PRECIPITATION OF PLUTONIUM(III) OXALATE AND CALCINATION TO PLUTONIUM DIOXIDE

by

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ABSTRACT

Procedures were developed for the precipitation of plutonium(III) oxalate from nitric acid, hydrochloric acid, and sulfamic acid solutions. The plutonium was adjusted to Pu(III) with ascorbic acid in the presence of an oxidation inhibitor. Plutonium dioxide was produced by calcining the oxalate in air at temperatures between 450 and 750°C.

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PRECIPITATION OF PLUTONIUM(III) OXALATE
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INTRODUCTION

The preparation of plutonium dioxide is often required in the processing of plutonium. The oxide is the desired final form for some applications, while for others oxide is an intermediate. Plutonium dioxide has been most often produced on a large scale by precipitation of plutonium(IV) peroxide or plutonium(IV) oxalate and subsequent calcination. The technology of these processes is well developed and is reported in the literature.[1,2] The peroxide precipitation has the advantage of providing more extensive purification of plutonium from cationic impurities than does the oxalate precipitation. On the other hand, plutonium(IV) oxalate is more easily filtered and handled than plutonium(IV) peroxide. In both precipitations, the solubility of the compounds is significant, and therefore, the loss of plutonium to the filtrates is relatively high; however, efficient processes have been developed for partial recovery of the plutonium losses. The necessity for recovery operations is considered to be the greatest disadvantage of these processes.

Another method for producing plutonium dioxide is by precipitation of plutonium(III) oxalate and subsequent calcination. The preparation and properties of plutonium(III) oxalate are well-known and have been the subject of a number of investigations.[2-9] Limited solubility data have been published.[3,5,10] The thermal decomposition of the oxalate to the oxide has been thoroughly investigated by thermogravimetric techniques.[8,9,11] Although the literature indicates that the precipitation of plutonium(III) oxalate is a simple procedure, the precipitation has seldom been used as a process step in the large-scale production of plutonium dioxide.

The neglect of plutonium(III) oxalate for process use may have been due to the lack of suitable reducing agents to adjust the plutonium to the Pu(III) state. Iodide ion has been employed successfully as a reductant prior to oxalate precipitation,[8] but the corrosiveness of iodide toward stainless steel has limited its use. Metal ions such as Fe^{2+} reduce plutonium to the Pu(III) state, but their use is undesirable because they form insoluble oxalates that precipitate with the plutonium. Hydroxylamine is a useful reagent for producing Pu(III) for oxalate precipitation[9]; however, the valence adjustment is slow and incomplete

under some conditions. The development of ascorbic acid (or isoascorbic acid) as a reductant for producing Pu(III)[12] has provided a highly satisfactory reagent for use in the oxalate precipitation. Ascorbic acid rapidly reduces plutonium to the Pu(III) state in various acid media over a useful range of concentrations.

Perhaps the greatest potential advantage of the plutonium(III) oxalate precipitation is that the loss of plutonium to the filtrate is sufficiently low under proper conditions to eliminate the necessity of recovery operations. Also, the oxalate precipitate is granular and easily filtered. The separation of plutonium from impurities is comparable to that obtained in the precipitation of plutonium(IV) oxalate.

The present investigation was undertaken to demonstrate the applicability and versatility of the plutonium(III) oxalate precipitation as a process route for plutonium dioxide production, and to develop the technical data and procedures necessary for plant applications.

SUMMARY

Procedures were developed for the precipitation of plutonium(III) oxalate from solutions of plutonium in nitric acid, hydrochloric acid, and sulfamic acid. In the preferred procedure, plutonium(III) oxalate is precipitated at room temperature by the slow addition of 1M oxalic acid to feed solutions containing from ~5 to >100 g/l of plutonium in 1M acid. Before precipitation, the plutonium is adjusted to Pu(III) by the addition of ascorbic acid in the presence of an oxidation inhibitor such as hydrazine or sulfamic acid.

Under the recommended conditions the loss of plutonium to the filtrate is usually less than 20 mg/l, and recovery operations are therefore not necessary. Solubility data for plutonium(III) oxalate in various acid solutions were determined to define optimum process conditions. The recommended precipitation procedure yields plutonium(III) oxalate that is coarse, dense, and easily filtered. Small particle sizes can be produced when desired by simple modifications of the procedure.

Plutonium dioxide is produced by calcining air-dried plutonium(III) oxalate in air at temperatures between 450 and 750°C. The particle size distribution of oxide produced by calcination of the coarse oxalate precipitates is mainly in the 15 to 40 micron range, while oxide with a large percentage of particles in the 1 to 10 micron range is produced from the finer precipitates.

DISCUSSION

EXPERIMENTAL METHODS

Solutions of plutonium in various acid media were prepared for precipitation tests by standard techniques.

- Solutions of Pu(IV) in nitric acid were prepared by anion exchange. A solution containing ~1 g Pu/l and 8M nitric acid was adjusted to 0.05M ferrous sulfamate and was heated briefly at 50°C to produce Pu(IV). The Pu(IV) was absorbed from this solution on a column of anion exchange resin, washed with 8M nitric acid, and eluted with 0.3M nitric acid.

- Solutions of Pu(III) in nitric acid were prepared by cation exchange. A solution containing ~1 g Pu/l and 0.3M nitric acid was adjusted to 0.05M hydroxylamine to produce Pu(III). The Pu(III) was absorbed from this solution on a column of cation exchange resin, washed with 0.3M nitric acid, and eluted with a solution containing 4.7M nitric acid and 0.3M sulfamic acid.

- Solutions of Pu(III) in hydrochloric acid or sulfamic acid were prepared by dissolution of plutonium metal in the respective acids.

The precipitation tests were performed in ordinary laboratory glassware scaled to accommodate from 1 to 100 g of plutonium. The precipitates were filtered by vacuum on medium-porosity fritted glass discs. The plutonium(III) oxalate was calcined to the dioxide in a tube-type furnace that was purged with air.

The equilibrium solubility of plutonium(III) oxalate in acid solutions was determined at room temperature. Pure plutonium(III) oxalate was equilibrated with solutions of known acid composition, and the solubility was determined at equilibrium. All plutonium analyses were by standard alpha counting techniques.

The particle size distribution of plutonium dioxide samples was determined by the Andreasen sedimentation technique.[13] With coarse oxide samples, 50 wt % sulfuric acid was used as the suspending medium; water served as the suspending medium for fine samples. With either medium, 0.05 wt % sodium pyrophosphate was added as a wetting agent. Plutonium analyses of the sedimentation fractions were performed by alpha counting techniques after dissolving the oxide samples in hot nitric acid solutions containing 0.05M potassium fluoride.

PRECIPITATION OF PLUTONIUM(III) OXALATE

Solubility Measurements

The solubility of plutonium(III) oxalate at room temperature as a
function of various acid and oxalate concentrations was determined
in order to establish the minimum plutonium loss attainable in the
oxalate precipitation and to define the conditions for minimum loss.
Solubility data for nitric acid-oxalic acid solutions are shown in
Figure 1; data for hydrochloric acid-oxalic acid and sulfamic acid-
oxalic acid solutions are shown in Figures 2 and 3. These solutions
all contained 0.05M ascorbic acid to stabilize the plutonium as Pu(III).
The data show that the solubility of plutonium(III) oxalate increases
rapidly with increasing nitric acid or hydrochloric acid concentration,
but is less strongly influenced by sulfamic acid concentration. How-
ever, the maximum concentration of sulfamic acid attainable is only
about 1.5M because of solubility limitations. The effect of increasing
the oxalic acid concentration in nitric acid and hydrochloric acid
solutions is to decrease the solubility, but this trend appears to be
reversed in sulfamic acid solutions.
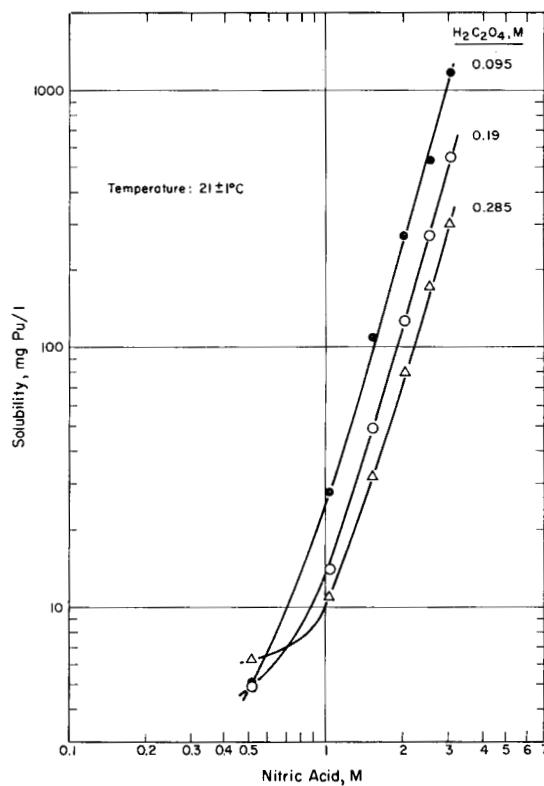

FIG. 1 EFFECT OF NITRIC ACID AND OXALIC ACID CONCENTRATIONS
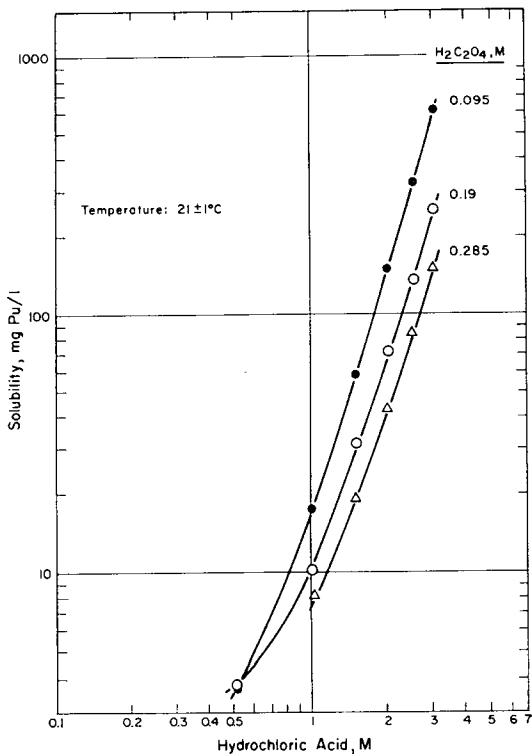ON THE SOLUBILITY OF PLUTONIUM(III) OXALATE

FIG. 2 EFFECT OF HYDROCHLORIC ACID AND OXALIC ACID CONCENTRATIONS
ON THE SOLUBILITY OF PLUTONIUM(III) OXALATE
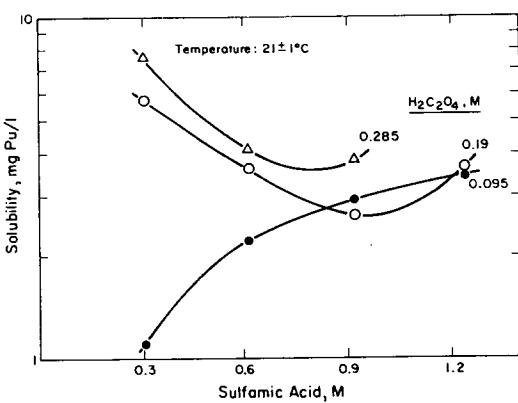

FIG. 3 EFFECT OF SULFAMIC ACID AND OXALIC ACID CONCENTRATIONS
ON THE SOLUBILITY OF PLUTONIUM(III) OXALATE

The solubility data show that plutonium(III) oxalate should be precipitated from nitric acid or hydrochloric acid feed solutions at an acidity of 1M, or lower, to minimize losses in the final slurry. Under these conditions, the recommended excess oxalic acid concentration is ~0.2M. Although this concentration of oxalic acid does not provide the lowest plutonium solubility, the volume of the filtrate is minimized (since the oxalic acid precipitant is added as 1M solution), and the total plutonium loss is thus near the minimum. The solubility data indicate that under these recommended conditions the loss of plutonium to the filtrate will be less than 20 mg Pu/l if equilibrium is attained.

The solubility data also show that plutonium(III) oxalate can be precipitated from sulfamic acid solutions with low plutonium loss without acid adjustment of most feed solutions. A 0.1M excess concentration of oxalic acid will minimize plutonium loss to the filtrate under most conditions. As the data show, the solubility is less than 10 mg Pu/l over a wide range of conditions. Thus, close control of acid and oxalate concentrations is not required when precipitations are from sulfamic acid solutions.

Precipitation Procedure

Plutonium(III) oxalate can be precipitated readily from nitric acid, hydrochloric acid, and sulfamic acid feed solutions containing from ~5 to >100 g Pu/l. The procedure is similar to that developed for precipitating neptunium(IV) oxalate[14]. The main difference in the procedures is that the neptunium process is operated most satisfactorily at elevated temperature, while the plutonium process can be operated at room temperature. An operating temperature of about 50°C is required with neptunium to assure rapid reduction of the neptunium to the Np(IV) state with ascorbic acid, and to produce a dense, granular precipitate. Elevated temperature is not required with plutonium because reduction to Pu(III) with ascorbic acid is rapid, and coarse precipitates are obtained at room temperature. In plutonium(III) oxalate precipitations, as with neptunium, an oxidation inhibitor such as sulfamic acid or hydrazine is needed in the feed solution to scavenge oxidants (nitrite, radiolysis products) that could consume the ascorbic acid reductant and oxidize the Pu(III) to higher valence states.

The same general procedure (except for the feed adjustment) can be applied to precipitate plutonium(III) oxalate from nitric acid, hydrochloric acid, and sulfamic acid feed solutions. The general procedure is as follows:

- Feed Adjustment

     Nitric Acid Solutions. Adjust the nitric acid concen-
tration to less than 1.5M, preferably to 1M or lower. Adjust to
0.05M hydrazine or sulfamic acid and mix for 10 minutes.

     Hydrochloric Acid Solutions. Adjust the hydrochloric
acid concentration to less than 1.5M, preferably to 1M or lower.
The use of an oxidation inhibitor is optional, but the addition
of hydrazine or sulfamic acid to 0.05M may be beneficial.

     Sulfamic Acid Solutions. No adjustment is required.

- Valence Adjustment

  Add the amount of 1M ascorbic acid stoichiometrically required
  to reduce the plutonium to Pu(III) and provide a 0.03M excess.
  Mix for 10 minutes.

- Precipitation

  Maintain efficient mixing. Add the stoichiometric amount of 1M
  oxalic acid plus a 0.2M excess at a controlled rate over a period
  of 30 to 45 minutes. (A 0.1M excess of oxalic acid is sufficient
  with sulfamic acid feed solutions.)

- Digestion

  Agitate the slurry for 30 minutes.

- Filtration

  Filter as rapidly as possible through a medium porosity frit.

- Washing

  Wash the precipitate on the filter frit with about three cake
  volumes of 0.5 to 1M acid (nitric, hydrochloric, or sulfamic)
  containing 0.2M oxalic acid.

- Drying

  Dry by aspiration of ambient air as required for subsequent
  processing.

The above procedure yields a precipitate that is dense and granular and is easily filtered, washed, and dried. The filtration requires only 2 to 2-1/2 times longer than the time required to filter an equal volume of water through the same filter under the same conditions. The precipitate dries to a free-flowing powder. The process is rather insensitive to most process variables except nitric acid or hydrochloric acid concentration. Under the recommended conditions, the loss of plutonium to the filtrate is usually less than 20 mg/l; the wash losses are approximately the same. This small quantity of plutonium normally does not warrant recovery. Recovery, if required, could be accomplished easily by anion exchange processing after acid and valence adjustment of the waste solutions.

A problem that may be encountered under abnormal processing conditions is oxidation of the precipitated plutonium from Pu(III) to Pu(IV). This phenomenon is most likely to occur in nitric acid systems. Oxidation can occur in the precipitator if the precipitate is not maintained in the slurried state. Stagnant layers of precipitate oxidize within several hours, the time depending upon the temperature and the nature and concentration of oxidants present. Oxidation of slurried precipitates will not normally occur unless the slurried precipitates are held until the reductant is depleted, usually after several days. Oxidation in the precipitator is highly undesirable because the solubility loss of plutonium is increased, and the oxidized precipitates are difficult to filter. Oxidation of filtered precipitates may occur upon standing, particularly if incompletely dried. Fully dried precipitates are rather stable toward oxidation under normal conditions. Oxidation of filtered precipitates may or may not be objectionable, depending upon the subsequent processing required. Both plutonium(III) and plutonium(IV) oxalate are readily calcined to the dioxide.

Typical performance data are shown in Table I.

TABLE I

Precipitation of Plutonium(III) Oxalate in Various Acid Media[a]

Nitric Acid

Feed Composition		Pu Loss in Filtrate	
HNO_3, M	g Pu/l	mg Pu/l	% Pu
1.0	28.1[b]	24	0.13
1.0	18.8[b]	20	0.16
1.0	18.8[b]	12	0.09
3.2	33.8[c]	100	0.46
2.5	22.6[c]	45	0.30
1.7	17.0[c]	21	0.18

Sulfamic Acid

Feed Composition		Pu Loss in Filtrate	
NH_2SO_3H, M	g Pu/l	mg Pu/l	% Pu
0.6	83.6	5	0.01
0.5	94.0	6	0.01
0.2	120.0	6	0.01

Hydrochloric Acid

Feed Composition		Pu Loss in Filtrate	
HCl, M	g Pu/l	mg Pu/l	% Pu
3.0	8.8	59	0.92
1.2	3.4	10	0.40
1.2	34.0	12	0.06

(a) All precipitations were made with 0.2M excess oxalic acid. Approximately 0.03M excess ascorbic acid reductant was added to all feeds. Plutonium isotopic composition was mainly [239]Pu.

(b) Plutonium feed solution was prepared by anion exchange and contained 0.05M sulfamic acid.

(c) Plutonium feed solution was prepared by cation exchange and contained 0.3M sulfamic acid.

Particle Size Distribution

The particle size distribution of a typical sample of plutonium dioxide prepared by the recommended general precipitation procedure and subsequent calcination at 750°C is shown in Figure 4. As the data show, the oxide is composed mainly of particles between 15 and 40 microns in size. Plutonium dioxide of finer particle size may be required for some applications, and can be produced without difficulty by simple modifications in the plutonium(III) oxalate precipitation step. Three modifications that yield plutonium dioxide composed of a high percentage of particles in the 1 to 10 micron size range are described below.

> Procedure A: Same as general procedure already described except that the 1M oxalic acid precipitant is added in 1 minute rather than in 30 to 45 minutes.

> Procedure B: Same as general procedure except that the plutonium feed solution is added to the 1M oxalic acid precipitant.

> Procedure C: Same as Procedure B except that 0.2M oxalic acid precipitant is used.

The particle size distributions of plutonium dioxide samples produced with these procedures are shown in Figure 4.
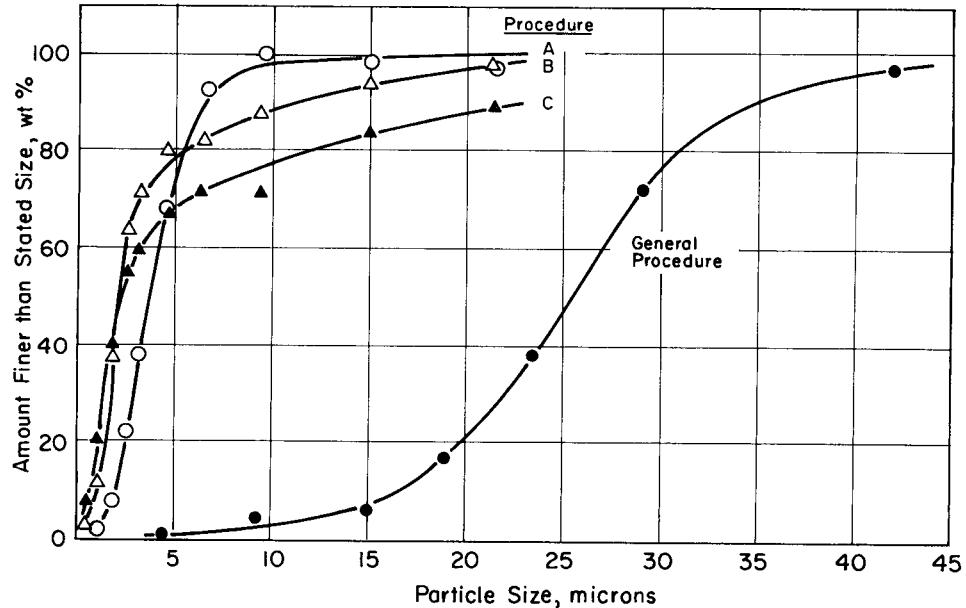

FIG. 4 PARTICLE SIZE DISTRIBUTION OF PLUTONIUM DIOXIDE

The above modifications give about the same loss of plutonium
to the filtrate as does the general procedure. Because of the smaller
particle size, however, the filtration time is increased by a factor
of about three and the time required for complete drying is greatly
increased. Occasional stirring of the filter cake will hasten drying
and will prevent cake hardening. If the precipitate is not fully dried
and powdered before calcination, the resulting oxide will contain many
large agglomerates, which can however be subdivided easily by mechanical
action.

Radiolysis Effects

The plutonium(III) oxalate precipitation was applied to various
compositions of plutonium isotopes, including plutonium that was pre-
dominantly ^{238}Pu, ^{239}Pu, or ^{242}Pu. Only in the case of ^{238}Pu were
radiolysis effects troublesome. The specific alpha activity of ^{238}Pu
is about 250 times that of ^{239}Pu. ^{238}Pu is also a source of low-energy
gamma radiation. The main effect of radiolysis in the precipitation is
to oxidize Pu(III) to higher valence states and thus cause increased
loss of plutonium to the filtrate and wash solutions. With the general
precipitation procedure already described, the ^{238}Pu loss to the filtrate
is 4 to 5 times that observed with ^{239}Pu, and the loss to the wash
solution is even higher. Increased concentrations of oxidation inhibitor
and reductant in the feed solution, and the inclusion of these reagents
in the wash solution decreases (but does not eliminate) the losses.
Increasing the rate of filtration also decreases the losses; but even
with these remedial procedures, the loss of ^{238}Pu is still 2 to 3 times
that observed with ^{239}Pu. The precipitation data in Table II demonstrate
these effects.

TABLE II

Precipitation of ^{238}Pu(III) Oxalate

| | Feed Composition | | | | Filtrate Loss[a] | | Wash Loss[b] | |
Run	g Pu/l[c]	HNO_3, M	N_2H_4, M	$C_6H_8O_6$[d], M	mg Pu/l	%	mg Pu/l	%
1	7.9	1.0	0.05	0.05	69	1.2	123	0.08
2	7.9	1.0	0.1	0.1	54	1.0	126	0.08
3	7.9	1.0	0.1	0.1	43	0.8	62	0.04
4	10.0	1.4	0.1	0.1	41	0.6	45	0.02
5	10.0	1.4	0.1	0.1	30	0.4	45	0.02
6	10.0	1.4	0.1	0.1	32	0.6	59	0.03

(a) Filtration times in Runs 4, 5, and 6 were 30 to 50% shorter than in other runs.
(b) Wash solution composition in Runs 1 and 2 was 1M HNO_3-0.2M $H_2C_2O_4$-0.05M N_2H_4.
In the remaining runs, 0.05M ascorbic acid was also present.
(c) Plutonium was approximately 80% ^{238}Pu.
(d) Ascorbic acid.

The radiolytic oxidation occurs most extensively within the filter cake—the plutonium concentration of the supernatant solution in the precipitator corresponds to the expected solubility, while the concentration in the filtrate and wash solutions is much higher. Thus, rapid filtration and washing of the precipitate is desirable. Centrifugation would probably result in lower losses than filtration. Since the plutonium content of the filtrate and wash solutions is in excess of the equilibrium solubility of plutonium(III) oxalate, and since excess ascorbic acid reductant is present, reprecipitation of the excess plutonium in these solutions will occur within several hours. The precipitate can be recovered by subsequent refiltration of the solutions through a clean filter, with the result that the over-all loss of plutonium is not significantly greater than the expected solubility loss.

^{238}Pu(III) oxalate can be prepared and isolated, but it cannot be preserved because of radiolytic decomposition. During the first few hours after ^{238}Pu(III) oxalate is filtered, the color gradually changes from the original bright green to a darker green; within 24 hours, the color changes to a dark brown. The precipitate undergoes a loss in weight concurrently with the color changes and after several days the weight loss usually corresponds to almost complete conversion to plutonium dioxide. Intermediate products in the course of the radiolytic decomposition could not be identified by X-ray diffraction analysis. Calcination at any stage of decomposition yields crystalline plutonium dioxide.

CALCINATION OF PLUTONIUM(III) OXALATE TO PLUTONIUM DIOXIDE

Thermogravimetric analyses[8,9,11] of air-dried plutonium(III) oxalate have shown its composition to be $Pu_2(C_2O_4)_3 \cdot 10H_2O$. These analyses have also shown that when the compound is heated in air, decomposition occurs in several stages yielding intermediate products and eventually plutonium dioxide. Decomposition to plutonium dioxide is appreciable at 300°C and is almost complete at 400°C. However, small additional weight losses will occur with continued heating to higher temperatures. For example, plutonium dioxide that has been calcined at 450°C will lose about 2% in weight upon heating to 800°C.

Plutonium dioxide was prepared in these studies by the following procedure: Air-dried plutonium(III) oxalate was heated under a stream of air from room temperature to 125°C over a 1-hour period and maintained at this temperature for 1 hour. During this step most of the water of hydration evolved. The temperature was then increased at the rate of 3 to 5°C per minute to the desired final calcining temperature, and was maintained at that temperature for 1 to 2 hours. The product

was cooled to room temperature under the air stream. The final calcination temperature ranged from 450 to 750°C depending on the intended use of the product.

The above procedure yields plutonium dioxide that is olive to olive-brown in color and has a tapped density usually between 2.0 and 2.5 g/cc. Oxide produced from coarse particle plutonium(III) oxalate is free-flowing and relatively dust-free. Oxide from small particle size oxalate is less free-flowing and tends to dust somewhat, but handling is not particularly difficult. Oxide produced by calcination within the specified temperature range is not refractory; it can be dissolved readily in hot concentrated nitric acid containing about 0.05M fluoride ion.

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