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PROPERTIES OF PLUTONIUM DIOXIDE

by

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CONTENTS

ABSTRACT

Selected physical and chemical properties of plutonium dioxide were investigated. Plutonium dioxide was prepared from the following plutonium salts: oxalate, nitrate, hydroxide, and peroxide. Calcination temperatures used were 240° C, 400° C, 600° C, 800° C, and 1000° C. The density, plutonium content, relative solubility, hygroscopicity, surface area, crystallite size, and thermogravimetric behavior of the oxides were measured.

SUMMARY AND CONCLUSIONS

To ship plutonium oxide safely and to measure the plutonium accurately, the calcination of the oxide and subsequent handling procedures must be controlled. Calcination temperatures between 400° C and 800° C yield oxides which are suitable for shipping and for subsequent dissolution. Humidity control of the glovebox atmosphere is necessary for accurate, repeatable samplings and analyses.

Oxide prepared from plutonium peroxide was found to be the most dense of those studied. Next in order of decreasing density were hydroxide, nitrate and oxalate (III and IV). The density of the material increased as the decomposition temperatures rose. Plutonium dioxide obtained by burning metal was found to be more dense than oxide prepared from peroxide.

The plutonium content of the dioxide increases with increasing temperature. The bulk of the anionic constituents, except sulfate, were removed at temperatures of approximately 400° C. A temperature greater than 600° C is necessary for sulfate decomposition. At 1000° C an O/Pu atom ratio of 2.06 (±0.01) was achieved for all of the salts investigated.

Nitric-hydrofluoric acid solutions were used in the solubility study. Nitric acid concentrations ranged from $6\underline{N}$ to $12\underline{N}$. The hydrofluoric acid concentrations were from 0.00 to $0.12\underline{N}$. The higher nitric acid ($12\underline{N}$) and higher hydrofluoric acid concentrations (0.06 and $0.12\underline{N}$) gave the most complete and rapid dissolution. Oxides obtained at lower decomposition temperatures were more soluble for any given acid level. Oxide obtained from plutonium peroxide had the best solubility characteristics. Oxide obtained by direct denitration had the poorest solubility characteristics.

The oxide specific surface areas decreased in the following order: oxalate >hydroxide >nitrate >peroxide. Oxalate oxide had a relatively large surface area, varying from 20 to 60 m^2/g, while the hydroxide oxides averaged 20 m^2/g. Nitrate oxides ranged from 6 to 12 m^2/g, and peroxide oxides were from 5 to 10 m^2/g. Other workers have found the reactivity of similar oxides to correlate with the surface area, (i.e., the greater the surface area, the more reactive the oxide).

In this study, the surface area did not correlate directly with the solubility. This was probably due to uncertainties in the specific surface area determination, and to uncontrollable variations in methods of preparing the oxides.

The crystallite size of the oxide particles increased as the decomposition temperature increased. Within a given system, (e.g., oxalate or peroxide) the solubility was greater for material with the lower crystallite size. This was not always true between systems. Oxide prepared from peroxide at 600° C (277A)* dissolved approximately twice as fast as oxide prepared from oxalate at 800° C (275A)*, and three times as fast as hydroxide prepared at 800° C (290A)*.

Plutonium oxide is hygroscopic. The extent and rate of water adsorption depends upon the surface area of the oxide and the humidity of the environment in which it exists. The greater the specific surface area and the higher the humidity, the more water is adsorbed. Water adsorption as great as 5 percent of the dry oxide weight was measured.

Thermograms of plutonium hydroxide and plutonium peroxide are given. The curve for the hydroxide was indicative of the drying of a hydrated oxide. This conclusion was verified by X-ray diffraction. The curve for the peroxide shows a three step decomposition: the peroxide linkage at ~150° C, the nitrate decomposition between 200° C-300° C, and a sulfate decomposition above 575° C.

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* The numbers in parentheses refer to the average diameter (expressed in angstrom units) of the crystallites making up the oxide particles.

INTRODUCTION

The work included in this report was sponsored by the Division of Nuclear Materials Management, USAEC, as part of a study on the use of plutonium dioxide as a shipping form. Included in the larger study are the development of handling and measurement procedures(4), and the design and testing of suitable shipping packages(1).

The properties of plutonium dioxide have been reported previously. One of the earliest reports in the literature was made by E. F. Westrum, Jr.(24). He describes oxides prepared from several starting materials, including $Pu(NO_3)_4$, $Pu(C_2O_4)_2$, and $Pu(OH)_4$. C. E. Holley and co-workers at LASL published a summary of the chemical, physical and thermodynamic properties of several of the oxides of plutonium(13). They describe several methods of preparing plutonium dioxide, including the preparation from plutonium peroxide. T. D. Chikalla and co-workers at HAPO have summarized the thermodynamic, crystallographic, and physical properties of plutonium-oxygen compounds(8, 9). Their work includes melting and dissociation temperatures, thermal expansion, lattice constants, and electrical resistivity determinations as well as structural stability data. J. L. Drummond and G. A. Welch investigated the preparation and properties of plutonium dioxide(11). They discuss composition and heat stability.

C. S. Caldwell and co-workers have reported a comprehensive study on oxide produced by the thermal decomposition of plutonium (III) and (IV) oxalates(5, 6, 7).

This report covers the effects of different preparation processes on those oxide properties which affect: (1) the accuracy of plutonium measurement, (2) the safety of shipment, (3) the amount of plutonium that can be shipped in a given volume, and (4) the subsequent processing of the plutonium. Comparisons of properties of oxides prepared from plutonium peroxide, plutonium nitrate, plutonium hydroxide, and plutonium (III) and (IV) oxalate are given. Where appropriate, comparisons are made with oxide produced by burning plutonium metal. Plutonium dioxide was prepared from the plutonium salts listed above by heating to temperatures of 240° C, 400° C, 600° C, 800° C, and 1000° C. The density, plutonium content, relative solubility, anionic composition, hygroscopicity, surface area, crystallite size, and thermogravimetric behavior of the oxides were measured.

EXPERIMENTAL

A. REAGENTS

The plutonium used in the major part of this study was purified prior to its use by either peroxide precipitation or by anion exchange. The plutonium peroxide was obtained from the Rocky Flats Metal Production process and calcined directly at the appropriate temperature. The plutonium oxalate, plutonium nitrate, and plutonium hydroxide starting materials were prepared in our laboratory. The starting materials always contained less than 5000 and usually less than 2500 parts of metallic impurities per million parts of plutonium.

B. PREPARATION OF OXIDES

The plutonium salts were placed in platinum dishes, dried for one hour at 120°C-140°C, and then heated to the desired temperature in a muffle furnace. The rate of temperature rise was controlled by a powerstat, and the maximum temperatures were controlled (±10°C) by a Foxboro temperature recorder-controller. Stirring of the bed during the heating cycle gave more uniform results. This was especially true at temperatures of 400°C and below. When stirring was omitted hard crusts formed on the surface which slowed thermal decomposition. This resulted in large, incompletely reacted agglomerates.

The lowest calcination temperature (240°C) investigated is on the edge of the normal thermal decomposition temperature range of all but the peroxide salt.

C. DENSITY MEASUREMENT

Density measurements were made by filling a tared 25-ml. graduated cylinder with oxide. During filling, the oxide was tumbled through a Scott Paint Pigment Volumeter prior to entering the cylinder. The volume was noted (approximately 20-25 cc) and the cylinder sealed. The cylinder was then affixed to a "tapping table" where the oxide was compacted for 2 hours. During this 2-hour period, the table fell 120 times through a distance of one inch onto a hard surface. The new volume was then noted, and the weight of the oxide measured. The bulk and tapped density were then calculated. The Volumeter and tapping table were used to provide a uniform, easily reproducible test.

D. SOLUBILITY TEST

Solubility tests of the various oxides were made in 100-ml. flat-bottomed boiling flasks. A reflux condenser was used during dissolution to minimize volume changes. Seven grams of the oxide and 35 ml. of the appropriate HNO_3-HF stock solution were normally used. All tests, except those labeled otherwise, were for 2 hours at reflux temperatures (110°C-112°C at this altitude of 6000 ft.). The solutions were allowed to cool 5 to 15 minutes and were then filtered through a tared fine-fritted glass filter. The filtrate volume was measured and the solution was analyzed for plutonium. The residue was washed with distilled water, and this filtrate volume was also measured and analyzed for plutonium content. The filter and residue were dried and weighed. From this information a material balance, and a dissolution percent were obtained. The dissolution percent is defined as:

$$\frac{\text{grams Pu (dissolver solution + wash solution)}}{\text{grams Pu (in solution + insoluble residue)}} \times 100$$

E. THERMOGRAVIMETRY

All thermogravimetric curves were made with an Ainsworth Vacuum Recording Balance. The balance pan hangs down into a horizontal tube furnace of special design. The system is capable of maintaining 10^{-3} mm Hg vacuum and controlled atmospheres. Weight gain-and-loss curves as a function of the controlled humidity atmosphere were made with the same equipment.

F. ANALYSES

The three methods of plutonium analysis used in this study were:

1. A reduction-oxidation titration using ceric sulfate(16).
2. An emission spectrographic method(22).
3. A vacuum fusion mass spectrometer method (for oxygen, then Pu by difference)(21).

The standard deviation of the ceric sulfate method, as used here on plutonium oxides, is approximately ±0.0006 g Pu/g. The emission spectrographic method is less precise, probably ±0.005 g Pu/g. The oxygen analysis is reliable to ±10 percent of the oxygen content.

The X-ray identification and crystallite size determinations were performed using standard diffraction techniques. Surface area measurements were made using a Perkin-Elmer Sorptometer, modified for use with plutonium.

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RESULTS

A. DENSITY MEASUREMENTS

The bulk and tap density of plutonium oxide are both dependent on the method of preparation. The factors which influence density most are the nature of the starting material (salt or metal), and the temperature and heating cycle to which the material has been subjected. Less important is the nature of the grinding and milling process.

Oxide density varies with the starting material used. Oxide densities vary in the following manner: oxalate <hydroxide <peroxide <metal. The range of densities obtained during this study was from 1 to 5 grams per cubic centimeter. Density of the oxides increased for each of the four salts investigated as the temperature of thermal decomposition increased. Grinding or milling appeared to increase the density.

Figure 1 illustrates these trends for bulk densities only.

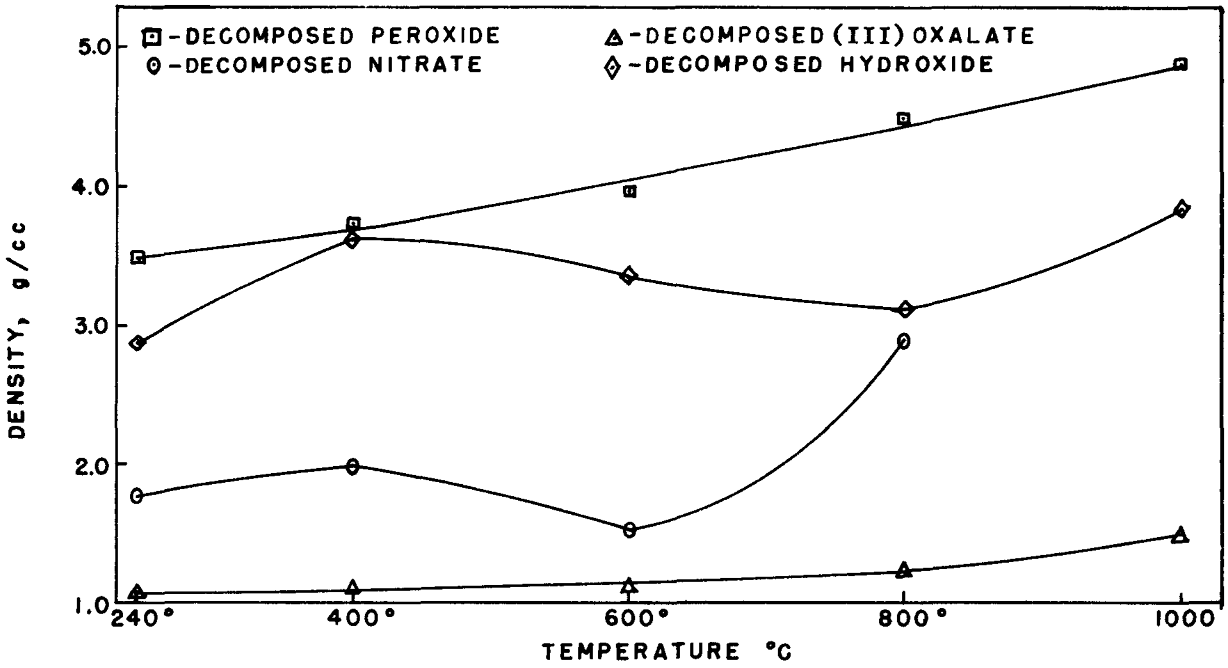

Figure 1. DENSITY OF PuO_2 AS A FUNCTION OF CALCINATION TEMPERATURE

Representative bulk and tap densities are given in Table I. The curve illustrating change of density with increasing temperature of decomposed plutonium peroxide decomposition is linear. The curve for hydroxide decomposition shows an irregularity at a calcination temperature of 400° C. The reason for this is not known. A speculation would be that a composition change occurred between 300° C and 500° C, i.e. from the hydroxide to the oxide. Thermogravimetric curves on a similarly prepared hydroxide showed that a change does occur at approximately 300° C (Fig. 2). The temperature at which the weight change occurs, and the shape of the weight loss curve is strongly suggestive of a drying period.

TABLE I

BULK AND TAP DENSITIES OF PLUTONIUM OXIDE PREPARED IN SEVERAL DIFFERENT WAYS

Starting Material	Decomposition Temperature	Bulk Density g/cc	Tap Density g/cc
Pu Nitrate	240°C	1 7	2 1
"	400.	1 9	2 4
"	600	1 7	1 8
"	800	2 9	3 6
"	1000	---	---
Pu Peroxide	240°C	3 5	4 1
"	400	3 8	4 3
"	600	3 9	4 4
"	800	4 5	4 8
"	1000	4 9	5 8
Pu (IV) Oxalate	240°C	1 0	1 4
"	400	1 1	1 5
"	600	1 2	1 5
"	800	1 4	1 7
"	1000	1 7	2 3
Pu Hydroxide	240°C*	2 9	3 2
"	400 *	3 7	4 2
"	600 *	3 5	4 0
"	800	3 2	3 7
"	1000	3 8	4 2
Pu Metal	unknown	4 8	5 3

* Average of two or more measurements Other data are single measurements

The change of density with decomposition temperature for oxide produced from plutonium nitrate is not linear. The shape of the curve is difficult to explain, for $Pu(NO_3)_4 \cdot xH_2O$ crystals are fully decomposed below 400° C(23). A sulfate impurity could have caused this density anomaly by decomposing between 550° C and 600° C. Sulfate decomposition would have increased porosity and lowered density of the oxide produced at 600° C. Further work is needed to definitely establish the cause.

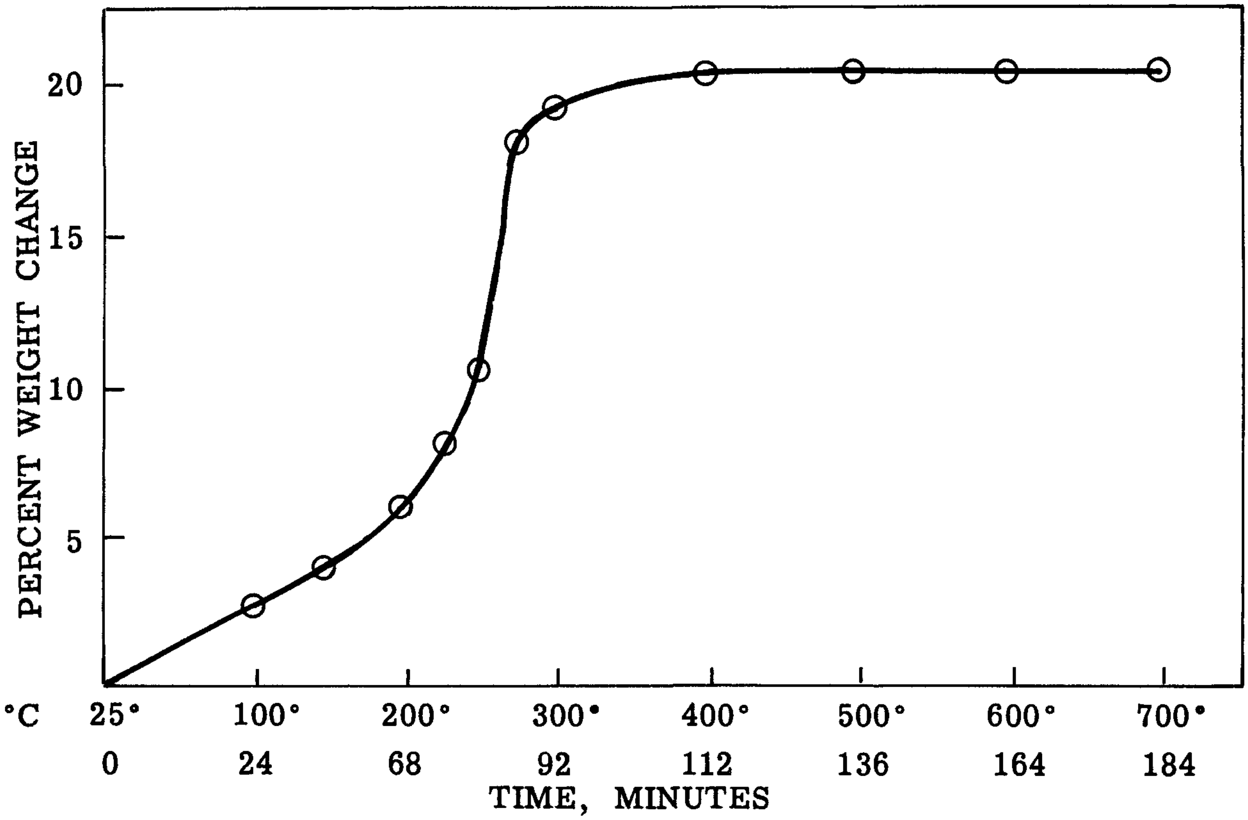

Figure 2. WEIGHT LOSS CURVE OF PLUTONIUM HYDROXIDE CONTAINING NITRATE IONS (1" DIA. Pt PAN, 300 mg SAMPLE, 2.5° C/MIN HEATING RATE)

The density of oxides produced from plutonium (IV) increases linearly with temperature. The oxalate begins to decompose below 400° C. Caldwell(3) also found that for oxides prepared from plutonium (III) and (IV) oxalates, the density increased linearly with increasing temperature. The slope of the curve reported by Caldwell is the same as shown for oxalate decomposition in Figure 1, but the intercept is displaced upward by 0.3 g/cc. The reason for this difference is believed to be the different preparative methods. Caldwell used 1M oxalic acid containing - 0.25 to 0.8M H_2O_2 solution to precipitate the oxalate. A 3.0M $H_2C_2O_4$ solution containing no H_2O_2 was used to precipitate the oxalates discussed in this report.

B. PLUTONIUM CONTENT

The plutonium content of the oxide is dependent upon its method of preparation(11). The three main variables affecting plutonium content are the furnace atmosphere, heating cycle, and decomposition temperature of the main anionic components. The lower temperature used in this study (240° C) is on the lower edge of the decomposition temperature of most of the compounds. Near stoichiometric oxides were obtained under the highest temperature condition examined (1000° C).

Temperatures in excess of 1200° C are required to give stoichiometric ratios of O/Pu(11). Plutonium salts decomposed above 870° C contain no anionic impurities, but do contain excess interstitial oxygen that is not fully removed until temperatures of 1200° C-1300° C are reached. The plutonium and oxygen contents of the high temperature oxides prepared in this study are given in Table II.

TABLE II

PLUTONIUM CONTENT OF OXIDES PREPARED FROM DIFFERENT STARTING MATERIALS[1]

Starting Material	Decomposition Temperature[2]	Pu Analysis g Pu/g[3]	Pu Analysis g Pu/g[4]	O_2 Analysis g O/g[5]
Pu Nitrate	240°C	0.8399	0.8428	---
"	400	0.8706	0.8650	---
"	600	0.8760	0.8778	0.121
"	800	0.8499	0.8697	0.124
"	1000	0.8737	0.8689	0.125
Pu Peroxide	240°C	0.7978	0.8005	0.162
"	400	0.8305	0.8325	0.130
"	600	0.8583	0.8594	0.125
"	800	0.8788	0.8771	---
"	1000	0.8790	0.8773	0.120
Pu (III) Oxalate	240°C	0.6925	0.7062	0.161
"	400	0.7345	0.7823	0.158
"	600	0.8429	0.8524	0.140
"	800	0.8705	0.8764	0.120
"	1000	0.8790	0.8791	0.123
Pu Hydroxide	240°C	0.6308	0.6091	0.194
"	400	0.8572	0.8633	0.113
"	600	0.8583	0.8690	0.118
"	800	0.8731	0.8689	0.117
"	1000	0.8748	0.8729	0.121

[1] The non-stoichiometry of the low temperature oxides is typical of plutonium oxide

[2] Dried at 140°C for one hour, then raised rapidly to the temperature listed and held for 4 hours

[3] Determined by ceric sulfate redox titration method

[4] Determined by an emission spectrograph impurity analysis by difference method

[5] Determined by vacuum fusion

The results agree favorably with those reported in the literature(11). The O/Pu atom ratios for the 1000° C oxides should be approximately 2.06, the 0.06 excess being interstitial oxygen.

Plutonium nitrate will thermally decompose to form the dioxide between 240° C and 300° C(23). The lower temperature gave a partially decomposed oxide of lower plutonium content. The decomposition reaction is dependent upon bed depth, product gas removal, and temperature. The authors feel that this is indicative of a diffusion-controlled decomposition reaction. The nitrate content for materials heated at 240° C for four hours was approximately 1 percent. The sulfate content was not reduced until temperatures of 575° C-600° C were achieved. The sulfate content of the oxides prepared between 600° C and 1000° C will depend on the sulfate content of the original solution (and therefore of the precipitate), the time it is held at temperature, the degree of bed agitation, and product gas removal. Material prepared at 400° C had a relatively high plutonium content. At 600° C the plutonium content was at the predicted level. The unexpectedly low plutonium content of the oxide at the 800° C and 1000° C temperature levels is thought to be due in part to a high sulfate content (2.0 and 1.4 percent respectively). The starting solution for the 800° C and 1000° C calcination levels was from a different batch. The only plausible explanation for the differences is that the starting solutions differed in sulfate ion content, and that the calcination conditions were not suitable for complete decomposition. The oxygen analyses of oxides produced at both levels agree reasonably well with the plutonium analyses.

The plutonium analysis using plutonium peroxide as a starting product varies with temperature in a logical manner. Plutonium peroxide is a complex precipitate and is generally thought to contain hydroxide, peroxide, hydroperoxide, nitrate, and sulfate linkages when precipitated under the conditions used here(17). Peroxide linkages break at 150° C, nitrate and hydroxide components decompose between 150° C and 300° C, and sulfate decomposition starts to occur at about 580° C. The peroxide decomposed at 240° C contained 3.8 w/o NO_3^- and 3.5 w/o $SO_4^=$, while the same material decomposed at 600°C contained 0.16 w/o NO_3^- and 2.70 w/o $SO_4^=$. Both the nitrate and sulfate decompositions are probably diffusion controlled. It is not until temperatures of 1000°C are achieved that both impurity levels are less than 0.1 percent.

The temperatures required for thermal decomposition of plutonium oxalate have been thoroughly studied(12, 15, 19). Decomposition does not approach completion until temperatures in excess of 300°C are achieved, and the oxide will not approach stoichiometry at temperatures less than 800°C. The lower temperatures give an abnormally low plutonium content due to the presence of gross amounts (~10 percent) of sulfate contamination. (The starting solution was found, upon subsequent examination, to contain sulfate ion.) The plutonium content is low and the sulfate content is high until a temperature capable of decomposing sulfate is achieved.

The trend in the plutonium hydroxide decomposition curve is also straightforward. The low temperature oxide (or hydroxide) contained large (>10 percent) quantities of nitrate. The remainder of the temperature levels (>400°C) are sufficiently high to remove the greater part of the nitrate impurity. A major problem in using $Pu(OH)_4$ as a starting material is that the precipitate is difficult to filter and wash.

Table III lists plutonium contents of several oxides prepared at

TABLE III

PLUTONIUM CONTENT OF PLUTONIUM OXIDES
PREPARED AT THE HANFORD PLANT
(BUILDING 234-5)

Starting Material and Decomposition Conditions		Pu Analysis g Pu/g	$SO_4^=$ Analysis g $SO_4^=$/g
H-633	Activated Nitrate, decomposed at 410°C	0.7406	0.1000
H-634	Purex Nitrate, decomposed at 410°C	0.8478	0.0300
H-635	Purex Nitrate, decomposed at 450°C	0.8652	0.0085
H-647	Oxalate, decomposed at 400°C	0.7576	0.0015
H-649	Oxalate, decomposed at 400°C	0.8196	0.0010

Hanford. For batch H-633, the denitration reaction was carried out in a pilot plant size continuous calciner. This denitrated oxide contains a large (~10 w/o) amount of sulfate ion. The oxides designated H-634 and H-635 follow the trend shown in Table II, while H-647 and H-649 do not follow this trend. The latter two samples were taken from a production calciner at Hanford at different times on the same day. The starting material used here was $Pu(C_2O_4)_2$. This difference (76 percent vs 82 percent) in Pu content points out the difference that may occur in a production calciner. The higher value is more characteristic of the oxide normally produced by this method(14, 20).

C. SOLUBILITY

Plutonium dioxide is difficultly soluble in most solvents. The best solvents are 12-16$\underline{M}$ HNO_3 with 0.01-0.1$\underline{M}$ HF, 5-6$\underline{M}$ HI, and 9$\underline{M}$ HBr(10, 13). Refluxing is necessary in all cases and the dissolution is slow. The nitric acid-hydrofluoric acid dissolution is preferred for plutonium recovery.

Rainey has studied the dissolution rates of high density oxide pellets(18). He pointed out the beneficial effect of fluoride ion concentration on the dissolution rate. Workers in Belgium state that the rate of dissolution of PuO_2 in greater than 10$\underline{N}$ HNO_3 increases linearly with increasing fluoride ion concentration between the limits of 0.07 and 0.3$\underline{M}$ HF(3).

Table IV lists the solubility characteristics of several oxides over a range of nitric acid and fluoride ion concentrations. These are the oxides previously discussed in parts A and B of this section. A number of factors are known to influence the solubility of oxides in a particular acid. Among these are the nature of the starting material, the maximum temperature to which the material has been subjected, the time at that temperature, and extent of impurities. The physical properties which possibly can be used to predict the relative solubility of an oxide include the crystallite size and the surface area. These two properties are, of course, related to the four factors mentioned above. The increasing refractory nature of PuO_2, as the decomposition temperature is increased, is thought to be due to the perfection of the crystal lattice as the temperature (and time at temperature) is increased[(2)].

TABLE IV

PERCENT OF PLUTONIUM OXIDE DISSOLVED IN THE LISTED SOLUTION
SEVEN GRAMS OF THE OXIDE WERE REFLUXED FOR 2 HOURS IN 35 ML. OF ACID

Type of Oxide*		6N HNO_3	9N HNO_3	12N HNO_3	12N HNO_3 0.002N F^-	12N HNO_3 0.005N F^-	12N HNO_3 0.01N F^-
Denitration,	240°C	3.20	4.72	5.78	4.46	6.15	10.2
"	400	1.24	0.90	2.44	---	---	---
"	600	0.63	0.14	0.48	---	---	---
"	800	4.32	5.29	6.50	11.49	30.41	41.74
"	1000	1.12	0.94	0.96	0.98	12.64	27.10
Peroxide,	240°C	96.50	99.44	99.67	99.20	99.48	99.66
"	400	11.57	94.39	99.76	99.66	99.76	99.78
"	600	4.24	4.15	2.31	3.81	15.60	57.38
"	800	0.73	0.75	1.16	0.67	15.05	34.01
"	1000	0.35	0.45	0.94	1.14	9.44	16.10
Oxalate,	240°C	75.64	87.20	93.31	92.54	98.12	99.46
"	400	48.30	63.76	65.94	69.26	88.07	99.50
"	600	7.83	9.70	10.34	7.07	13.03	62.50
"	800	1.73	1.53	1.63	0.41	1.35	29.84
"	1000	0.89	1.54	1.93	1.01	14.72	30.62
Hydroxide,	240°C	---	---	6.56	99.56	99.85	99.95
"	400	---	---	6.80	5.74	6.75	13.23
"	600	---	---	1.01	0.32	0.59	2.28
"	800	---	---	0.52	0.20	2.08	18.55
"	1000	---	---	0.50	0.01	8.33	41.33

* Each oxide sample was heated slowly to 140°C, then rapidly to the indicated temperature. They were held for 4 hours at temperature.

There are some exceptions in the data in Table IV, but in general, a higher calcining temperature produced a less soluble oxide. Oxides prepared from oxalates and peroxides followed this trend very well. It was not as evident in the case of oxides prepared by denitration and by calcination of hydroxide. In both of the latter cases, the solubility increased between 600° C and 800° C. The suspected reason for this is the presence and subsequent decomposition of sulfate in the starting material (plutonium nitrate solution). The densities (Table I, Fig. 1) of these oxides are believed to have varied peculiarly for the same reason.

Table IV also illustrates the effect of the solvent on the solubility. Increasing acidity and increasing fluoride ion content generally increase the extent of dissolution under the conditions studies. For many processes, a high fluoride ion content is undesirable, due to its complexing and corrosive properties. It appears however, that a fluoride ion concentration of $0.01\underline{M}$ (or greater) is needed for rapid and complete dissolution of these particular oxides.

If high solubility and relatively low fluoride ion concentration in the resultant solution are desired, then oxides produced by the decomposition of plutonium nitrate and plutonium hydroxide are less desirable in this characteristic. If fluoride ion concentration is of no concern, then any one of the four may be considered.

Workers at Hanford have also found denitrated plutonium oxide to be unreactive with respect to chlorination(12). Their solution is to "activate" the oxide by the addition of sulfate.

Since direct denitration of plutonium nitrate offers several advantages in equipment and operating personnel cost savings, it was decided to repeat several of these tests. Table V lists the data

TABLE V

ADDITIONAL DISSOLUTION STUDIES ON OXIDES PREPARED BY DENITRATION
SEVEN GRAMS OF THE OXIDE WERE REFLUXED FOR 2 HOURS IN 35 ML. OF ACID
(Dissolution in percent.)

Calcination Temperature*	$12\underline{N}$ HNO_3	$12\underline{N}$ HNO_3 $0.002\underline{N}$ F^-	$12\underline{N}$ HNO_3 $0.005\underline{N}$ F^-	$12\underline{N}$ HNO_3 $0.01\underline{N}$ F^-	$12\underline{N}$ HNO_3 $0.06\underline{N}$ F^-	$12\underline{N}$ HNO_3 $0.12\underline{N}$ F^-
240°C	3.04	4.46	6.15	10.20	---	---
350	1.30	1.49	2.16	3.54	98.40	99.95
400	0.28	0.38	0.55	2.85	---	---
400	1.02	0.90	1.08	2.34	98.30	---
400	0.81	0.90	1.42	2.66	98.44	---
400	0.49	0.68	0.80	1.94	91.58	---
600	0.03	0.45	27.23	62.94	---	---
600	0.08	0.14	3.25	40.99	88.41	---
800	3.03	13.59	29.59	43.38	---	---

* Each batch was heated slowly to 140°C, then rapidly to the indicated temperature. Calcination time was 4 hours.

obtained. The trend of increasing solubility with higher fluoride ion concentration is observed. In addition to those levels listed in Table IV, tests at higher fluoride concentrations were performed. At higher fluoride ion concentrations these oxides were found to be more soluble.

Table VI lists solubility data on some oxides prepared at Hanford.

TABLE VI

DISSOLUTION TESTS ON OXIDES PREPARED AT HANFORD
SEVEN GRAMS OF OXIDE WERE REFLUXED FOR 2 HOURS IN 35 ML. OF ACID
(Dissolution in percent.)

Type of Oxide		$12\underline{N}\ HNO_3$	$12\underline{N}\ HNO_3$ $0.002\underline{N}\ F^-$	$12\underline{N}\ HNO_3$ $0.005\underline{N}\ F^-$	$12\underline{N}\ HNO_3$ $0.01\underline{N}\ F^-$	$12\underline{N}\ HNO_3$ $0.06\underline{N}\ F^-$
H-633	Denitration at 410°C for ~30 minutes, activated	49.09%	51.17%	62.52%	78.71%	98.04%
H-634	Denitration at 410°C for ~30 minutes, semi-activated	5.40	6.28	9.27	25.7	78.92
H-635	Denitrated at 450°C for ~30 minutes, non-activated	2.32	2.80	3.13	4.97	86.22
H-647	Oxalate decomposition, at 400°C for ~30 minutes	51.76	52.35	---	54.95	99.95
H-649	Oxalate decomposition, at 400°C for ~30 minutes	---	31.83	31.41	34.93	99.98

Oxide H-633 is "activated" (contains 10 w/o $SO_4^=$). H-634 is "semi-activated" (contains 3 w/o $SO_4^=$). H-635 is "non-activated" (~1 w/o $SO_4^=$). The effect of increasing the fluoride ion concentration is illustrated here also.

Sample H-647 was decomposed at 400°C. The decomposition was apparently incomplete, leaving some of the material as the oxalate. This is reflected in both the solubility data and plutonium content (Table III). Sample H-649 was more completely decomposed, but probably had some plutonium present as the oxalate.

Table VII lists the solubility data for an oxide prepared from plutonium oxalate. The material was heated to 400°C for one-half hour, removed from the furnace, ground with a ceramic pestle, and then replaced in the furnace for an additional half hour. The solubility is low except in the solution containing $0.06\underline{N}$ fluoride ion. Table VIII is a study of the effect of fluoride ion concentration and time on the extent of dissolution. The oxide used in Tables VII and VIII is from the same batch.

TABLE VII

DISSOLUTION TESTS ON OXIDES PREPARED BY THERMAL DECOMPOSITION OF $Pu(C_2O_4)_2$*

(Dissolution in percent.)

Temperature	$12\underline{N}$ HNO_3	$12\underline{N}$ HNO_3 $0.002\underline{N}$ F^-	$12\underline{N}$ HNO_3 $0.005\underline{N}$ F^-	$12\underline{N}$ HNO_3 $0.01\underline{N}$ F^-	$12\underline{N}$ HNO_3 $0.06\underline{N}$ F^-
1 hour at 400°C	6.72%	9.06%	11.43%	16.28%	99.77%

* Seven grams of oxide were refluxed for 2 hours in 35 ml. of acid.

TABLE VIII

DISSOLUTION TESTS ON OXIDES USING TIME AT REFLUX CONDITIONS AND INITIAL FLUORIDE ION CONCENTRATION AS THE VARIABLES

(The oxide is from the same batch as that illustrated in Table VII.)

		Time at Reflux, Hours			
Type of Oxide	Type of Acid	1	2	3	4
400°C oxalate	0.01 F^- + $12\underline{N}$ HNO_3	8.67%	15.40%	21.40%	31.80%
400°C oxalate	$0.03\underline{N}$ F^- + $12\underline{N}$ HNO_3	19.48	40.79	98.85	99.36
400°C oxalate	$0.03\underline{N}$ F^- + $12\underline{N}$ HNO_3	16.40	34.29	96.86	99.29

D. SURFACE AREA

Surface area measurements were made on selected samples of oxides prepared from the five starting materials. The specific surface area of the oxides increased in the order: metal >peroxide >nitrate >hydroxide >oxalate. Except for the nitrate and hydroxide, this is the order of decreasing bulk density. Table IX lists some

TABLE IX

SURFACE AREA MEASUREMENTS OF
TYPICAL OXIDES PREPARED IN THIS STUDY

Oxide Type	Time at Temp.	Specific Surface Area, M^2/g
H-633 activated nitrate, decomposed at 410°C		7.59
H-634 nitrate, decomposed at 410°C		5.71
H-635 nitrate, decomposed at 450°C		6.20
H-647 oxalate, decomposed at 400°C		22.7
Oxalate, decomposed at 400°C		41.4
Nitrate, decomposed at 400°C	4 hours	11.9
Nitrate, decomposed at 400°C	4 hours	11.2
Nitrate, decomposed at 400°C held at 140°C	6 months	10.6
Peroxide, decomposed at 600°C	30 minutes	8.9
Dried (138°C for one hour) plutonium peroxide		10.1
Air dried plutonium peroxide, not decomposed		4.7
Hydroxide, decomposed at 240°C	3 hours	22.7
Hydroxide, decomposed at 400°C	3 hours	22.1
Hydroxide, decomposed at 600°C	3 hours	22.3

typical specific surface area values. The oxides labeled with the H prefix are the same ones whose solubility is illustrated in Table VI. The surface area of the burned metal oxide is remarkably low by contrast. It is seen that the surface area is a characteristic of the starting material. This metal oxide was also nearly insoluble compared to the oxides prepared by decomposition of the salts.

The degree of correlation expected was not found between the surface area of the salts and the other properties, notably solubility, measured in this study. Caldwell has reported(5) a correlation between calcination temperature and surface area of oxides prepared from plutonium (IV) oxalate. He found that the surface area of oxide powders decreased with increasing temperature. The values reported ranged from 10 m^2/g of PuO_2 to 60 m^2/g, the variation due primarily to the heat treatment applied. The lack of direct correlation with solubility in our study was probably due to the relatively long times that the samples were held at the maximum temperature. This would smooth out differences between samples due to sintering effects.

The attempt in this part of the study has been to establish relative surface area ranges for particular types of oxides.

E. CRYSTALLITE SIZE

Crystallite size determinations were made on a number of oxides prepared from various starting materials. The crystallite size increased as the calcination temperature increased. The crystallite size, as well as the surface area, was used as a means of predicting and correlating reactivity.

The trends seen in Table X , when compared to the dissolution test data given in Table IV, show that a correlation does exist. The correlation is not exact, i.e. an oxide with a crystallite size determination of 100A will not necessarily dissolve at a rate faster than one with a crystallite size determination of 200A. The tendency is assured between an oxide having a crystallite size of 100A and one having a crystallite size of 1000A. This lack of exact correlation is thought to be due in part to a lack of accuracy in the crystallite size determination itself, for it is an empirical measurement. Another and perhaps more important reason is the effect of other parameters such as surface area and impurity content in improving or inhibiting dissolution characteristics.

Table XI lists the crystallite size determinations of oxides prepared at Hanford. The crystallite sizes fall within the range established in Table X.

TABLE X

CRYSTALLITE SIZE MEASUREMENTS MADE ON REPRESENTATIVE OXIDES
(The values are obtained by X-ray diffraction.)

Oxide Type		Crystallite Size, A
Nitrate,	240°C	115
	400	130
	600	118
	800	1000
	1000	1000
Peroxide,	240°C	38
	400	52
	600	277
	800	480
	1000	1000
Oxalate,	240°C	41
	400	57
	600	137
	800	275
	1000	1000
Hydroxide,	240°C	56
	400	61
	600	100
	800	291
	1000	550

If the data in Table XI are compared with the data in Table VI, one sees that a correlation can be made between crystallite size and solubility for four of the five oxides. The exception is oxide H-633, the "activated" oxide. The reason for this anomaly, other than the obvious reason of sulfate impurity, is not clear. It is apparent that although crystallite size is indicative of the solubility to be expected, other parameters also affect solubility.

TABLE XI

CRYSTALLITE SIZE DETERMINATIONS MADE ON OXIDES PREPARED AT HANFORD

Oxide Type		Crystallite Size, A
H-633	activated nitrate, calcined at 410°C	197
H-634	nitrate, calcined at 410°C	155
H-635	nitrate, calcined at 450°C	155
H-647	oxalate, calcined at 400°C	42
H-649	oxalate, calcined at 400°C	42

F. PARTICLE SIZE DETERMINATION

Due in a large part to the methods of preparation used in this study, no correlation was observed between temperature of decomposition and particle size.

The oxide obtained by batch preparation in a muffle furnace was almost always crusty and agglomerated. Either during or immediately following the decomposition period, the material was pulverized. The degree of pulverization appeared to affect the measured particle size more than the nature of the starting material or the temperature of decomposition.

G. EMISSION SPECTROGRAPHIC ANALYSES OF METALLIC IMPURITIES

The plutonium nitrate starting material used in this study was pure enough to preclude any measurable effect from metallic impurities. The starting materials always contained <5000 ppm and usually <2500 ppm of metallic impurities per gram of plutonium.

H. WATER CONTENT

Plutonium oxide is hygroscopic. When the oxide is prepared at temperatures in excess of 400°C and in a dry atmosphere (<5°F dew point) adsorbed water will not be a problem in measuring and assaying plutonium oxide. At lower calcination temperatures, or higher relative humidities, problems arise. In our investigation, the hygroscopic character was a problem in sampling and analysis(4). The samples adsorbed sufficient water during sampling and analytical weighing periods to cause detectable errors. Conversely, samples with large amounts of adsorbed water lost this water when placed in desiccators.

Caldwell has found that moisture pickup is a function of surface area, relative humidity, and time(6, 7). Plutonium oxide prepared from oxalate (60 m^2/g) gains 1.0 weight-percent in 2 hours, and 1.9 weight-percent in 10 hours in a 76 percent relative humidity atmosphere. Plutonium oxide prepared from oxalate (10 m^2/g) gains 0.1 weight-percent in 20 minutes, 0.25 weight-percent in one hour and 0.3 weight-percent in 2 hours. No further weight change was noted at the end of 3 hours.

Caldwell further reports(5) that in a 33 percent relative humidity atmosphere the equilibrium water adsorption is about one-third of that at 76 percent relative humidity. In a 53 percent relative humidity atmosphere the equilibrium water adsorption is two-thirds of that at 76 percent relative humidity.

Calcined plutonium peroxide (pre-dried, then heated at 400°C for one hour, specific surface area = 20 m^2/g) was found to gain as much as 3.5 weight-percent in 24 hours in a >95 percent relative humidity atmosphere at room temperature. Figure 3 shows the

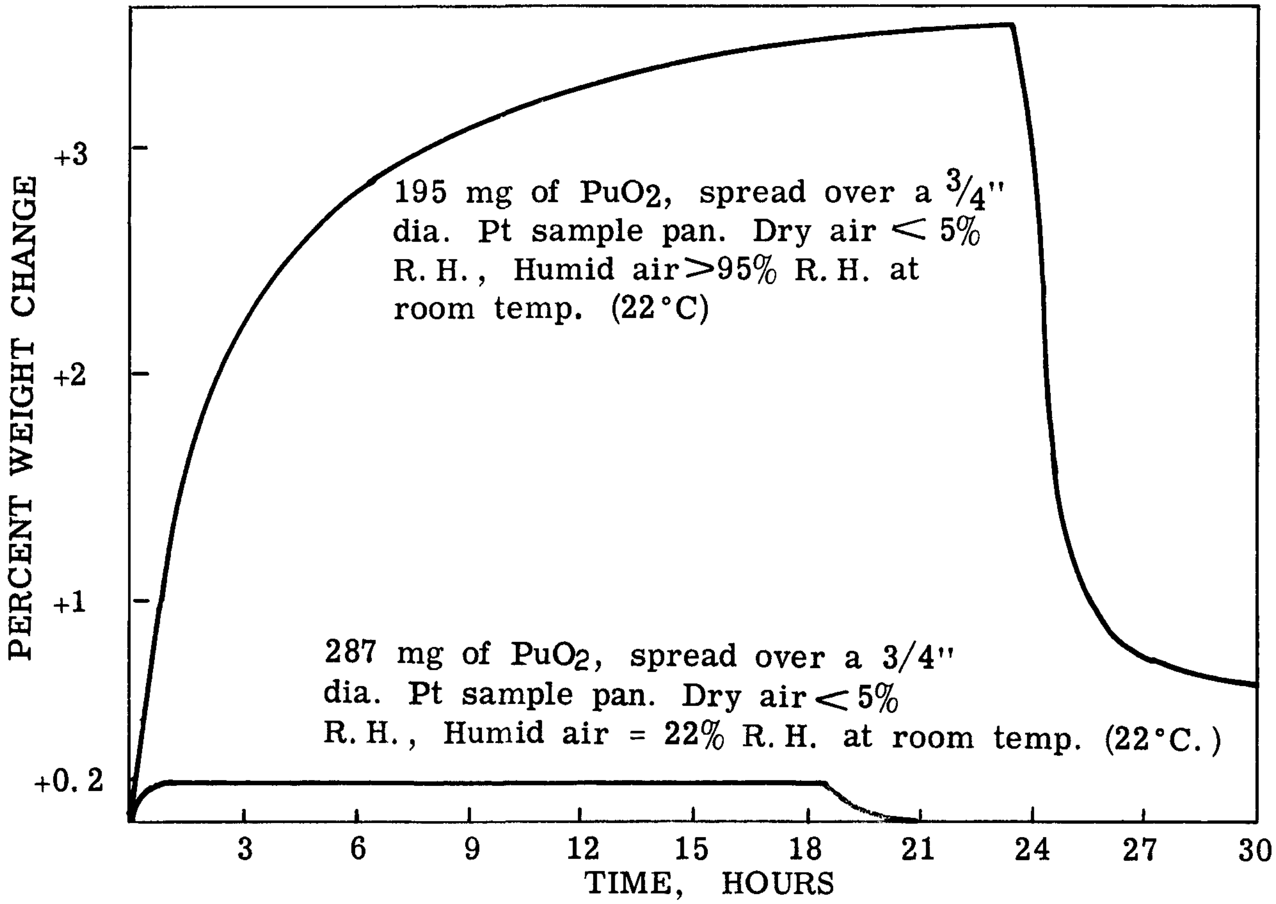

Figure 3. MOISTURE ADSORPTION AND DESORPTION CURVES ON SAMPLES OF PuO_2 CONTACTED WITH DRY, THEN HUMID, THEN DRY ATMOSPHERES. SPECIFIC SURFACE AREA = 20 m^2/g.

moisture adsorption and desorption curves of this calcined peroxide oxide at 22 percent and >95 percent relative humidity. The humidity of the atmosphere is shown to be a very significant factor in the rate and extent of moisture pickup and loss. The weight gain in the 22 percent relative humidity atmosphere, 0.2 percent, is small but would still be of significance in a sampling or analytical procedure where a high degree of precision was expected. The measurements reported in Figure 3 were made using an Ainsworth Vacuum Balance with the sample pan hanging into a controlled atmosphere. The samples were evenly spread over a three-quarter inch diameter sample pan. This provided a near optimum environment for weight gain, and may account for the difference in these values and in the values reported by Caldwell. The largest weight gain measured in this laboratory was 5 percent. No desorption measurements were made and the surface area was not measured for this latter sample.

I. THERMOGRAVIMETRIC CURVES

Thermogravimetric curves for decomposition of plutonium nitrate and plutonium oxalate have been published(19, 23). Curves for plutonium hydroxide and plutonium peroxide are shown in Figures 2 and 4.

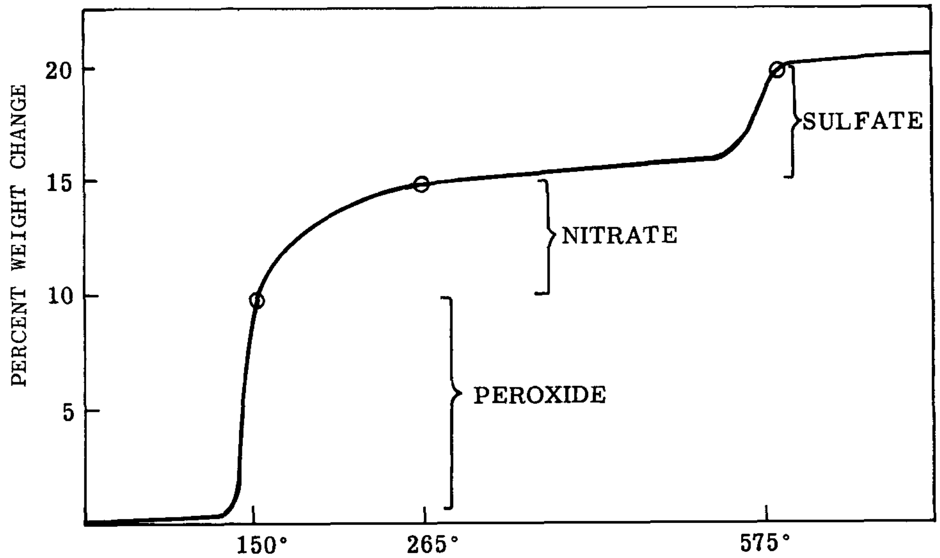

Figure 4. WEIGHT LOSS CURVE OF PLUTONIUM PEROXIDE CONTAINING NITRATE, AND SULFATE IONS. (1" DIA. Pt PAN, 250 mg SAMPLE, 2.5°C/MIN. HEATING RATE)

Thermograms show that a significant loss of weight occurs from hydrated $Pu(NO_3)_4$ above 60° C. The weight loss is rapid from 90° C to slightly above 300° C, at which point a near stoichiometric oxide ($\sim PuO_{2.1}$) occurs under thermobalance conditions. The weight loss is very gradual above 350° C.

Plutonium (IV) oxalate is hydrated when prepared from nitric acid solutions. After drying at temperatures below 80° C, the anhydrous salt is obtained(19). The oxalate decomposes to the oxide between 160° C and 350° C. As with similar oxides, these samples continue to lose weight gradually until temperatures greater than 1000° C are reached.

Plutonium (IV) peroxide is also hydrated when precipitated from nitric acid solutions. The peroxide composition is variable, depending upon the precipitation conditions(15). The crystals contain Cl^-, NO_3^-, OH^-, $SO_4^=$, and $C_2O_4^=$ when the anions are present in the original solution. A typical thermogravimetric curve is shown in Figure 4. These crystals were prepared from a nitric acid solution containing sulfate ions. The peroxide linkages decompose between 140° C and 150° C. The nitrate ions are decomposed below 320° C, and sulfate decomposition is complete above 575° C.

Plutonium hydroxide is considered to be a hydrated oxide, and not a true hydroxide compound. This supposition is based largely on X-ray diffraction data. Figure 2 lends credence to this idea. The first part of the weight curve is characteristic of a drying process. This is followed by a portion of the curve suggestive of a nitrate decomposition. Prior to the running of the thermogram, the precipitate was dried in a dry helium atmosphere until a near constant weight was achieved. The thermogram suggests that, except for sulfate impurities, a temperature of 400° C is adequate for decomposition.

RECOMMENDATIONS FOR FUTURE WORK

The effect of radiation on undecomposed anions ($SO_4^{=}$, NO_3^{-}, $C_2O_4^{=}$, etc.) in the oxide matrix is not known. This effect is apparently negligible on well calcined materials for short periods of time(4), i.e. 2 to 3 months unvented storage. The effect of radiation on incompletely calcined materials during long storage periods is not known. If long storage periods are anticipated, additional information on radiolysis effects should be obtained.

The effect of sulfate additions on density and reactivity of plutonium oxide is not well understood. Preliminary work at Hanford(14) shows that the addition of sulfate increases the reactivity. The probable mechanism is an increase in porosity due to escaping gases during the thermal decomposition. If solubility of the oxide is important, the effect of sulfate should be determined.

The relationship between surface area and reactivity, as measured by dissolution or hydrofluorination, is not clear. A more complete study is needed to determine if solubility characteristics for plutonium oxide can be improved.

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