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Dissolution of High-Fired Plutonium Oxide

***H. A. Woltermann, T. L. Ulrick
and D. Antion***

March 9, 1973

MASTER

AEC Research and Development Report

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U. S. Government Contract No. AT 33-1-GEN-53

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National Technical Information Service
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Springfield, Virginia 22151
Price: Printed Copy \$3.00; Microfiche \$0.95

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ABSTRACT

A new method of dissolution of high fired plutonium oxide using a Teflon-lined acid-digestion bomb permits a more rapid and efficient dissolution than previously obtained in a Teflon beaker. Analytical results subsequent to dissolution indicate that the acid-digestion bomb is far superior to the Teflon beaker method in quantitative handling of plutonium oxide samples.

INTRODUCTION

Mound Laboratory has been engaged in the production of cermet discs of molybdenum-coated plutonium dioxide and molybdenum-coated solid solution (approximately 90% PuO_2 - 10% ThO_2) for use as heat sources for the Pioneer and Transit Programs.¹ Adequate quality control required the determination of plutonium and thorium in the solid solution samples.

High-fired ($>1600^\circ\text{C}$) plutonium dioxide has been difficult to dissolve,² and the solid solution samples were equally resistant to dissolution. Previously, plutonium dioxide was dissolved in a Teflon beaker with boiling concentrated nitric acid to which small quantities of hydrofluoric acid were added. Even if the oxide is ground to a fine powder in a mortar and pestle prior to dissolution, as much as five working days may be needed for complete dissolution. Periodic operator attention is required to ensure that the boiling nitric acid does not "bump" and that the solution is not baked to dryness. The large volume of samples required by this program made this method of dissolution unacceptable.

In the new method developed, a Teflon-lined acid-digestion bomb is used to dissolve high-fired plutonium oxides.

EXPERIMENTAL

Teflon Beaker Method Oxide samples are ground to a fine powder in a mortar and pestle and placed in a 250 ml Teflon beaker. The beaker is filled with 150 ml of concentrated nitric acid with a few drops of hydrofluoric acid (48%). The beaker is placed on a hot plate and the acid is heated to boiling until dissolution is completed. Repeated additions of acids are required.

Teflon-Lined Acid-Digestion Bomb Method Teflon-lined acid-digestion bombs were purchased from Paar Instrument Company*. The bombs are approximately 9 cm in height by 6 cm in diameter. They consist of a nickel-coated brass housing containing a 25 ml capacity Teflon cup (Figure 1).

These bombs proved unsatisfactory for routine work because the small amount of nitric acid which leaked from the bombs during dissolution reacted with the nickel-coated brass housing. Upon cooling of the bombs, the resultant metal solution was drawn back into the Teflon cup thus

*Paar Instrument Company, Moline, Ill. Catalogue No. 4747.

contaminating the sample. A similar bomb housing was constructed of stainless steel in our machine shop**.

Also a Teflon cup and lid were fabricated which employed two delta seals instead of the one found in the commercial Paar bomb (Figure 2). This design allowed repeated use of the acid digestion bomb without sample contamination.

Oxide samples were ground to a fine powder in an agate mortar and pestle. Approximately 0.15 g of the oxide is placed in the Teflon cup with 10 ml of concentrated nitric acid and 0.020 ml of hydrofluoric acid (48%). The bombs are sealed and placed in a drying oven for 40 hr at 150°C. The oven was controlled by a controlling pyrometer*** with a limiting pyrometer**** back-up system. Both pyrometers were a fail-safe design in case of thermocouple failure.

After dissolution the bombs are cooled and then opened, and the contents are transferred to a Teflon beaker with nitric acid. The contents of the beaker are fumed to a low volume to remove HF and thus dissolve any ThF_4 precipitate.

FIGURE 1 - Paar Instrument Company acid-digestion bomb.

**Since completion of this work the Paar Instrument Company has marketed a stainless steel version of the bomb.

***Versatroniks controlling pyrometer, Model R7161G.

****API pyrometer, Model 503K, Assembly Products Inc., Chesterland, Ohio.

FIGURE 2 - Seals between Teflon cup and cap.

RESULTS

Table 1 and 2 compare the precision in the subsequent plutonium determination³ on duplicate, routine, solid samples dissolved by the Teflon beaker method and the Teflon-lined, acid digestion bomb, respectively. The relative standard deviation of samples dissolved by the acid digestion bomb was 0.47% which compares favorably with the relative standard deviation of 0.43% attained on plutonium-238 solution samples. The precision of plutonium determinations after dissolution in a Teflon beaker is much poorer because of the excessive handling of samples by this method. In addition, the plutonium values obtained after dissolution in a Teflon beaker often were low indicating loss of sample.

Table 3 relates the summation of plutonium and thorium determination values expressed as the oxide with the impurities found in the fuel after dissolution in the Teflon-lined acid-digestion bomb. The data indicate that no detectable sample is lost during this process.

Table 1
DUPLICATE PLUTONIUM RESULTS ON SOLID-SOLUTION SAMPLES
AFTER DISSOLUTION IN A TEFLON BEAKER

Sample No.	% Pu		Avg % Pu
	Duplicate A	Duplicate B	
1	78.16	78.39	78.28
2	77.96	78.20	78.08
3	77.60	77.12	77.36
4	72.82	72.89	72.86
5	78.48	77.80	78.14
6	79.61	81.04	80.32
7	71.21	69.70	70.46
8	82.70	81.63	82.16
9	79.28	81.15	80.22
10	79.91	79.32	79.62

Relative Standard Deviation (%) - 0.91.

Table 2

DUPLICATE PLUTONIUM RESULTS ON SOLID-SOLUTION SAMPLES
AFTER DISSOLUTION BY THE TEFLON-BOMB TECHNIQUE

Sample No.	% Pu		Avg % Pu
	Duplicate A	Duplicate B	
1	79.20	79.44	79.32
2	80.74	79.28	80.01
3	80.75	80.80	80.78
4	80.84	80.95	80.90
5	80.23	80.30	80.26
6	78.77	78.66	78.82
7	80.79	80.98	80.89
8	80.23	80.83	80.53
9	79.23	78.71	78.97
10	79.66	79.65	79.66
11	78.71	79.23	78.97
12	80.79	80.98	80.89
13	77.30	77.91	77.61
14	78.96	78.94	78.95
15	78.75	79.60	79.29

Relative Standard Deviation (%) = 0.47.

Table 3

PLUTONIUM AND THORIUM RECOVERED FROM SOLID-SOLUTION SAMPLES
AFTER DISSOLUTION BY THE TEFLON-BOMB TECHNIQUE

No.	% Pu	% PuO ₂	% Th	% ThO ₂	% Recovery*
1	78.72	89.26	8.40	9.55	98.8
2	79.32	89.95	7.99	9.08	99.0
3	80.01	90.73	7.60	8.64	99.4
4	79.43	90.07	7.88	8.96	99.0
5	78.71	89.25	7.90	8.98	98.2
6	78.32	88.81	8.73	9.93	98.7
7	79.46	90.11	8.24	9.36	99.5
8	78.14	88.69	8.77	9.97	99.1
9	79.49	90.14	7.35	8.35	98.5
10	79.92	90.63	7.81	8.87	99.5

Average percent recovery 99.0

*Percent recovery does not include uranium build-up from plutonium-238 decay (approximate average of 0.6% as U₃O₈) or impurities (approximate average of 0.2% as metal oxides). This would add approximately 0.8% to the recovery values.

SUMMARY

The acid digestion bomb is a quantitative, efficient, and relatively rapid method of dissolving high-fired plutonium oxides. It is now used routinely at Mound Laboratory in the dissolution of all high-fired plutonium oxides.

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