water and mixtures of nitric and oxalic acid solutions have been used for washing plutonium(IV) oxalate. When washing by decantation, the best results (lowest plutonium solubilities and turbidity of supernatants) came from the use of wash solution containing two molar nitric acid and 0.05 molar oxalic acid. When the cake was washed on a filter, wash solutions ranging in composition from water to four molar nitric acid, 0.05 molar oxalic acid were used with little difference in plutonium solubility (0.03 to 0.06 grams per liter). Water peptized the oxalate somewhat, but would be a good final wash if it were desired to reduce the acid content of the cake. The plutonium oxalate solubility increased greatly with increases in the nitric acid concentration of the wash solutions above five molar (Table XVII).

Twenty grams of wash solution per gram of plutonium are adequate for washing plutonium(IV) oxalate cakes prepared from either P-2 cake solution or Redox PR solution.

Cake Properties

Color

Freshly precipitated plutonium(IV) oxalate $(Pu(C_2O_4)_2 \cdot 6H_2O$(15, 16) has a cream to tan color, normally within the Munsell(17) color range of 2.5 Y 8/4 to 2.5 Y 7/10. The most common color (2.5 Y 7/6) is that of Figure 1. The color is lighter for finely divided precipitate than for coarse precipitate. Traces of plutonium(III) oxalate give the precipitate a green color, and plutonium(VI) oxalate contributes a salmon tint. On standing, plutonium(IV) oxalate develops a green color (more rapidly when damp than when dry), which is probably due to some plutonium(III) oxalate formation, but the change has no observed effect on subsequent dry chemistry operations.

[redacted]

FIGURE 1

COLOR OF TYPICAL PLUTONIUM(IV) OXALATE

Bulk Density

The fresh precipitate settled to a deposit containing 0.1 to 0.4 grams of plutonium per cubic centimeter, with an average of 0.3. The filtered precipitates contained 0.4 to 0.7 grams of plutonium per cubic centimeter, with an average of 0.6. There was no apparent change in bulk density during the removal of free water from the filter cakes, but their bulk density increased approximately 25 per cent upon removing the water of hydration.

Dry Chemistry

Myers(18) found that in air, plutonium(IV) oxalate lost its water of hydration at 100 to 140 C and decomposition of the oxalate began below 140 C. An investigation now in progress(19) indicates that plutonium(IV) oxalate loses some water of hydration at room temperature in air containing about 20 per cent humidity.

[redacted]

Plutonium(IV) oxalate has been fluorinated directly(20) to plutonium tetrafluoride or converted to plutonium dioxide(21) before further processing.

Purification Factors

The plutonium(IV) oxalate precipitation is depended upon for the final plutonium purification. The major impurities which may have to be removed in processing at Hanford include aluminum, uranium, lanthanum, stainless-steel corrosion products (iron, chromium, nickel), and fission products (ruthenium, zirconium-niobium).

Chemical Separation Factors

The average separation factors obtained by means of a plutonium(IV) oxalate precipitation and normal cake washing were 100, 120, 1.5, 115, and 60 for Al, Cr, La, Ni, and U, respectively, with 100,000 parts of impurity per million parts of plutonium in the feed solutions. With 5,000 parts of impurity per million parts of plutonium in the feed solutions, the factors were ten to twenty for Al, Cr, Fe, Ni and U, and approximately one for La. Additional separation factors of 40 to 80 were obtained for Al and Cr during the reduction of plutonium tetrafluoride to plutonium metal. More complete data are shown in Tables I and XVIII through XXIII.

Fission Product Decontamination

Decontamination factors of 1, 12, and 3 to 6 were obtained for Am, Ru, and Zr-Nb, respectively, by plutonium(IV) oxalate precipitations from Redox solutions containing 10 to 60 grams of plutonium per liter. Complete data are shown in Table XXIV.

Little, if any, separation of tracer thorium(UX_1) from plutonium was achieved by plutonium(IV) oxalate precipitation.

Supernatant Treatment

The equilibrium solubility, at 25 C, of plutonium(IV) oxalate in mixtures of nitric acid and oxalic acid is shown by Figure 2. By chilling

[redacted]

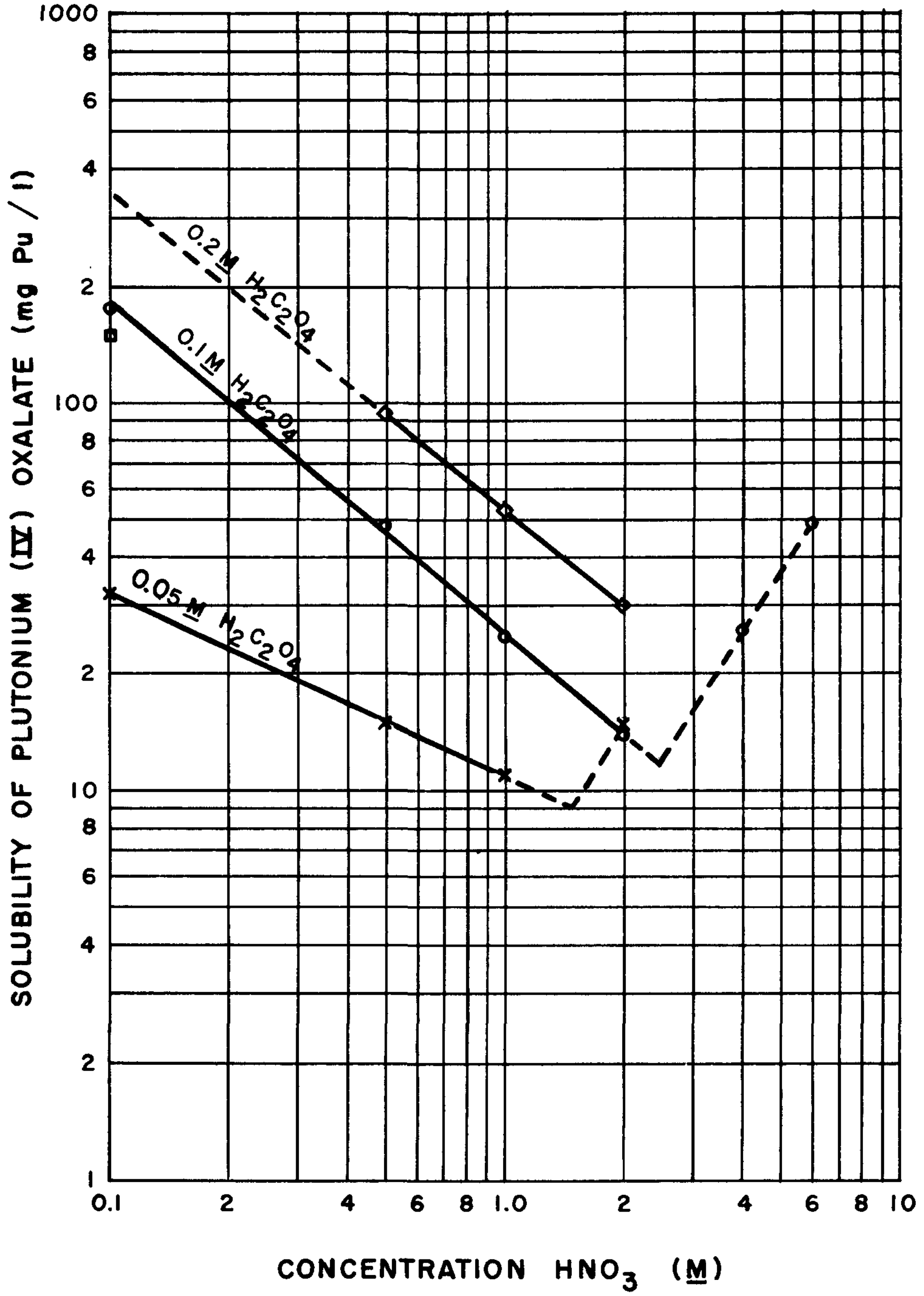

FIGURE 2
EQUILIBRIUM SOLUBILITY OF PLUTONIUM (IV)
OXALATE IN $HNO_3-H_2C_2O_4$ SOLUTIONS AT 25±2 C.
(DATA TAKEN FROM REPORT CN-1702)

[redacted]

plutonium(IV) oxalate slurries to less than 10 C during processing, the plutonium concentration of the supernatants may be reduced almost to the 25 C equilibrium values (i.e., twenty to fifty milligrams of plutonium per liter).

Before recycling to recovery the filtrates or supernatants from plutonium(IV) oxalate precipitations, the oxalic acid and any plutonium(IV) oxalate solids may be destroyed by: evaporating the solutions to a nitric acid concentration of greater than ten molar;(21) adding potassium permanganate solution and heating; or adding a mixture of nitric acid and hydrogen peroxide and heating if required. The last procedure is not applicable to plant processing, because the reaction is too vigorous to be completed in vessels with limited free space. The reaction is useful in the laboratory for dissolving plutonium(IV) oxalate without introducing foreign ions.

Under unusually favorable conditions, plutonium(IV) oxalate will dissolve completely in an excess of more than eight molar nitric acid, but normally a large percentage of cream-colored, gum-like, residue will be produced if some hydrogen peroxide or potassium permanganate is not included with the nitric acid. Formation of the gum-like residue was not observed when two to four molar nitric acid was used as the solvent, but dissolution rates were too low for process use.

ACKNOWLEDGEMENT

The data included in this report were obtained by G. E. Benedict, J. F. Facer, Jr., M. N. Myers, and R. A. Pugh; and are to be found in the following secret laboratory notebooks; HW-3409-T, HW-4055-T, HW-4494-T, HW-4498-T and HW-4626-T.

J. F. Facer Jr.
J. F. Facer, Jr.

K. M. Harmon
K. M. Harmon

JFF, Jr.:KMH:ag:lj:ms

[redacted]

TABLE I

Spectrochemical Analyses* of Plutonium Feed Solutions, Plutonium(IV) Oxalates, and Plutonium Metal from Typical Laboratory Processing Data

Runs	160 to 165 and 168			191		
Element	AT Starting Sol.	Oxalate Cake	Plutonium Metal	3-BP Starting Sol.	Oxalate Cake	Plutonium Metal
Al	<5		<20	$5x10^4$	50	1
Bi	500	200-500	< 1	100		< 1
Ca	200	130-500	30-100	<130	<50	<10
Cr	500	5-50	2-10	2000	20	2
Fe	>1000	500-20000	70-180	5000	350	135
K	500	500-1000	<10	1000	400	2
La	20000	3000-10000	2000	800	130	400
Mn	200	3-50	5-50	1000		100
Na	1500		200-500	1000		20
Ni	100		50-1000	1000	30	50
P	>1000	>1000	<100	< 200		<200
Si	< 5	< 5	10-20	> 2000	100	10

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* Parts of impurity element per million parts of plutonium by weight. AT Starting Solution contained 60 grams of plutonium per liter and 2 $\underline{M}$ HNO_3. 3 BP Starting Solution was a filtered solution containing 12 grams of plutonium per liter and 6 $\underline{M}$ HNO_3.

TABLE II

Effect of Hydrogen Ion Concentration Upon Filtration Rates and Plutonium Oxalate "Solubility" with Different Valence-Adjustment Procedures

	Procedure 1 a*		Procedure 1 b*		Procedure 2*	
Feed Solution	g/l Pu in filtrate	Filtration Minutes	g/l Pu in filtrate	Filtration Minutes	g/l Pu in filtrate	Filtration Minutes
10 g/l Pu, Pure Stock:						
2.68 M HNO_3	.017	12	.013	23	.017	21
3.78 M HNO_3	.020	12.5	.014	10.3	.009	14
4.87 M HNO_3	.139	102	.013	10.5	.034	11
5.96 M HNO_3	.148	80	.029	25.5	.037	24
10 g/l Pu, Redox PR:**						
1.7 M HNO_3					5.17	4.5
2.0 M HNO_3	.057	4.7	.035	15	--	3.0
3.2 M HNO_3	.049	4.1***	.037	14.5***	3.83	18.4***
4.5 M HNO_3			.033	15	.29	12
4.7 M HNO_3	.049	>90	.025	60	.034	15
5.0 M HNO_3	.26	>120***	2.18	>60***	1.07	7.2***

All strikes were made at 35 C, and except where otherwise noted, 5 to 6 gram plutonium batches were filtered by 60 ml, Corning M, sintered pyrex filters, with 20 inches Hg vacuum.

* See text, Plutonium Valence Adjustment, for details of procedures.

** Redox PR solutions from plant runs S-53-01-L-22, S-53-02-L-24, S-53-03-L-37 and S-53-03-L-44.

*** Filtration times for one-gram, plutonium batches through 15 ml, Corning M, sintered pyrex filters.

TABLE III

Effect of Strike Temperatures(13) Upon Plutonium(IV) Oxalate Process Variables

Strike Temp. (Degrees C)	Valence Adjustment Time (Minutes)	Precipitate Settling Time (Minutes)	Filtration Time (Minutes)	Per Cent Recycle
30	35	10	6.5	--
50	6	2.5	3.5	0.24
60	3.5	1.75	6	0.25
70	2.6	2	7	0.31
80	0.6	1	13*	0.42

All strikes were made from the same Redox PR solution, using one hour for oxalic acid addition, thirty minutes for chilling to 5 C, and filtering a two gram batch of plutonium through a 100 ml, Corning, medium porosity, sintered pyrex funnel.

* Gummy Oxalate.

[redacted]

TABLE IV

Laboratory Precipitation of Plutonium(IV) Oxalate from Task I Type Feed Solutions

Feed Solution		Procedure 1 a		Procedure 1 b		Procedure 2	
		g/l Pu in filtrate	Filtration Minutes	g/l Pu in filtrate	Filtration Minutes	g/l Pu in filtrate	Filtration Minutes
HNO_3, mole/liter	Solution from Plant Run No.						
2.2	S-53-03-L-44	.190	2.0	.234	2.0	.102	2.9
3.6	S-53-01-L-110					.064	16.5
4.5	S-53-01-L-94			.077	2.7*		
5.0	S-53-01-L-110					.041	13
5.8	S-53-01-L-44	.048	4.0*	.062	4.2	.100	3.0
6.0	S-53-01-L-105	.174	4.0***			.170	6.0**
7.2	S-53-01-L-94					.413	10 **

All strikes were made from Redox PR solutions which had been concentrated in the laboratory from 10 g/l plutonium, diluted to 60 g/l plutonium, and filtered. Strikes were made at 50 C, using six gram plutonium batches, 30 minute oxalic acid addition, 0.1 molar oxalic acid concentration in the slurries, and a final digestion temperature of 7 C.

Oxalates were filtered by 60 ml, Corning M, pyrex filters, using 20 inches Hg vacuum.

* Very vigorous pre-reduction with some reactor overflow.

** Thixotropic precipitate - still muddy after one hour of air flow through the cake.

TABLE V

Effect of Feed Composition Upon Filtration Time

Feed Solution	Filtration Time, Minutes					
	3.78 $\underline{M}$ HNO_3			4.87 $\underline{M}$ HNO_3		
	Procedure 1 a	Procedure 1 b	Procedure 2	Procedure 1 a	Procedure 1 b	Procedure 2
Pure stock solution	12.5	10.3	14.0	102	10.5	11.0
100,000 ppm Al in stock solution	10.5	27.0	9.5	---	19.5	14.0
100,000 ppm Al and 3,000 ppm Fe in stock solution	---	30	11	---	---	---

All strikes were made at 35 C, with 1 per cent hydrogen peroxide; 12 minute, oxalic acid addition times; and slurries chilled to 7 C before filtration.

5 gram batches of plutonium as 10 g/l plutonium solution were used for each run. Slurries were filtered by a 60 ml, Corning M, pyrex filter, with a 20 inch Hg vacuum.

TABLE VI

Effect of Increased Temperature and Digestion Time Upon Filtration Time and Plutonium "Solubility"

Strike Temperature, C	35			50		
Valence-Adjustment Procedure	1 a	1 b	2	1 a	1 b	2
Run No. S-53-03-L-37: 2.74 M HNO_3*						
Filtrate, g/l Plutonium	.457	.100	5.95	---	---	.033**
Filtration Time, Min.	4.4	7.5	3.7	---	---	4.6**
5.0 M HNO_3						
Filtrate, g/l Plutonium	.258	2.18	1.07			
Filtration Time, Min.	>120	>60	7.2			
Run No. S-53-03-L-44: 3.84 M HNO_3						
Filtrate, g/l Plutonium		.76	3.12	.101	.012	.020
Filtration Time, Min.		15.5	8.2	4.3	4.7	7.0
5.0 M HNO_3						
Filtrate, g/l Plutonium				.056	.021	.076
Filtration Time, Min.				6.0	5.8	3.7

One gram plutonium batches of Redox PR solution (nominal 10 g/l plutonium) were used for all strikes, and all slurries were filtered by a 15 ml, Corning M, sintered pyrex filter at 20" Hg vacuum. All 35 C strikes were made with 12 minute oxalic acid addition and, with one exception, 50 C strikes were made with 30 minute, oxalic acid addition.

* Strikes at 2.74 and 3.84 M HNO_3 made from PR solution as received; at 5.0 M, from PR solution diluted with conc. HNO_3.

** 45 minute oxalic acid addition plus another 45 minutes of digestion at 50 C.

[redacted]

TABLE VII

Effect of Slurry Digestion at 35 C upon Plutonium "Solubility"*

HNO_3 in Feed Solution, mole/liter**	2.0		5.0	
RC - Run No.	163	165	164	166
Digestion time in minutes after oxalic acid addition	0	30	0	30
g/l Plutonium in Filtrate	6.25	0.13	0.23	1.21
Filtration Time, *** Minutes	1.75	2.0	2.5	2.0

* All strikes were made at 35 C with the hydrogen peroxide and oxalic acid added as a mixture over a 12 minute period.

** Redox PR solution from plant run S-53-02-L-24 was concentrated in the laboratory to 300 grams of plutonium per liter, cooled to room temperature, filtered to remove any solids, and diluted to 10 g/l plutonium.

*** A one gram batch of plutonium was filtered by a 60 ml Corning M pyrex glass filter at 20 inches Hg vacuum.

TABLE VIII

Variation of the Plutonium Concentration in Filtrates from Plutonium(IV) Oxalate Precipitations with Concentration of Oxalic Acid in the Slurry (Ten Grams of Plutonium Per Liter of Starting Solution)

Run No.	Starting Solution	Starting $\underline{M}$ HNO_3	Slurry $\underline{M}$ $H_2C_2O_4$	Gms Plutonium per liter of filtrate
RC-68	Button Solution	2.0	0.05	0.012
RC-77	Button Solution	2.0	0.05	0.015
RC-78	Button Solution	2.0	0.05	0.016
RC-67	Button Solution	2.0	0.08	0.017
RC-69	Button Solution	2.0	0.14	0.020
RC-74	Button Solution	8.1	0.05	0.89
RC-73	Button Solution	8.1	0.08	0.91
RC-72	Button Solution	8.1	0.11	0.74
RC-71	Button Solution	8.1	0.14	0.99
RC-103	3BP	4.6	0.07	0.024
RC-104	3BP	4.6	0.10	0.055
RC-106	3BP	4.6	0.10	0.042
RC-105	3BP	4.6	0.13	0.025
RC-107	3BP	4.6	0.18	0.015
RC-108	3BP	6.0	0.07	0.026
RC-109	3BP	6.0	0.13	0.024

All strikes were made at 25 C, with a 30 minute pre-reduction, 15 minute oxalic acid addition time and 7 to 8 C final digestion temperature. The concentration of oxalic acid in the slurry was calculated on the assumption that all of the plutonium had reacted to form $Pu(C_2O_4)_2$ and that no other ions had reacted with oxalic acid.

[redacted]

TABLE IX

Variation of the Plutonium Concentration in Filtrates from Plutonium(IV) Oxalate Precipitations with Concentration of Oxalic Acid in the Slurry (60 to 75 grams of Plutonium Per Liter of Starting Solution)

Run No.	Starting Solution	Starting M HNO_3	Slurry M $H_2C_2O_4$	Gms Plutonium per liter of filtrate
RC-43	Button Solution	2.1	0.05	0.051
RC-65	Button Solution	2.1	0.07	0.022
RC-59	Button Solution	2.1	0.08	0.023
RC-47	Button Solution	2.1	0.11	0.034
RC-60	Button Solution	2.1	0.13	0.032
RC-56	Button Solution	2.1	0.15	0.040
RC-57	Button Solution	2.9	0.07	0.041
RC-58	Button Solution	2.9	0.09	0.012
RC-61	Button Solution	3.9	0.07	0.037
RC-62	Button Solution	3.9	0.09	0.018
RC-66	Button Solution	3.9	0.11	0.017
RC-52	AT	3.0	0.05	0.151
RC-63	AT	3.0	0.075	0.032
RC-54	AT	3.0	0.10	0.016
RC-53	AT	4.5	0.05	0.062
RC-64	AT	4.5	0.075	0.013
RC-55	AT	4.5	0.10	0.36

All strikes were made at 25 C, with a 30 minute pre-reduction, 15 minute oxalic acid addition time and 7 to 8 C final digestion temperature. The concentration of oxalic acid in the slurry was calculated on the assumption that all of the plutonium had reacted to form $(Pu(C_2O_4)_2$ and that no other ions had reacted with oxalic acid.

[redacted]

TABLE X

Plutonium(IV) Oxalate Precipitation in the Presence of Aluminum, Chromium and Iron, from Solutions Containing Ten Grams of Plutonium Per Liter

Run Number RC-	41	39	42	37	40	38	36
Impurity Concentration, g/l	0	2.04 Cr	2.20 Fe	1.06 Al	0	2.04 Cr	1.06 Al
$H_2C_2O_4$ in Slurry; mole/liter:							
assuming no tie-up of oxalate by impurities	0.05	0.05	0.05	0.05	0.106	0.106	0.106
assuming $R_2(C_2O_4)_3$ formation	0.05	*	*	*	0.106	0.05	0.05
Pu in Filtrate, g/l	0.053	0.075	0.123	2.35	0.150	0.120	0.046
Pu in Wash, g/l	0.029	0.035	0.057	0.088	0.017	0.230	0.048

* Very slight oxalic acid deficiency

The starting solution for all runs contained 9.4 g Pu/l and 2.7 M HNO_3. Strikes were made at 25 C with an 8 C final digestion temperature. Oxalic acid was added in fifteen minutes.

TABLE XI

Plutonium(IV) Oxalate Precipitation in the Presence of Aluminum, Chromium and Iron, from Solutions Containing Sixty Grams of Plutonium Per Liter

Run Number RC-	43	44	51	45	46	47	48	49	50
Impurity	None	Al	Al	Cr	Fe	None	Al	Cr	Fe
$H_2C_2O_4$ in slurry; mole/liter:									
assuming no tie-up of oxalate by impurities	0.05	0.05	0.05	0.05	0.05	0.11	0.16	0.10	0.10
assuming $R_2(C_2O_4)_3$ formation	0.05	*	*	0	0	0.11	0.05	0.05	0.05
Pu in Filtrate, g/l	0.051	0.057	0.043	1.10	0.67	0.034	0.022	0.029	0.087

* Slight oxalic acid deficiency

The starting solution for all runs was a pure plutonium solution containing 60 g/l Pu and 2.1 $\underline{M}$ HNO_3. 50,000 parts of impurity were added per million parts of plutonium. Strikes were made at 25 C, with 15 minute oxalic acid addition and 8 C final digestion temperature.

TABLE XII

Variation of Filtration Time and Plutonium Recycle with Oxalic Acid Addition Time: Synthetic Redox PR Solution

Run No.	Minutes to add $H_2C_2O_4$	Plutonium in Filtrate, g/l	Minutes to filter batch*
RC-155	3	0.021	16.7
RC-153	12	0.018	11
RC-152	0.33	0.030	19
RC-145	12	0.019	14

* Five grams of plutonium per batch, using a 60 ml, Corning M, sintered pyrex filter. Starting solution for all runs was a pure plutonium solution (10 g/l) spiked with 100,000 ppm Al. Runs 153 and 155 were from 3.78 M HNO_3 solution, and runs 145 and 152 were from 4.87 M HNO_3 solution. All strikes were made at 35 C with a 7 C final digestion temperature.

TABLE XIII

Variation of Plutonium Recycle with Oxalic Acid Addition Time: Diluted AT Solution

Run No.	Oxalic Acid Addition Time	Plutonium in Filtrate, g/l
RC-81	0.33 Minutes	0.056
RC-79	3.5 Minutes	0.018
RC-82	15 Minutes	0.020
RC-80	20 Minutes	0.019

Starting solution was cut AT solution containing 60 g/l plutonium and 2.9 M HNO_3. Strikes were made at 25 C; and immediately after the oxalic acid addition, slurries were chilled to 8 C and filtered. Six-gram batches of plutonium were used.

TABLE XIV

Variation of Plutonium Tetrafluoride Caking with the Strike Temperature for Plutonium(IV) Oxalate Precipitation

Run Number RO-	30	31	33
Strike temperature, degrees C	25	55	60
Pu in filtrate, g/l	0.053	0.049	0.035
Plutonium loss to recycle, per cent	0.23	0.20	0.14
Per cent free-flowing PuF_4 obtained by hydrofluorinating the product oxalate	100	75	65

Starting Solution:	45 grams/liter Pu; 2 M HNO_3. Stock solution, prepared by dissolving laboratory buttons.
Strike:	10 minute oxalic acid addition. 20 minute digestion while cooling. 25 C final digestion and filtration temperature.
Washes:	Four washes of filter cake with 7.5 ml of 1.0 M HNO_3 - 0.02 M $H_2C_2O_4$ per gram of plutonium per wash.

TABLE XV

Variation of Plutonium Concentration in Supernatants with Final Digestion Temperature

		Plutonium in Filtrate, g/l		
Final Digestion Temperature		25 C	50 C	75 C
Run No.	158	0.027		
	159	0.031		
	160	0.031		
	163	0.021		
	161		0.049	
	162		0.082	
	164			0.423
	165			1.163

All strikes weremade from the same batch of cut AT solution (2 M HNO_3 and 60 g Pu/liter), using 10 minute oxalic acid addition and 20 minute digestion. Oxalic acid addition, digestion, and decantation were all done at the same temperature for a given strike.

[redacted]

TABLE XVI

Effect of Agitation Speed(9) upon the Filterability of the Resulting Plutonium(IV) Oxalate

		Feed Concentration		Time in Minutes				
Run	Agitator Speed rpm	g/l Pu	g/l H^+	Oxalic Acid Addition	Digestion	Cooling	Settling	Filtering
1	1700	12.3	2.4	60	0	30	3.7	3.2
2	300	12.3	2.4	60	0	30	4.5	2.5
3	1700	62.6	3.5	30	0	30	2.7	1.9
4	300	62.6	3.5	30	0	30	1.5	1.6
5	1700	60.9	4.7	1	30	30	2.9	3.2
6	300	60.9	4.7	1	30	30	3.0	2.1

Strikes were made at 50 C, from Redox PR solution or from concentration prepared from Redox PR solution. Three-gram batches of plutonium were filtered through a 100 ml, Corning, medium porosity, sintered pyrex funnel.

TABLE XVII

Variation of Plutonium Content of Wash Solutions with Acidity

	Wash Composition		
Run Number	$H_2C_2O_4$, mole/liter	HNO_3, mole/liter	grams/liter Pu
RC-24	0.05	2	0.022
RC-25	0.05	2	0.020
RC-26	0.05	2	0.033
RC-22	0.05	4	0.037
RC-30	0.05	4	0.031
RC-31	0.05	4	0.057
RC-11	0.05	6	0.119
RC-13	0.05	6	0.257
RC-15	0.05	6	0.239
RC-16	0.05	6	0.152
RC-17	0.05	6	0.133
RC-18	0.05	6	0.147
RC-12	0.05	8	0.447

All strikes were made from Redox 3-BP solution containing approximately ten grams of plutonium per liter.

TABLE XVIII

Uranium Separation by Plutonium(IV) Oxalate Precipitation

Run No.	HNO_3 in mole/liter	Parts of Uranium per Million Parts of Uranium				
		Feed Solution	$Pu(C_2O_4)_2$ No Washes	$Pu(C_2O_4)_2$ One Wash	$Pu(C_2O_4)_2$ Three Washes	$Pu(C_2O_4)_2$ Five Washes
RC-28	3.2	100,000	41,000	9,600	2,400	2,000
RC-27	3.2	10,000	1,200	280	160	140
RC-29	3.2	10,000	1,500	500	150	110
RC-33	3.2	1,000	410	150	70	36
RC-32	6.4	100,000	11,400	3,200	990	860
RC-31	6.4	10,000	5,200	1,100	570	410
RC-30	6.4	1,000	110	80	70	65

The same pure stock solution (60 g Pu/l) was used for all runs. Solid uranyl nitrate was added to spike the stock solution to the desired uranium concentrations. All strikes were made at 25 C, with 30 minute pre-reduction, 15 minute oxalic acid addition time, 20 minute digestion, and no chilling. Supernatant liquids and washes were removed by decantation. Each wash consisted of 20 ml of 2 M HNO_3 - 0.05 M $H_2C_2O_4$ per gram of plutonium.

TABLE XIX

Aluminum Separation by Plutonium(IV) Oxalate Precipitation

	Starting Solution		Parts of Aluminum per Million Parts of Plutonium		
Run No.	Type	g/l Pu	Feed Solution	$Pu(C_2O_4)_2$ Cake	Button
192	Spiked 3-BP	60	300,000	1750	40
193	Spiked 3-BP	60	300,000	1550	20
163	Cut AT	60		800	20
RC-99	Spiked Stock	223	10,000	640	--
191	3-BP	10	50,000	50	1
153	Synthetic 2-BP	10	14,000	20	--

All strikes were made at 25 C, with 30 minute pre-reduction, 30 minute oxalic acid addition and digestion, and no chilling. Supernatant liquid from the strikes and washes was separated by decantation. Sufficient oxalic acid was used to react with all of the plutonium to form $Pu(C_2O_4)_2$ and to make the slurry 0.05 molar in oxalic acid if no other ion reacted with the oxalic acid. Two washes of 20 ml of 2 $\underline{M}$ HNO_3 - 0.05 $\underline{M}$ $H_2C_2O_4$ per gram of plutonium were used for each run.

[redacted]

TABLE XX

Chromium Separation by Plutonium(IV) Oxalate Precipitation

	Starting Solution		Parts of Chromium per Million Parts of Plutonium		
Run No.	Type	g/l Pu	Feed Solution	$Pu(C_2O_4)_2$ Cake	Button
192	Spiked 3-BP	60	200,000	200*	40
193	Spiked 3-BP	60	200,000	200*	4
174	Synthetic 3-BP	60	100,000	800	<10
163	Cut AT	60	500	50	2
153	Synthetic 2-BP	10	141,000	80	
191	3-BP	10	2,000	20	2

* Values are about one fifth as great as might be expected on a straight dilution basis.

All strikes were made at 25 C, with 30 minute valence adjustment, 20 minute oxalic acid addition and digestion, and no chilling. Supernatant liquid from the strikes and washes was separated by decantation. Sufficient oxalic acid was used to react with all of the plutonium to form $Pu(C_2O_4)_2$ and to make the slurry 0.05 molar in oxalic acid if no other ion reacted with the oxalic acid. Two washes of 20 ml of 2 $\underline{M}$ HNO_3 - 0.05 $\underline{M}$ $H_2C_2O_4$ per gram of plutonium were used for each run.

TABLE XXI

Iron Separation by Plutonium(IV) Oxalate Precipitation

	Starting Solution		Parts of Iron per Million Parts of Plutonium		
Run No.	Type	g/l Pu	Feed Solution	$Pu(C_2O_4)_2$ Cake	Button
RC-99	Spiked stock	223	10,000	950	--
RC-101	Spiked stock	100	10,000	310	--
192	Spiked 3-BP	60	5,000	--	230
193	Spiked 3-BP	60	5,000	--	200
191	3-BP	10	5,000	350	135
169,170	Synthetic 3-BP	10	4,000	--	170
153	Synthetic 2-BP	10	1,000	100	--

All strikes were made at 25 C, with 30 minute pre-reduction, and 30 minute oxalic acid addition and digestion. Sufficient oxalic acid was used to react with all of the plutonium to form $Pu(C_2O_4)_2$ and to make the slurry 0.05 molar in oxalic acid if no other ion reacted with oxalic acid. The oxalate cakes were washed with 20 to 40 ml of 2 M HNO_3 - 0.05 M $H_2C_2O_4$ per gram of plutonium.

TABLE XXII

Nickel Separation by Plutonium(IV) Oxalate Precipitation

	Starting Solution		Filtrate	$Pu(C_2O_4)_2$	
Run No.	g/l Pu	g/l Ni	g/l Pu	ppm Ni	Ni DF
RC-68	10	0	0.012	0	--
191	10	0.01	---	30	33
RC-86	10	0.5	0.030	500	100
RC-76	10	10	1.11	2500	400

The same pure stock solution (2 M HNO_3 and 10 g/l Pu) was used for all runs except 191, which was made with 3 BP. All strikes were made at 25 C, with 30 minute pre-reduction, 15 minute oxalic acid addition time and 7 to 8 C final digestion temperature. Sufficient oxalic acid was used to react with all of the plutonium to form $Pu(C_2O_4)_2$ and to make the slurry 0.05 molar in oxalic acid if no other ion reacted with the oxalic acid.

Nickel was added to the stock solution as solid nitrate. Oxalate cakes were washed with 40 ml of 2 M HNO_3 - 0.05 M $H_2C_2O_4$ per gram of plutonium.

TABLE XXIII

Lanthanum Separation by Plutonium(IV) Oxalate Precipitation

	Starting Solution		Filtrate	$Pu(C_2O_4)_2$	
Run No.	g/l Pu	g/l La	g/l Pu	ppm La	La DF
RC-68	10	0	0.012	0	--
RC-85	10	0.2	0.085	3×10^4	1
RC-84	10	2.0	0.089	8×10^4	2.5
RC-83	10	10.0	0.627	1×10^5	10

The same pure stock solution (2 M HNO_3)was used for all runs. All strikes were made at 25 C, with 30 minute pre-reduction, 15 minute oxalic acid addition time and 7 to 8 C final digestion temperature. Sufficient oxalic acid was used to react with all of the plutonium to form $Pu(C_2O_4)_2$ and to make the slurry 0.05 molar in oxalic acid if no other ion reacted with the oxalic acid. Lanthanum was added to the stock solution as the solid nitrate. Oxalate cakes were washed with 40 ml of 2 M HNO_3 - 0.05 M $H_2C_2O_4$ per gram of plutonium.

TABLE XXIV

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

				Fission Product					
Strike Conditions			Pu	Ru		Zr - Nb		Am	
Run	M HNO$_3$	g/l Pu	c/min./sample*****	DF	c/min./sample	DF	c/min./sample	DF	c/min./sample
162	2.0	1	6.45×10^5	15	****	6.2	0.28×10^5	0.7	8.42×10^5
160	5.0	1	4.93×10^5	2.3	3.14×10^5	1.8	0.74×10^5	1.0	4.52×10^5
163	2.0	10	3.80×10^5	10.6	0.52×10^5	6	****	0.8	4.44×10^5
164	5.0	10	4.14×10^5	15	****	6	****	1.1	3.74×10^5
161	2.0	60	5.57×10^5	15	0.52×10^5	3.8	0.39×10^5	1.2	4.37×10^5
159	4.9	53	4.78×10^5	10.2	0.64×10^5	2.4	0.57×10^5	1.2	3.98×10^5
3-BP	**		4.50×10^5	--	6.87×10^5	---	3.66×10^5	---	4.52×10^5
3-BP	***		5.22×10^5	1.0	7.72×10^5	2.8	1.52×10^5	1.0	5.08×10^5
158	5.0	11.5	5.52×10^5	9.4	0.92×10^5	5.9	0.81×10^5	1.0	5.46×10^5

---

* Strike at 35 C, by addition of mixed H_2O_2 - $H_2C_2O_4$; no pre-reduction.

** Solution as received in PR can from Redox. Starting solution for run 158.

*** Starting solution for runs 159 - 162 inclusive. This was prepared by evaporating 3-BP solution to 300 g/l Pu, diluting to 60 g/l Pu, and filtering.

**** Not detectable.

***** Each sample contained 3 ml of 10 g/l Pu solution.

TABLE XXV

Precipitation of Plutonium(IV) Oxalate from Concentrated Plutonium Solutions

Run Number RC-	101	100	99	102	142
Starting Solution:					
g/l Pu	100	150	223	393	550
M HNO_3	4.0	5.1	6.3	12	9.63
ppm* Al	10000	10000	10000	>10000	Nil
ppm Fe	10000	10000	10000	>10000	Nil
ppm U	10000	10000	10000	10000	Nil
Pu in Filtrate:					
g/l	0.055	0.027	0.078	1.21	0.053
Pu in Washes:					
g/l	0.025	0.027	0.037	2.42	---
Per Cent Recycle	0.19	0.12	0.22	8.8	---
Product Cake:					
ppm Al	---	250	640	640	---
ppm Fe	310	180	950	700	---
ppm U	55	21	550	9000	---

---

* ppm = parts of impurity per million parts of plutonium

Each strike was made at 35 C with one minute pre-reduction, 15 minute oxalic acid addition, 0.1 M $H_2C_2O_4$ in the slurry, and 7 C final digestion temperature. Eleven grams of plutonium were used for each run. Spiked plutonium stock solutions were used for runs 99, 100 and 101, spiked 3 BP was used for run 102, and a pure stock solution was used for run 142. Three washes, 10 ml of 2 M HNO_3 - 0.05 M $H_2C_2O_4$ per gram of plutonium per wash, were used for each run.

TABLE XXVI

Percentage of Plutonium Recycled in Filtrates from Typical Plutonium(IV) Oxalate Strikes Made at Different Acidities and Final Digestion Temperatures

Final Digestion Temperature, Degrees C	10	10 to 20	20 to 30
$\underline{M}$ HNO_3 in Starting Solution			
2	0.16		
3	0.18		0.5
4		1.7	
5	1.4	3.3	3.3
6	3	5.6	
7			12
8			40

Starting solution for all runs was 3 BP solution containing 10 grams of plutonium per liter. All strikes were made at 25 to 30 C.

Final oxalic acid concentration in the slurry was 0.05 molar in all runs.

[redacted]

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