Dr-887

180/8-8-74
● MLM-2153

MLM-2153

Plutonium-238 Dioxide Dissolution Study

D. E. Etter and W. R. Herald

July 31, 1974

MASTER

MOUND LABORATORY

Miamisburg, Ohio

operated by

Monsanto

MONSANTO RESEARCH CORPORATION

a subsidiary of Monsanto Company
for the

U. S. ATOMIC ENERGY COMMISSION

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

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Plutonium-238 Dioxide Dissolution Study

D. E. Etter and W. R. Herald

July 31, 1974

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

PRINTED IN THE UNITED STATES OF AMERICA

Available from
National Technical Information Service
U. S. Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22151
Price: Printed Copy \$4.00 Microfiche \$1.45

MONSANTO RESEARCH CORPORATION

A Subsidiary of Monsanto Company

MOUND LABORATORY

Miamisburg, Ohio 45342

operated for

UNITED STATES ATOMIC ENERGY COMMISSION

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

MASTER

7-6
14

ABSTRACT

The effects of calcination temperature, HF concentration, HNO₃ concentration, and HNO₃ volume on the dissolution of oxalate-precipitated ²³⁸PuO₂ were investigated. A calcination temperature of 500°C is recommended because of the assurance of complete decomposition of the oxalate and subsequently a reasonable dissolution rate. The study shows that if the HF-to-PuO₂ ratio is maintained at 10 mg/g, the volume of concentrated HNO₃ can be varied from 2 to 7 ml/g of PuO₂ without affecting dissolution. In this case, the HF molarity varied from 0.071 to 0.25 molar. This work also shows that complete dissolution can be achieved in 8 hr at 30°C, when the HF-to-PuO₂ ratio is increased to 15 mg/g.

INTRODUCTION

In the preparation of $^{238}\text{PuO}_2$ particles by the hydroxide method, oxalate-produced $^{238}\text{PuO}_2$ is dissolved in a HF-HNO_3 acid medium as the primary step of this production process. In the course of this dissolution, small amounts (<1 wt %) of oxalate-produced $^{238}\text{PuO}_2$ often remain undissolved after a normal 48-hr acid treatment. The original intent of this study was to determine the cause of and subsequently eliminate this residue. The residue consisted of very large (390 μm), refractory-type, $^{238}\text{PuO}_2$ particles. These large residual particles are believed to have resulted from material which had been calcined to higher than normal temperatures, perhaps because of significant thermal gradients within a batch of material during calcination. The apparent lower dissolution rate of this residual material could be caused by either the lower surface area/mass ratio or the postulated high calcination temperature or both. In either case, the study of this residual material precipitated an extensive study of the entire dissolution process of oxalate-precipitated $^{238}\text{PuO}_2$. Detailed discussion of this residue and photomicrographs illustrating the comparison of the residue to the normally small, oxalate-precipitated, $^{238}\text{PuO}_2$ particles were reported earlier.¹

Other investigators^{2,3} have shown that increasing HNO_3 acidity and increasing fluoride ion content generally increase the extent of dissolution. Moseley² has also shown that calcination has a marked effect on dissolution.

The standard production dissolution procedure for 600 g of $^{238}\text{PuO}_2$ entails introducing 120 drops of 48% HF into three to four liters of concentrated HNO_3 (15.8 N). The specification for calcination of the oxalate-precipitated plutonium oxide is to heat to a minimum of 650°C for a minimum of 1 hr. Both of these operations have a relatively wide latitude in areas which could be critical.

EXPERIMENTAL

The material used for this study was taken directly from the Mound Laboratory recovery process as freshly precipitated plutonium oxalate. The isotopic ratio of plutonium was nominally 80 wt % 238, 16 wt % 239, 3 wt % 240, and the remaining 1% 236, 241, and 242. The maximum metallic impurity content was 1500 ppm. Other individual actinide concentrations were less than 0.5 wt %.

Because of the self-heating characteristics of plutonium-238, quantities were calcined in a tube furnace to ensure a uniform temperature throughout the sample.

All dissolutions were performed, without auxiliary heating, in a tantalum beaker.

Plutonium solution concentrations were analyzed by the alpha counting technique.

RESULTS

Results of the investigation of calcination temperature and HF concentration as a function of dissolution are shown in Figure 1. The effect of calcination temperature is very pronounced. The 800°C calcination curve exhibits a marked resistance to dissolution and even at an HF concentration of 14 mg HF/g $^{238}\text{PuO}_2$, only 27% of the material was dissolved, whereas 73% of the material calcined at 400°C was dissolved under the same conditions.

Also illustrated in the data presented in Figure 1 is the marked effect of HF concentration. The 400°C material, which is the material least hindered by calcination effects, was only 50% dissolved after 3 hr at an HF concentration of 7 mg HF/g $^{238}\text{PuO}_2$; however, the amount dissolved increased to 73% for an HF concentration of 14 mg HF/g $^{238}\text{PuO}_2$.

FIGURE 1 - The effect of calcination temperature and HF concentration on PuO_2 dissolution.

Figure 2 illustrates the dependence of HNO_3 concentration on dissolution. In this study, the HF concentration, as a function of the mass of $^{238}\text{PuO}_2$, was held constant while the normality of the HNO_3 with respect to the mass of $^{238}\text{PuO}_2$ was varied. Very little dissolution occurred below a HNO_3 concentration of 10 N. Above 10 N the amount dissolved increased rapidly with increased HNO_3 normality. Thus, by far, concentrated HNO_3 (16 N) should be used, as is presently the case.

FIGURE 2 - The effect of HNO_3 concentration on PuO_2 dissolution; HF concentration held at 10 mg/g $^{238}\text{PuO}_2/3$ cc HNO_3 .

However, in marked contrast to the dependence on HNO_3 normality is the independence on the quantity or volume of concentrated HNO_3 , as evidenced by the data in Table 1. These results demonstrate that the volume of concentrated HNO_3 can be varied between the investigated limits without dissolution effect provided the HF concentration is held constant as a function of the mass of $^{238}\text{PuO}_2$. The calculated HF molarity exhibits a considerable range, while the HF/ PuO_2 ratio remains constant. These data show that production quantities (575 g $^{238}\text{PuO}_2$) can be dissolved in less than half of the volume presently employed.

The above studies were intentionally terminated short of complete dissolution in order to compare the amount dissolved and, subsequently, the effect of the variable under investigation. The desire to know the behavior of selected conditions for complete dissolution instigated the experiment shown in Figure 3. The conditions selected were based on the previous data, and the variable employed was the concentration of 10 and 15 mg HF/g PuO_2 . The results exhibit very little difference up to about 3 hr, at which time the higher concentration of HF becomes quite beneficial for dissolution. After 8 hr, the sample containing 15 mg HF/g

Table 1
EFFECT OF CONCENTRATED HNO_3
VOLUME ON PLUTONIUM DIOXIDE DISSOLUTION^a

HNO_3 Volume Per Gram PuO_2 (cm^3)	Amount Dissolved in 3 Hr (%)	HF Concentration (M)
2	55.7	0.25
3.5	55.5	0.142
5	54.3	0.1
7	54.0	0.071

^aDissolution Conditions: PuO_2 Calcined at 500°C for 1 hr
10 mg HF/g PuO_2

Temperature: 30°C , 1-g PuO_2 Samples

FIGURE 3 - Dissolution of PuO_2 as a function of time and HF concentration.

PuO_2 was completely in solution while the lower HF concentration sample was only 70% dissolved. The lower HF concentration sample was 88% dissolved after 24 hr. These data are indicative of the necessity of a specific level HF concentration for rapid, complete dissolution at 30°C.

Since the results of the calcination temperature dependence suggest the use of lower temperatures, it became necessary to investigate the temperature dependence of oxalate decomposition to ensure complete decomposition to the oxide phase, and thus, eliminate any hazard of CO_2 evolution during further processing. Published thermogravimetric analysis studies⁴ report that no further decomposition occurs above 400°C. Also, an experiment was completed using a stainless steel storage container that had been modified to permit pressure measurement. This container was loaded with 330 g of $^{238}\text{PuO}_2$ that had been calcined at 500°C for 1 hr. The filled container was allowed to reach equilibrium (center temperature was 400°C), then the pressure gage was screwed into place. There was a 7 psi increase within 3 min, then no further increase was observed for the remainder of the 24-hr test period. The initial 7 psi increase was probably due to the trapped gas in the pressure gage subsequently expanding when equilibrium temperature was reached. The absence of a continual pressure increase is indicative of no decomposition.

CONCLUSIONS

The conclusions drawn here are based on the above data and that reported earlier.^{1,5} The highest dissolution rate is obtained from those particles calcined at the lowest temperatures. However, to ensure complete decomposition of the oxalate and yet maintain a reasonable dissolution rate, a calcination temperature of $500 \pm 50^\circ\text{C}$ is suggested. It must be emphasized that this temperature must be carefully maintained and thermal gradients that exceed this range must be rigidly eliminated.

The HF concentration must be considered as a function of the mass of $^{238}\text{PuO}_2$ to be dissolved. An HF concentration, or more appropriately, as an HF-to- $^{238}\text{PuO}_2$ mass ratio, of 10 mg HF/g $^{238}\text{PuO}_2$ is suggested as this ratio yields a reasonable dissolution rate. However, a ratio of 15 mg HF/g $^{238}\text{PuO}_2$ for material calcined at 500°C is necessary for rapid complete dissolution at 30°C. It is also desirable to maintain the HF concentration at the least amount necessary, yet yielding a reasonable rate, to minimize reaction with and possible impurities from the various reaction vessels, handling equipment, and transfer lines.

As long as the suggested HF-to- $^{238}\text{PuO}_2$ ratio is maintained and concentrated HNO_3 is used, the volume of concentrated HNO_3 can be varied widely from 2 to 7 ml/g PuO_2 without appreciably affecting the dissolution rate.

The employment of the above conditions should considerably shorten the present 48-hr dissolution time required for 400-g quantities of PuO_2 . The heat (90°C) inherently associated with this quantity will most likely increase the rate of dissolution somewhat over the data presented here, since this work was conducted at 30°C. In addition, the lower and more uniformly controlled calcination temperature should eliminate the occurrence of the large residual $^{238}\text{PuO}_2$ particles whose presence instigated this study.

REFERENCES

1. Mound Laboratory Isotopic Power Fuels Programs: July-September, 1972, MLM-1983, (November 30, 1972), pp. 19-21.
2. J. D. Moseley and R. O. Wind, Properties of Plutonium Dioxide, USAEC Report RFP-503, Dow Chemical Co., Golden, Colorado (Aug. 24, 1965).
3. R. C. Smith, Plutonium: Steam Oxidation and Oxide Dissolution, USAEC Report HW-66431, Hanford Atomic Product Operations, Richland, Washington (Aug. 12, 1960).
4. G. S. Rao, M. S. Subramanian, and G. A. Welch, "Thermal Decomposition of Plutonium Oxalates," J. Inorg. Nucl. Chem., 25, 1294 (1963).
5. Mound Laboratory Isotopic Power Fuels Programs: October-December 1972, MLM-2014 (January 31, 1973), pp. 15-18.