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PLUTONIUM:  
STEAM OXIDATION AND OXIDE DISSOLUTION

By

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PLUTONIUM:  
STEAM OXIDATION AND OXIDE DISSOLUTION

I. INTRODUCTION

Plutonium metal, particularly in the form of turnings or skulls, is quite reactive under normal atmospheric conditions. A safety hazard arises due to its pyrophoric character, as well as its toxicity. Dangerous metal fires have occurred during processing, even in aqueous nitric-hydrofluoric acid dissolutions. The highly-exothermic reaction upon burning plutonium in air or oxygen is dangerous, difficult to control, and produces a sintered dioxide which is difficult to dissolve and reclaim.

This document outlines a method of oxidizing plutonium metal and skulls with steam to a low temperature, relatively soluble dioxide. The method is safe, produces a stable, easily-stored powder, and eliminates hazards of pyrophoricity associated with the handling, storage, and dissolution of metallic plutonium.

II. SUMMARY AND CONCLUSIONS

Plutonium skulls and turnings have been oxidized by steam in an inert atmosphere at temperatures from 200 to 500 C. With a four-inch diameter steel reactor, rates up to 250 grams per hour have been obtained. The resulting powder is finely-divided, free-flowing, and more reactive than normal dioxide to further processing or dissolution.

Plutonium dioxide dissolution rates as high as 1000 grams per hour have been obtained during initial dissolution periods, and appear possible under continuous dissolving conditions. On a batch basis, a two-hour cycle gave an average recovery of in excess of 99 percent\* using 15.7 M  $\text{HNO}_3$  - 0.2 M HF at an average solution concentration of 154 g/l, and from 94 to 100 percent recovery in 13 M  $\text{HNO}_3$  - 0.2 M HF at an average solution concentration of 132 g/l.

III. EXPERIMENTAL

The major portion of the large-scale work was accomplished using an iron reactor vessel made from four-inch diameter schedule 40 pipe. A piece of 21-micron porosity stainless filter material was welded near the top and bottom of the pipe at the gas inlet and outlet to prevent plutonium dioxide powder losses. The gas inlet and outlet were 3/8" steel tubing.

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Argon and steam were mixed prior to entering the reactor, and the entire reactor was heated by a pot furnace. A thermocouple well was welded through the side of the reactor, and a chromel-alumel thermocouple used to determine the internal temperature.

An oxidation run consisted of placing the plutonium on a ceramic-magnesium oxide disk over the bottom of the reaction vessel, closing the vessel, and putting it in the furnace. The furnace was turned on and the reactor flushed with argon while warming to 100 C. At 100 C internal temperature, steam was mixed with argon to about a 25 percent steam, 75 percent argon ratio. The oxidation reaction usually started by the time the temperature reached 175 C. When the oxidation started, the internal temperature increased rapidly, the furnace temperature was then lowered, and the oxidation reaction allowed to produce its own heat. Temperature control was maintained by the steam-to-argon ratio. When the temperature exceeded 400 C, the steam was decreased (or momentarily stopped); and when the temperature fell below 250 C, the steam flow was increased. An argon flow of about two liters per minute remained constant. The reaction was considered complete and the run stopped when the temperature fell below 200 C with a 75 percent steam, 25 percent argon flow ratio.

The off-gases were bubbled through a water trap, then passed into the hood atmosphere.

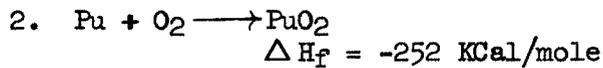
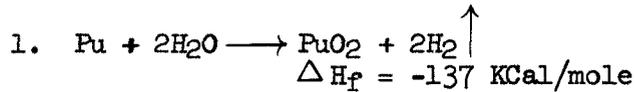
The oxide dissolutions followed normal procedures. The dry oxide was poured into a dry vessel first, then the premixed nitric and hydrofluoric acids were added. Throughout the experimental work, 1.5 liters of acid was added to each run. A water-cooled reflux condenser was used to limit the acid loss, and the solution was gently refluxed on a hot plate for the prescribed length of time.

#### IV. DISCUSSION

##### A. Steam Oxidation

Studies of "reactive" samples of plutonium dioxide indicate the reactivity could be attributed to the highly distorted, impure plutonium lattice produced at low temperature. The reactivity decreases as the lattice is perfected by higher temperature treatments up to 1000 C. No attempt has been made to determine the crystal structure of steam-oxidized plutonium dioxide. It is not known at what temperature the "reactivity" is lost, or even if it is lost.

The resultant total heat of reaction is considerably less for the steam oxidation process than for oxygen, as shown by equations 1 and 2.



It is, therefore, quite possible that considerably higher temperatures could be used during the steam oxidation, with resultant increases in the oxidation rate.

Thermodynamically, the reaction of the water to form plutonium dioxide and hydrogen decreases the overall heat of reaction, provides some measure of control, and allows the formation of the low temperature oxide. Presumably this oxide would sinter and form the less soluble oxide form if held at a high temperature. This has not been investigated to any degree, although short bursts of temperature up to 800 C were not noticeably detrimental to dissolution rates.

The presence of hydrogen from the steam decomposition poses a question concerning the formation of hydrides. Mixtures of plutonium dioxide and plutonium hydride have been found. These are slate-like in appearance, easily recognizable, and were obtained in the attempts to steam-oxidize massive pieces of plutonium metal. This characteristic of massive metal oxidations is the reason only plutonium skulls, turnings, or metal chipped into small pieces is recommended for the steam oxidation process. The black-slate oxide-hydride mixture does not dissolve as rapidly as yellow oxide. It appears to be quite stable and has been ground to a powder without sparking; but metal must always be suspected which would constitute a fire hazard.

The use of a ceramic disk as the base upon which the plutonium is oxidized is a factor not fully investigated. Experimentally, the skulls were never completely oxidized when placed directly upon the steel frit, whereas complete oxidation occurred when a 1/8" thick ceramic plate was interposed between the metal frit and the plutonium. The theoretical explanation is not known.

Batch sizes up to 900 grams have been oxidized by this method without difficulty. However, care must be taken with large batch sizes to exercise prompt and exact steam ratio control at the start of the oxidation reaction. An excess of steam left on for only one-half minute can result in a temperature jump of 600 C or more. Cutting the steam flow stops the reaction.

Nearly a dozen attempts were made to oxidize massive pieces of metal by this steam method. Yields of 30 to 50 percent good powder were obtained, along with a black-slate appearing material which x-ray analysis showed to be a mixture of plutonium hydride and oxide. The hydrogen appeared to penetrate the solid metal and react in a way which

made it partially resist oxidation. Vibrating the reactor during the oxidation did not appear to break this material and allow its complete oxidation. A rerun on the material after it had been broken up usually resulted in an acceptable oxide, but the results were unpredictable. The steam oxidation of massive pieces of pure metal is, therefore, not recommended.

#### B. Oxide Dissolution

The "refractory" nature of highly-ignited plutonium dioxide assures its stability, but makes it very difficult to reclaim. There is no effective dissolution method known for plutonium dioxide. The best solution rates are obtained by using concentrated phosphoric acid at 200 C, but the difficulties associated and the product formed make nitric-hydrofluoric acid the preferred media despite its slower dissolution rate.

Steam-oxidized plutonium dioxide was found to dissolve more rapidly and completely in nitric-hydrofluoric acid than either metal or the usual dioxide.

Dissolution rates are difficult to compare due to the variability of the oxide available. In reality there is no NORMAL oxide, and each batch dissolves at a rate related to its past treatment.

Laboratory dissolution procedure in which 250 to 450 grams of oxide are dissolved consists, on the average, of three steps: (1) the oxide is refluxed for three hours in 1-1/2 liters of 13 M HNO<sub>3</sub> - 0.2 M HF; (2) the solution is filtered and the residue refluxed in a second one-liter of acid for three hours; then (3) filtration and third treatment with fresh acid for two hours is usually required for complete dissolution.

Discussions with off-site personnel corroborate this general procedure as necessary for a consistent recovery of 95 percent or better.

Production facilities utilize two dissolvers--a large 400-liter unit and a smaller 3-liter unit. In the large dissolver, 400 grams are dissolved in about 125 liters of 5.5 M HNO<sub>3</sub> - 0.25 M HF in a three-hour period. The oxide is considered 90 percent dissolved; however, the solution is mixed with ANN and decanted into the process, so accurate recovery figures or rate data are not available.

The smaller unit takes a charge of 800 grams. About 50 percent, or 400 grams, are dissolved in three hours. The batch is made back up to 800 grams for the next run. This historical experience indicates 100 to 135 grams per hour as a maximum rate.

Dissolution rates of 1000 grams per hour have been obtained on steam-oxidized plutonium dioxide, as indicated in Table I, Run 14.

At the end of this high rate period, the oxide was 83 percent dissolved and the solution concentration was 223 g/l plutonium. Such a rate appears obtainable with a continuous dissolver unit; and even greater rates may be obtained if the product concentration were decreased.

Three variables were tested in the dissolution studies: (1) the concentration effect, (2) the dissolver material, and (3) the acid concentrations.

The concentration of plutonium in solution as a nitrate is known to have a retarding effect on the dissolution rate. In the past, concentrations of 175 g/l have been obtained only with great difficulty and long dissolution periods. It was doubtful whether they were reached by actual oxide dissolution or merely volume concentration. However, with steam-oxidized material, a concentration of 223 g/l was reached in 20 minutes' dissolving time. Although the concentration at which the dissolution rate is appreciably decreased is up considerably, it is still believed that high concentrations in solution reduce the dissolution rate.

Most of the laboratory work was done in glass equipment. It was expected that the chemical attack of the glassware would decrease the fluoride ion concentration to a degree detrimental to the process. Limited tests were made in a stainless steel vessel to verify this assumption, but no trend was obtained. In two of the high concentration tests, more rapid and complete dissolutions were obtained in the glass vessel. Although more exhaustive tests should be made, the present work indicates this factor to be negligible.

Four different acid conditions were tested: (1) 13 M  $\text{HNO}_3$  - 0.2 M HF, (2) 15.8 M  $\text{HNO}_3$  - 0.20 M HF, (3) 15.8 M  $\text{HNO}_3$  - 0.25 M HF, and (4) 15.8 M  $\text{HNO}_3$  - 0.20 M HF with periodic HF additions.

There was no discernable difference in the dissolution rate or completeness between initial HF concentrations of 0.20 M and 0.25 M. Increasing the  $\text{HNO}_3$  concentration from 13 M to 15.8 M definitely resulted in quicker and more complete dissolutions. Three 200-gram scale dissolutions with 15.8 M  $\text{HNO}_3$  were all 99 percent or better dissolved; whereas the completeness of dissolution in the 13 M acid runs varied from 94 to 100 percent complete after two hours' dissolution time.

It was also found in the larger scale runs (250 - 400 g) that periodic additions of HF increased the dissolution completeness. This has been verified by studies at the Rocky Flats Plant, where plutonium fluoride is added to the dissolution runs to provide a constant source of fluoride ion throughout the dissolution.

TABLE I

DISSOLUTION OF STEAM-OXIDIZED PLUTONIUM  
IN NITRIC AND HYDROFLUORIC ACID (0.2 - 0.25 M)

Run No.	Batch Size - Grams	Grams Dissolved After			Percent Dissolved After			HNO <sub>3</sub> Conc. - M	Conc. Of Solution After 1 hr. - g/l
		20 min.	1 hr.	2 hrs.	20 min.	1 hr.	2 hrs.		
1	150	-	143	150	-	96	100	13	84
2	211	189	198	198	89	94	94	13	126
3	205	160	186	194	78	91	95	13	124
4	217	199	198	217	92	91	100	16	141
5	215	215	215	215	100	100	100	16	152
6	212	208	210	212	98	99	100	16	152
7	216	182	191	216	84	88	100	16	132
8	251	215	248	251	86	99	100	16	193
9	255	172	203	255	67	80	100	13	195
10	250*	158	176	230	63	70	92	13	109
11	255*	175	180	250	69	70	98	13	110
12	250*	149	163	216	60	65	86	13	110
13	402	322	320	378	80	80	94	16	222
14	406	335	355	372	83	89	92	16	245

(\*) Those runs in which the black slate-like oxide-hydride mixture obtained from attempts to oxidize chunks of pure metal was included in the dissolution.

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One final note on dissolution efficiency. The addition of a small amount of ANN to the hot solution at the end of the run (ca 0.15 M) also increased the percent recovery.

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