PROGRESS REPORT

For Period July 1 through September 30, 1961
AEC R&D Contract AT(30-1)-2389

DEVELOPMENT
OF
PLUTONIUM BEARING FUEL MATERIALS

NUMEC P-80

Nuclear Materials and Equipment Corporation
Apollo, Pennsylvania

~~For Official Use~~ Only, ~~Pending Patent Release~~

DISCLAIMER

External Distribution List

U. S. Atomic Energy Commission, New York Operations Office
- M. Balicki
- H. S. Potter
- Leonard Topper
- Seymour Zirin

U. S. Atomic Energy Commission, Washington
- F. Charles Moesel (2)
- J. M. Simmons (5)
- M. Whitman
- M. Zeibold
- Reports and Statistics Branch

U. S. Atomic Energy Commission, Chicago Operations Office
- Bruce Anderson

U. S. Atomic Energy Commission, National Laboratories
- F. Foote, Argonne
- H. Young, Argonne (4)
- E. A. Evans, Hanford
- L. H. McEwen, Hanford
- O. J. Wick, Hanford
- J. Musser, Hanford
- I. D. Thomas, Hanford
- W. Cashin, KAPL
- H. Rizzo, Lawrence Radiation (3)
- R. D. Baker, Los Alamos
- L. B. Jones, Mound
- R. L. Mettler, Oak Ridge (3)
- D. F. Cope, Oak Ridge
- E. S. Bomar, Oak Ridge
- A. Squire, Westinghouse-Bettis

U. S. Atomic Energy Commission, Contractors
- W. J. O'Leary, Allis Chalmers Manufacturing Company
- R. W. Dayton, Battelle
- W. Duckworth, Battelle
- G. M. Butler, Jr., Carborundum Company
- R. H. Gale, Combustion Engineering
- A. D. Schwope, Clevite Research Center
- L. A. Matheson, Dow Chemical Company
- G. Spaulding, Electric Autolite Company
- W. Alter, General Electric Company, Vallecitos
- L. D. Harris, National Carbon Company
- A. Strasser, Nuclear Development Corporation of America
- R. W. Hartwell, Power Reactor Development Company
- D. E. Hamby, Union Carbide Metals Company
- Olin Mathieson Chemical Corporation

NUMEC Distribution List

R. J. Atkins
A. Biancheria
F. M. Cain
C. S. Caldwell
B. Cinai
J. Eck
G. Ehrlich
F. Forscher
R. Frumermann
H. J. Garber
E. E. Garcia
J. Goodman
O. S. Gray
E. K. Halteman
R. M. Horgos
R. A. Jaroszeski
L. J. Jones
W. Judd
A. Kasberg
H. Krake
A. L. Maharam
J. Marley
O. Menis
J. Miles
L. P. Pepkowitz
K. H. Puechl
P. Rey
D. G. Ross
J. E. Ross
W. G. Ross
J. Ruzbacki
J. Scott
Z. M. Shapiro
J. Stoner
M. M. Turkanis
B. Vondra
L. Weber
A. M. Weis
Library (5)

Previous Quarterly Progress Reports issued in this series are:

Number	For the Period Ending
NUMEC P-10	December 31, 1959
NUMEC P-20	March 31, 1960
NUMEC P-30	June 30, 1960
NUMEC P-40	September 30, 1960
NUMEC P-50	December 31, 1960
NUMEC P-60	March 31, 1961
NUMEC P-70	June 30, 1961

TABLE OF CONTENTS

PROJECT AND FACILITY ADMINISTRATION

Task 1.00
K. H. Puechl

Revised Scope of Work

During this period, Task 6.00, Fuel Reprocessing, was phased out since the AEC had decided to concentrate all efforts in this area at ORNL. As a replacement for this work, Task 11.00 has been initiated to allow investigation of the preparation and coating of spherical oxide PuO_2 and PuO_2-UO_2 particles. Metallic coatings will be investigated first; future effort may be expended on oxide coatings as well. PuO_2 coated particles will be prepared and evaluated for possible use in dispersion-type fuel elements; PuO_2-UO_2 coated particles will be similarly prepared and evaluated for possible use as feed material for mechanical packing of fuel rods.

General Plant Operations

Two more glove boxes have been completely outfitted and have passed leak testing specifications. These are the NaK canning box and the plasma torch box. Operations with plutonium will be initiated therein early in the next quarter. In addition, the corrosion test box is undergoing final leak testing, and the decontamination box is in the final stages of outfitting. These boxes will also be brought on stream shortly.

Since the last report period, an additional sixteen gloves have failed and have been successfully changed without any evidence of alpha contamination external to the glove boxes. In most cases, initial discovery of the defective gloves has been made through monitoring of the surgeon-type glove used by glove box operators as a secondary barrier. It is believed that this procedure has resulted not only in protecting the hands of the glove box operators from contamination but, in addition, in curbing the spread of contamination to surfaces external to the glove boxes.

Two minor in-box fires have occurred. Both were readily extinguished with the designed fire-fighting systems, with no danger to the glove box operators and with minor equipment damage. In one case, the fire was quickly extinguished by flooding the glove box with nitrogen.

Two intentional breaks into the sealed glove box system have been undertaken without radiological hazard. During repair of a sintering furnace, it was found necessary to drill into the steel jacket of the furnace which serves as a primary alpha barrier to the room atmosphere. Results of air sampling in the immediate area during the operation and of smear samples following the operation showed no evidence of the release of alpha contamination. The drill used was found to be contaminated with 550 dpm of removable

alpha. The second operation involved breaking into the box air exhaust system in order to tie in another glove box. This duct system is protected from contamination by in-line high efficiency filters at each glove box. The total absence of alpha activity in the ductwork verified good filter performance.

Summary of Experimental Activities

Four additional lots of PuO_2 have been prepared by the continuous oxalate precipitation process. These, as well as lots prepared previously, are now being fully characterized. Results show that the PuO_2 surface area decreases almost linearly with calcination hold time at 760°C; therefore, surface areas can be controlled in this manner over the range of 4 to 12 M^2/gm. As pointed out in previous progress reports, still higher surface areas can be attained with lower calcination temperatures. Sintering studies, however, have shown that the lower surface areas give adequate activity for sintering and minimize powder handling problems and shrinkage.

The decomposition of plutonium oxalate in both a nitrogen and air atmosphere has been investigated with the use of a thermogravimetric balance. The results show formation of an initial stable compound (at about 100°C) and a stable intermediate at about 300°C. These results differ from those obtained at the Los Alamos Scientific Laboratories and Harwell, hence point out the effect of preparation history on powder properties.

During this period, two more continuous PuO_2-UO_2 coprecipitation runs and one batch precipitation run were also carried out. Most of the produced material is scheduled to be used in the in-pile rabbit test samples. For the UO_2-5% PuO_2 material, a 6 ± 2 M^2/gm surface area was specified and a 6.2 M^2/gm surface area was obtained; this again shows that the understanding of preparation variables has progressed sufficiently to allow control of this product characteristic.

A simple method has been developed for obtaining the total porosity of a powder. The method consists of determining the amount of water required to initiate caking tendencies. Since this can be done simply and rapidly, the method may be a valuable aid to quality control.

Preliminary blending studies have been performed using PuO_2 and UO_2 powders in order to isolate important parameters. These studies show that mixing of two powders having almost the same surface areas tends towards a more homogeneous product than blending powders having widely divergent surface characteristics.

Studies have also been initiated to produce high-density coarse particles directly using proper chemical control, thereby eliminating the need for further processing to produce suitable feed for mechanical packing and

swaging. The homogeneous oxalate process is being investigated first, and preliminary results are encouraging.

Sintering studies have been continued on both mechanically mixed oxide and coprecipitated material. Incomplete interabsorption of PuO_2 and UO_2 was found in the mechanically mixed oxide pellets indicating that the blending and mixing procedures were unsatisfactory.

Considerable effort has been expended in order to elucidate upon various aspects associated with the formation of a second phase in PuO_2 pellets sintered under certain conditions. It now appears that the second phase is probably Pu_2O_3 and that its formation can be readily controlled.

Reactor Physics Studies

One paper entitled, "An Approach to Reactor Physics Using Results of Integral Experiments--Part II", has been published in the September 1961 issue of Nuclear Science and Engineering. Two more papers concerned with the potential of plutonium as a fuel in near-thermal converter and burner reactors have been accepted for publication in the same journal.

PREPARATION AND CHARACTERIZATION OF FUEL MATERIALS

Task 2.00
C. S. Caldwell

R. J. Atkins
A. Biancheria
G. Ehrlich
E. E. Garcia
J. Goodman
R. A. Jaroszeski
H. Krake
O. Menis
P. Rey

Plutonium Oxide Preparation and Powder Characterization

Preparation conditions and product characteristics of several lots of PuO_2 prepared by calcination of short-run continuously precipitated plutonium (IV) oxalate were presented in the last progress report(i). During the current report period, characterization work on this material continued, and four additional lots of PuO_2 (1 kg) were prepared in longer runs using the continuous oxalate process. Blending trials with UO_2 have been carried out on material from two of these lots. The material is also being utilized for various fabricability trials and for fabrication of in-pile test specimens.

Continuous Process PuO_2 Preparation (Runs 297-Pu-9, Lots I, II, III, IV): The general method used for preparation of PuO_2 by the continuous oxalate process has been described previously(i); specific process conditions used for the 297-Pu-9 preparation are presented in Table 2.1. Holdup times in the precipitator were controlled in the range 24-30 minutes, and steady state conditions were maintained for extended periods (7-12 percipitator throughputs) to simulate production processing operation. Properties of the resultant PuO_2 powder are summarized in Table 2.2. The usefulness of variable calcination time as a practical means of controlling surface area can be seen by comparing the characterization and fabrication results for Lots II and IV. When the results from 297-Pu-4-5 and 297-Pu-5-5 (5 minute calcination) are also included, it is seen that PuO_2 surface area, over the range of 4 to 12 M^2/gm, decreases almost linearly with calcination hold-time at 760°C. The hold times (5-30 minutes) are also compatible with continuous calcination equipment for production purposes. Handling properties of the oxalate precipitate have remained good for all batch and continuous runs, and filtrate losses have remained well below 50 mg/liter. Precipitation control near room temperature appears to be comparable with higher temperature (55°C) operation.

(i) NUMEC P-70, Progress Report, "Development of Plutonium Bearing Fuel Materials", pages 10 and 12.

Table 2.1

Summary of Conversion Processing Data
Plutonium Oxide Materials

End Product	297-Pu-7 UO_2-20% PuO_2	297-Pu-8 UO_2-5% PuO_2	297-Pu-9 Lot I PuO_2	297-Pu-9 Lot II PuO_2	297-Pu-9 Lot III PuO_2	297-Pu-9 Lot IV PuO_2	297-Pu-10 UO_2-20% PuO_2
Precipitation Conditions							
Method	Batch	Continuous	Continuous	Continuous	Continuous	Continuous	Continuous
Temperature, °C	58	57	33	35	35	35	45
Feed Composition							
gm Pu/liter	20	5	100	100	100	100	20
gm U/liter	80	95	-	-	-	-	80
H^+, molarity	3	1	3	3	3	3	1
Strike Solution Composition			100% Excess	73% Excess	74% Excess	62% Excess	
$H_2C_2O_4$, Molar			1	1	1	1	
H_2O_2, Molar			0.8	0.8	0.8	0.8	
NH_4OH, Molar	3.5	3.5					3.5M
Precipitation Average Holdup, minutes	-	33	30	24	25	25	36
Total No. Throughputs	-	9	7	12	9.7	10.6	13
Furnace Conversion Temperature, °C	540 and 740	740	760	760	350	760	740 followed by 780
Gas Atmosphere	6% H_2-94% N_2	6% H_2-94% N_2	Air	Air	Air	Air	6% H_2-94% N_2

PuO_2 Powder Characterization: Characterization data of the 297-Pu-4 and 297-Pu-5 PuO_2 samples are summarized in Table 2.2. For ease of comparison, the parameters are also plotted against calcination temperature in Figures 2.1 and 2.2 along with some of the data previously reported[1]. These data show the trend of increasing bulk and tap densities and air-permeability average particle size with increasing calcination temperature. The large decrease in surface area observed for the 297-Pu-4-5 and 297-Pu-5-5 samples, Figure 2.2, is attributed mainly to loss of internal surface and roughness since the external surface as measured by air-permeability, Figure 2.1, does not undergo a similar reduction.

The per cent carbon impurity in these samples is also shown in Table 2.2. The form in which the carbon exists is not known. It may be in the form of free carbon, oxalic acid, $Pu(CO_3)_2$ or some other intermediate, or as a mixture of these. The presence of the carbon, however, does indicate that a weight loss, in addition to that due from water loss, is expected on sintering. The presence of carbon may also result in a partial reduction of the PuO_2 at sintering temperatures.

A slight, but definite shift in properties was observed between the two sets of samples. This shift may be related to the generally better pressing qualities of the 297-Pu-4 samples (see Fabrication and Evaluation of Fuel Shapes). Within each set of samples, the low surface area powders (10 M^2/gm), 297-Pu-4-5 and 297-Pu-5-5, yielded the highest green densities. The sinterability data available to date indicates that all samples attained high and nearly equal densities, hence less shrinkage occurred in these two particular samples. To minimize shrinkage on sintering, in addition to easing the handling problems (higher bulk densities, less water pick-up), the lower surface area samples, therefore, appear to be more favorable. This conclusion is in agreement with experience on UO_2 which indicates that surface areas of the order of 6 M^2/gm provide more than ample activity for sintering.

It is to be noted that the surface areas reported here for the 297-Pu-5-1, 297-Pu-5-3, and 297-Pu-5-5 samples are not in agreement with those previously reported[1]. This is the result of an apparent increase in surface area with exposure to glove box atmosphere as previously observed with sample 297-Pu-1[ii]. Repeat measurements on samples 297-Pu-1 and 297-Pu-5-1 have shown that the observed surface area stabilizes after approximately 30 days. In order to allow comparison, the results reported here are those obtained from stabilized samples. Subsequent to stabilization, it was noted that the rate of out-gassing was greatly enhanced over prior determinations; this suggests that a slow reaction of the chemically bound surface constituents had occurred.

(i) NUMEC P-70, Progress Report, "Development of Plutonium Bearing Fuel Materials", page 12.

(ii) NUMEC P-70, Progress Report, "Development of Plutonium Bearing Fuel Materials", page 13.

Table 2.2

Characterization Parameters of PuO_2 Samples
Prepared by the Continuous Oxalate Preparation Method

Sample	Calcination		Bulk Density	Tap Density	Air Permeability Avg. Dia.*	B.E.T. Surface Area	50% Particle Size	Carbon Content
	Temp °C	Time min	gm/cc	gm/cc	microns	M^2/gm	microns**	w/o
297-Pu-4-1	350	35	1.38	1.82	1.7	57	7.8	0.283
297-Pu-4-2	420	5	1.30	1.80	1.7	51	9.9	0.375
297-Pu-4-3	490	5	1.42	1.85	1.8	53	12.0	0.279
297-Pu-4-4	560	5	1.42	2.03	1.9	39	9.3	0.163
297-Pu-4-5	760	5	1.70	2.36	2.0	9.9	9.0	0.000
297-Pu-5-1	350	35	1.34	1.72	1.9	59	11.4	2.102
297-Pu-5-2	420	5	1.55	2.00	2.2	69	11.8	0.303
297-Pu-5-3	490	5	1.63	2.05	2.1	60	10.2	0.223
297-Pu-5-4	560	5	1.63	2.16	2.4	45	10.9	0.195
297-Pu-5-5	760	5	1.93	2.60	2.6	11.7	12.0	0.0285
297-Pu-9-Lot I	760	30	1.97	2.62	2.1	3.4		
297-Pu-9-Lot II	760	30	1.76	2.30	2.6	5.4		
297-Pu-9-Lot III	350	30				43		
297-Pu-9-Lot IV	760	17				7.5		

* Calculated from data employing one-half the required sample weight.
** Mine Safety centrifugal particle size analysis.

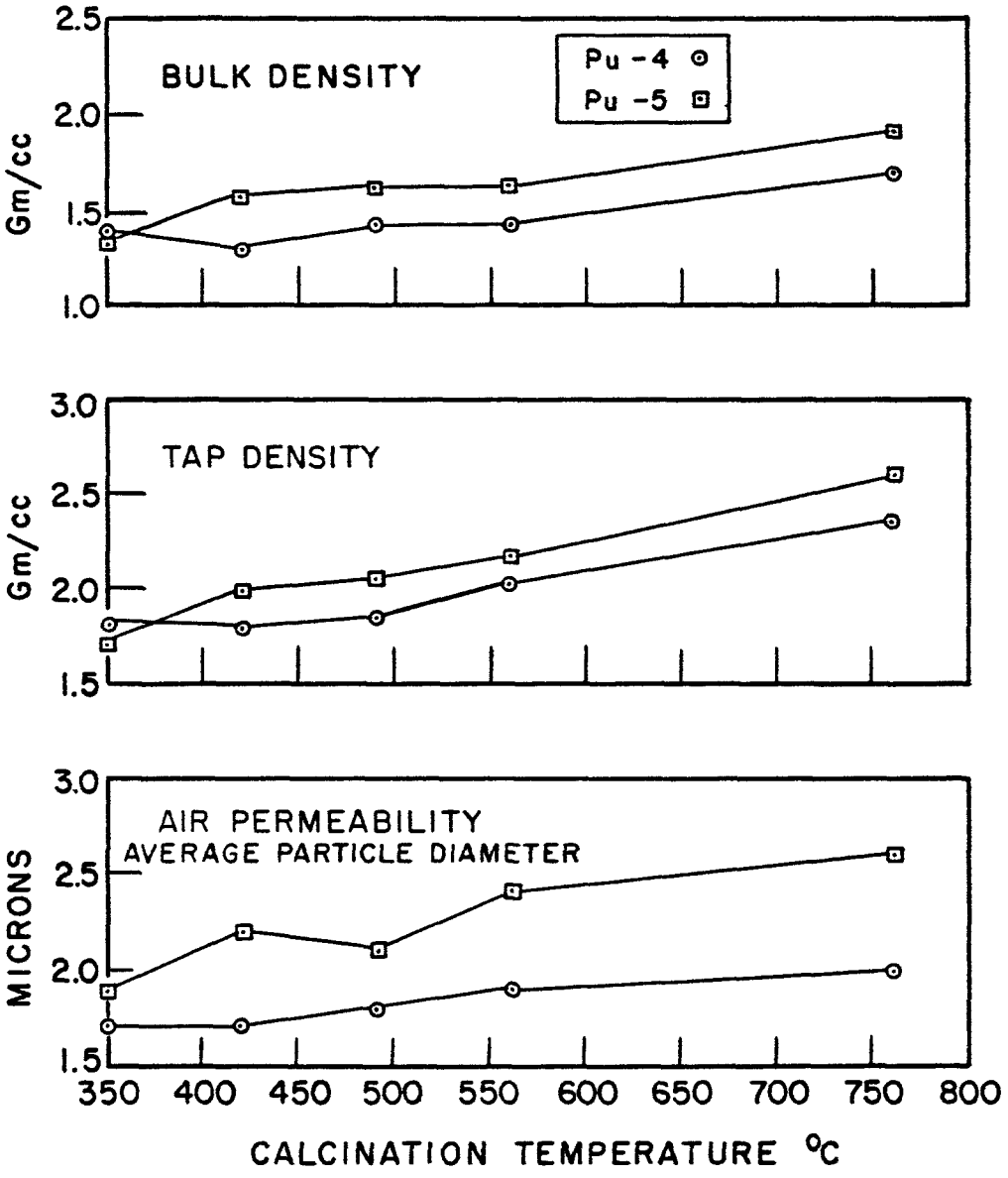


Figure 2.1

VARIATION OF PuO_2 POWDER PROPERTIES WITH CALCINATION TEMPERATURE (HOLD TIME - 5 MIN. AT TEMPERATURE)

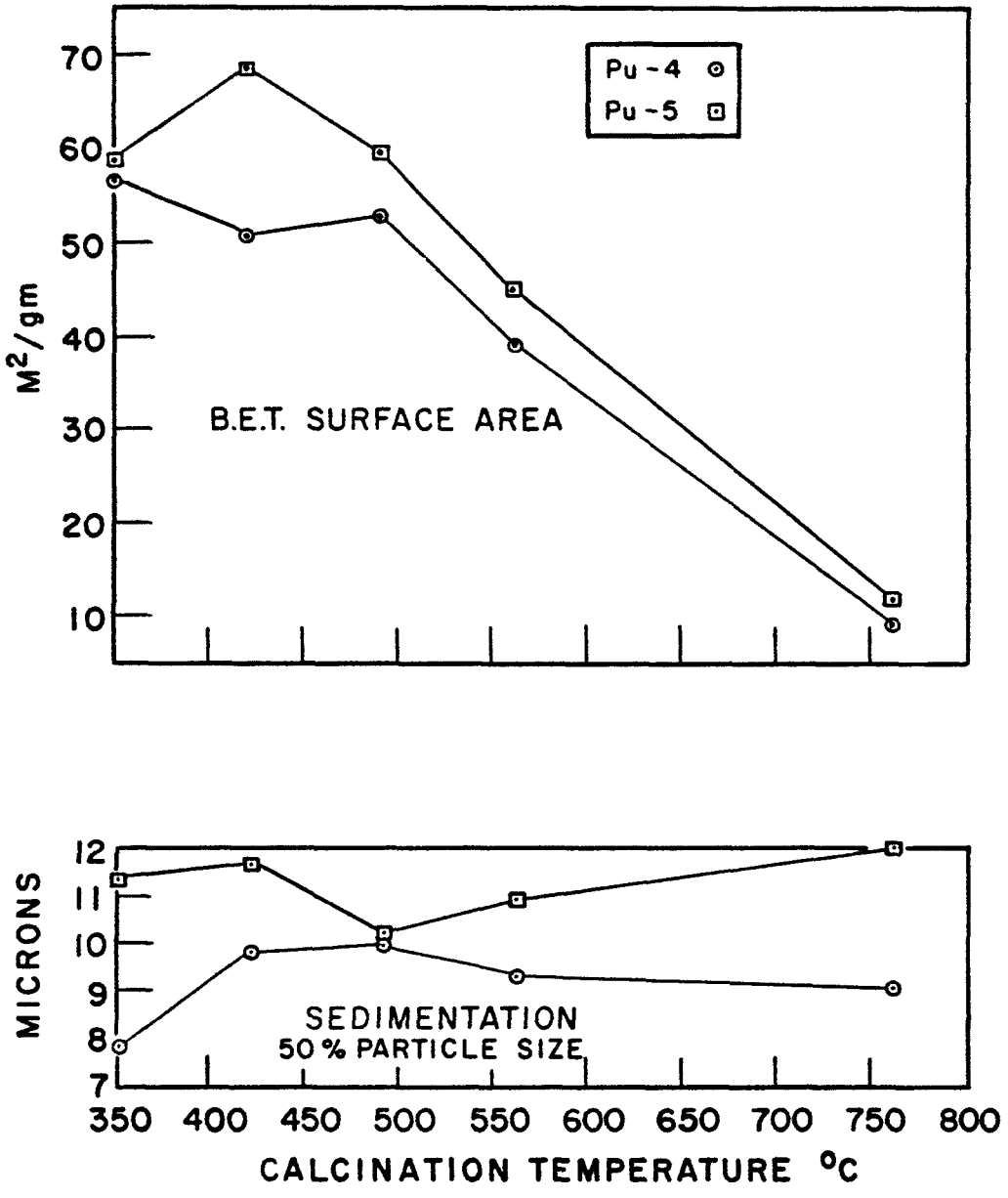


Figure 2.2

VARIATION OF PuO_2 POWDER PROPERTIES WITH CALCINATION TEMPERATURE (HOLD TIME -5 MIN. AT TEMPERATURE)

To further investigate and thereby to allow understanding of the origin of the high surface areas, measurements on a sample of plutonium oxalate, $Pu(C_2O_4)_2$ were carried out at various stages of decomposition. This was accomplished by heating the sample in situ in the B.E.T. apparatus. The temperature was raised to a predetermined value and held for approximately 20 minutes to accomplish any decomposition that might occur and then lowered approximately 50°C and held until out-gassing was complete. The initial weight of $Pu(C_2O_4)$ was obtained after the first heating period at 125°C, and the PuO_2 product weight was obtained at the end of the experiment. To avoid exposing the sample, no intermediate weights were obtained. The surface area of the $Pu(C_2O_4)_2$ based on its actual weight was 1.83 M^2/gm; for the PuO_2 end product the surface area was 37.7 M^2/gm. The surface areas based on the weight of the final PuO_2 powders are shown as a function of calcination temperature in Figure 2.3.

A sudden rise in total available surface area is seen to occur between 225 and 315°C. This does not necessarily imply a concomitant splitting of particles or agglomerates since the escaping decomposition gases can leave behind an intricate internal pore structure of high surface area without completely disintegrating the particles. Particle size and air-permeability measurements on the oxalate samples will be made shortly to aid in interpreting the physical mechanism of the decomposition. One would expect the end product to be less sensitive to precipitation variables if the particles and agglomerates were split during decomposition; however, if they were not split, then one would expect that particle and agglomerate size (and configuration) are determined to a large degree in the precipitation step.

T.G.A. Studies: The decomposition of plutonium oxalate, $Pu(C_2O_4)_2$, sample Pu-Ox-9-Lot I, was examined in the thermogravimetric balance. The results, corrected for a dummy run, are shown in Figure 2.4 and 2.5. The sample was obtained from a continuous precipitation processing run, was air dried, and was subsequently stored in a desiccator. The powders were dried to constant weight in the thermogravimetric balance at a temperature below 100°C in a stream of nitrogen prior to initiating a heating schedule of 6°C/minute. In one case, Figure 2.4, the experiment was carried out in a nitrogen atmosphere, while in the other, Figure 2.5, the gas flow was switched to air after the initial drying period. The difference between the two is striking in that the decomposition at the second stage is almost instantaneous in air compared to a more gradual loss in nitrogen. The second stage also occurs at a lower temperature in air, 310°C compared to 440°C in nitrogen.

A significant similarity in the curves is the apparent formation of a stable intermediate (280°C in air, 300°C in nitrogen) as well as a stable initial compound (after drying) between 100-160°C. Results obtained

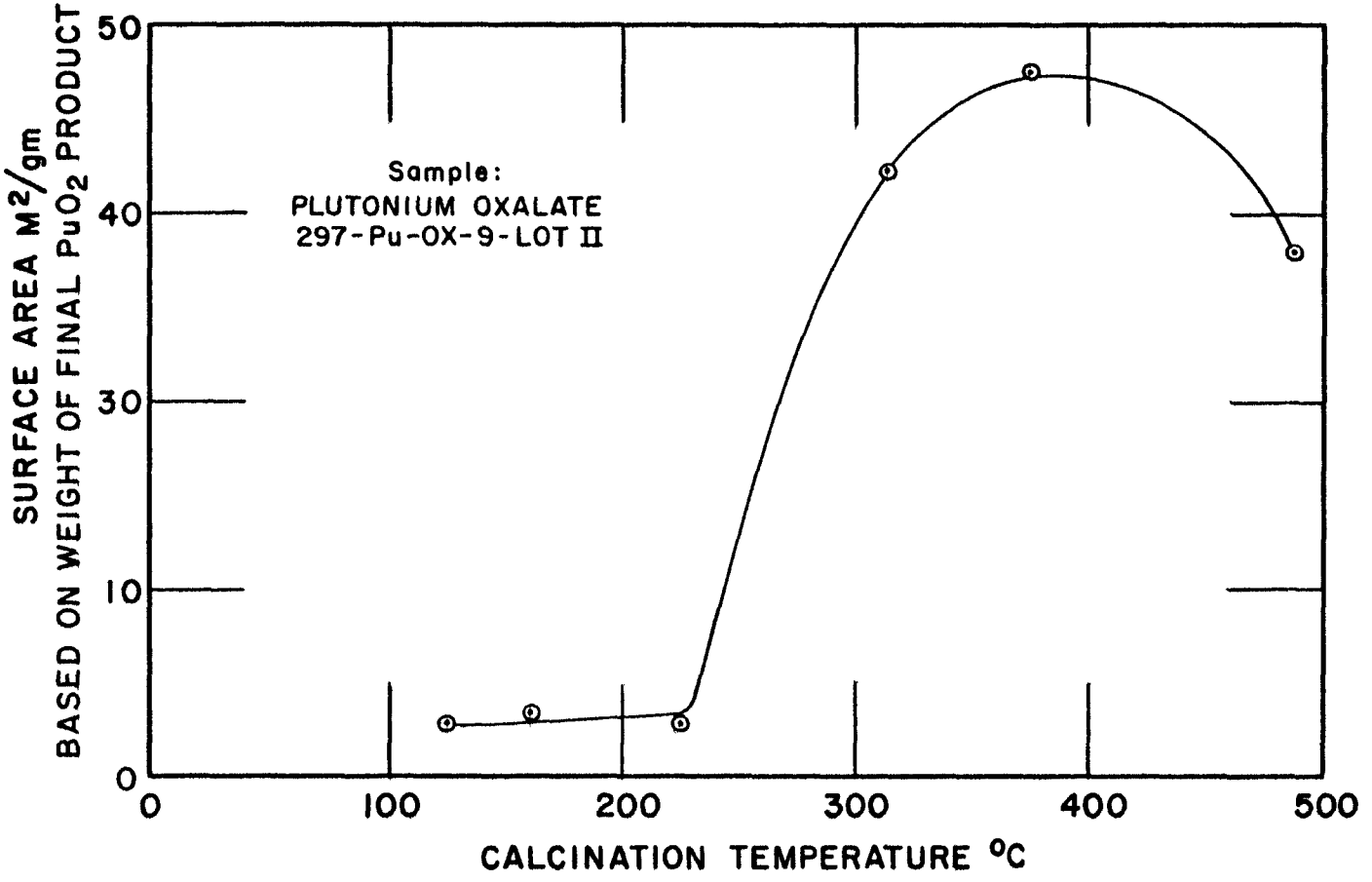


Figure 2.3

SURFACE AREA OF PLUTONIUM OXALATE
DECOMPOSED IN SITU IN B.E.T. APPARATUS

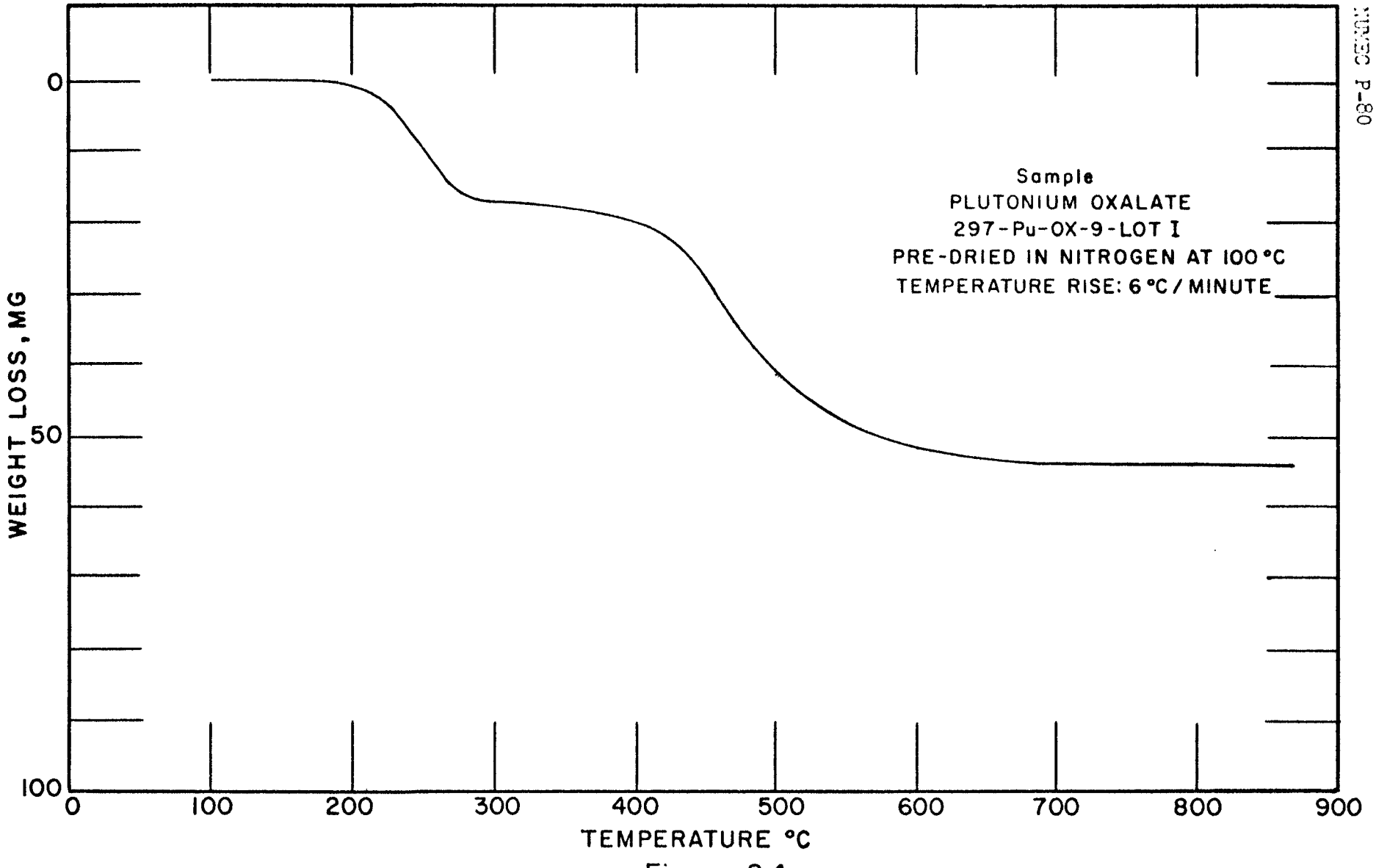


Figure 2.4

THERMOGRAVIMETRIC DECOMPOSITION CURVE

NITROGEN ATMOSPHERE

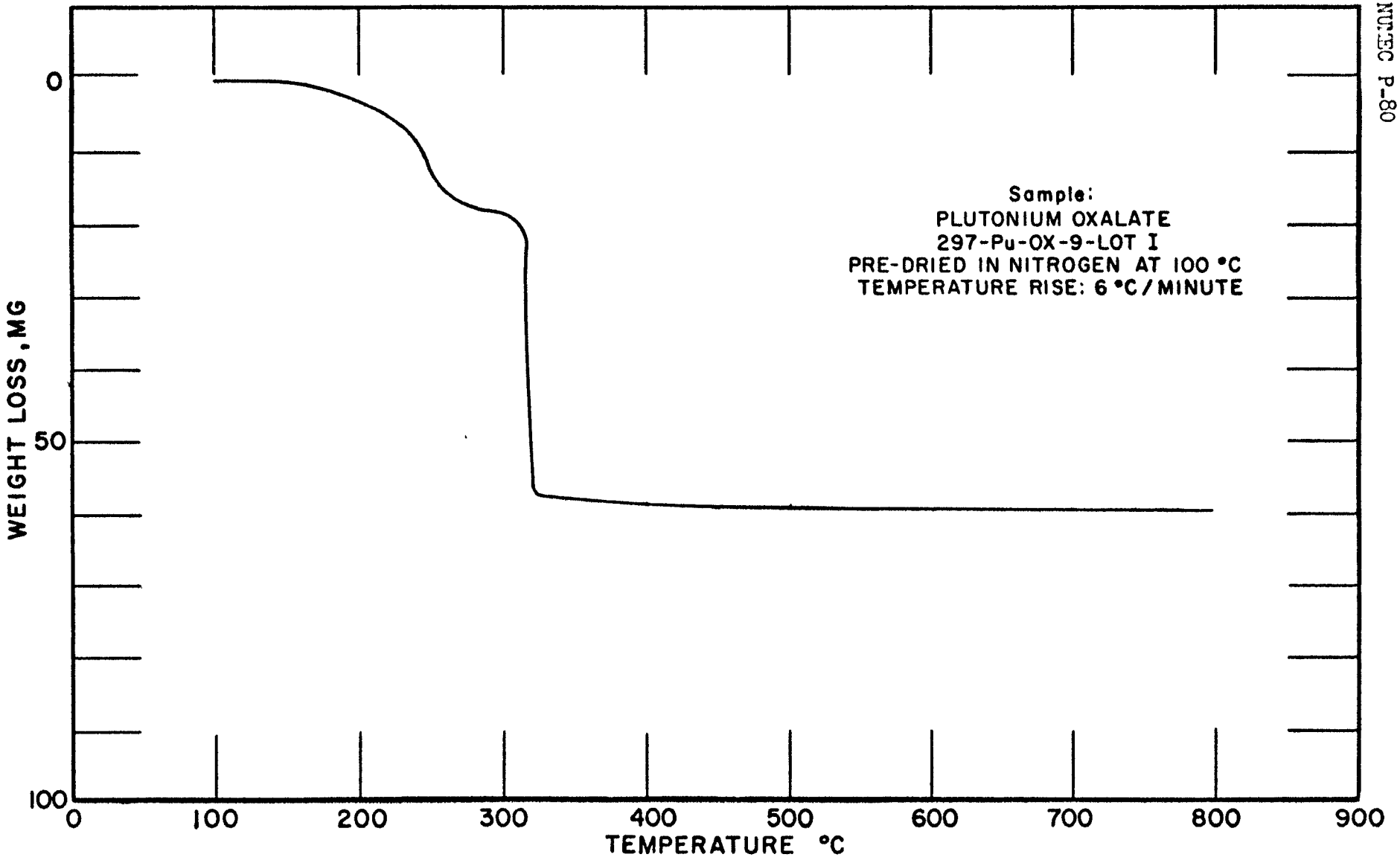


Figure 2.5

THERMOGRAVIMETRIC DECOMPOSITION CURVE

AIR ATMOSPHERE

at the Los Alamos Scientific Laboratories[(i)] indicate that no stable compounds are formed during decomposition, while results from Harwell[(ii)] show one slight arrest at approximately 350°C. The arrests observed in Figure 2.4 and 2.5, however, correspond to formation of $Pu(CO_3)_2$ (based on the final PuO_2 weight), while in the Harwell work no such corresponding arrest was observed. This again points out the effect of preparation history on powder properties.

While the second stage corresponds to $Pu(CO_3)_2$ on a weight basis, the weight loss at the first stage is insufficient to account for the expected CO loss on the basis of the reaction

$$Pu(C_2O_4)_2 \longrightarrow Pu(CO_3)_2 + 2CO\uparrow$$

This is related to the fact that the initial weight (after drying) is not sufficient to yield the final weight of PuO_2 obtained. Since a stable compound is maintained between 100-160°C, it is assumed that no oxalate decomposition occurs during the drying period. One possible explanation is that a mixture of $Pu_2(C_2O_4)_3$ and $Pu(C_2O_4)_2$ are formed during precipitation. Analysis on this basis yields, for the nitrogen run, a predicted weight loss of 12.6% compared to 10.2% for the first step and a predicted loss of 23.4% compared to an observed 24.5% for the second step.

To determine if a mixture does exist and if a stable carbonate is formed, chemical and x-ray analysis on the initial powder are planned, and an attempt will be made to isolate and analyze the compound formed after the first stage of decomposition.

In another run, 297-Pu-4 oxalate was heated to 350°C and held for two hours; actually the temperature rose from 345 to 360°C. The heating schedule was the same as used in processing (6°C/minute rise). Subsequently, the temperature was raised to 865°C to complete the conversion to PuO_2. After 35 minutes (the time used in processing) at this temperature, the conversion to PuO_2 was only 95% complete. This incomplete decomposition correlates with the residual carbon contents and the high weight losses observed on sintering the 297-Pu-4-1 and 297-Pu-5-1 samples (see Fabrication and Evaluation of Fuel Shapes).

(i) G. R. Waterbury, R. M. Douglass, C. F. Metz, Anal. Chem., 33, 1018 (61).
(ii) J. K. Dawson, R. M. Elliott, "The Thermogravimetry of Some Plutonium Compounds", A.E.R.E. C/R, 1207.

Weight Pick-Up Studies:

Because of the large weight losses observed on sintering and the large weight pick-up observed for the 297-Pu-4 and 297-Pu-5 powders (see Fabrication and Evaluation of Fuel Shapes), a study was initiated during this period to obtain more basic information on this phenomenon. Preliminary evidence indicates that the weight pick-up is not solely due to water and that the subsequent desorption is not a simple process. Initially, the samples are being examined for water adsorption employing humidity chambers controlled at 33, 53.5, 76, and 96.5% relative humidity. These data will be reported as accumulated. Weight pick-up at various CO_2 partial pressures with controlled humidities are also planned.

Plutonium-Uranium Oxide Preparation and Characterization

Previous co-precipitation run information and characterization data were reported(i) for small-lot preparations of UO_2-0.5% PuO_2 and UO_2-20% PuO_2 powder. During the current report period, two more continuous runs (1 kg) and one batch co-precipitation run were completed. Five additional continuous co-precipitation runs, using the ammonium uranate-plutonium hydroxide method, will be carried out during the next reporting period. The objective of the current series of preparation runs is to determine methods of controlling product surface area and fabrication characteristics.

Other co-precipitation methods are also being investigated to determine their suitability for the production of high-density granular or spherical oxide materials which are desired for mechanical packing or swaging.

Preparation of UO_2-5% PuO_2 and UO_2-20% PuO_2 (Runs 297-Pu-7, 8, 10): With the objective of preparing co-precipitated oxide for use in fabrication of in-pile test specimens, two continuous precipitation runs were made under conditions chosen to yield products of specified surface area (6 ± 2 M^2/gm). The general preparation method has been described previously(i) and specific process conditions are given in Table 2.1. The first of these, 297-Pu-8, yielded a UO_2-5% PuO_2 product having an average surface area of 6.2 M^2/gm using a precipitator holdup time of 33 minutes, an ammonia concentration of 3.5 M, and a reduction furnace temperature of 740°C (see Table 2.1). By isolating the starting and final transient products from the steady-state product and then separately characterizing the two sub-lots, it was determined that the surface area did not vary from start to finish (see Table 2.3) and that the target surface area had been achieved by proper initial choice of preparation conditions.

(i) NUMEC P-60, Progress Report, "Development of Plutonium Bearing Fuel Materials", pages 16 and 18.

Table 2.3

Summary of Co-precipitated UO_2-PuO_2 Parameters

Sample Identity	% PuO_2	Aqueous NH_3 Concentration (M)	Calcination[a] Temperature °C	Surface Area M^2/gm	Bulk Density gm/cc	Tap Density gm/cc
297-Pu-6	20	14.5	590	17.5		
297-Pu-6	20	14.5	640	12.7		
297-Pu-6	20	14.5	690	10.2		
297-Pu-6	20	14.5	740	7.1	1.80	2.18
297-Pu-7	20	3.5	540	20.7	1.14	1.29
297-Pu-7	20	3.5	740	19.8	1.31	1.53
297-Pu-8[b]	5	3.5	740	6.4		
297-Pu-8[c]	5	3.5	740	6.1	1.45	1.61

(a) 6% H_2-94% N_2 Atmosphere.
(b) Composite of startup and end of run product from continuous precipitation.
(c) Steady-state product from continuous precipitation.

In regard to the preparation of UO_2-20% PuO_2 (297-Pu-7 and 297-Pu-10), it had been learned from an initial trial preparation[i] that the powder prepared by slow 540°C reduction tended to oxidize during storage in air despite the use of precautions which had proven adequate for stabilizing UO_2 prepared under similar conditions. The most obvious difference between UO_2-20% PuO_2 and UO_2 prepared under identical conditions was that the mixed oxide had twice the surface area of the pure uranium oxide (Table 2.3).

The surface area measurements summarized in Table 2.3 indicate that the UO_2-20% PuO_2 samples precipitated with dilute ammonia (3.5 M) are more resistant to heat treatment than those precipitated with concentrated ammonia (14.5 M). The surface area of sample 297-Pu-6, precipitated with concentrated ammonia, is decreased from 17.5 to 7.1 M^2/gm with an increase in conversion temperature from 590° to 740°C. On the other hand, lot 297-Pu-7, precipitated with dilute ammonia shows only a slight decrease, 20.7 to 19.8 M^2/gm, when the conversion temperature is increased from 540 to 740°C. Comparison of the bulk and tap densities of the 297-Pu-6 and 297-Pu-7 samples calcined at 740°C indicates that the concentrated ammonia also results in more favorable bulk properties. The 297-Pu-7 sample calcined at 740°C could not be sufficiently compressed to give a reading on the Fisher Sub-Sieve Sizer even though the sample size was reduced by one half. It appears, then, that the combination of ammonia concentration and calcination temperature can be used to obtain and control the desired surface area. The fabricability and sinterability properties of powders prepared under these conditions are yet to be determined. Samples from additional continuous precipitation runs using dilute ammonia are being measured and evaluated to determine reproducibility and to provide further information for the control of processing variables.

Total Porosity: Previous work with UO_2 and other powders has indicated the importance of the pore structure in determining powder behavior. Porosity is expected to have an effect on sinterability, compressibility, trapping of impurities, and necessary binder addition. Based on earlier work[ii], a method has now been developed for obtaining the total porosity (micro and macro) by a simple test.

The method consists of determining the amount of water required to initiate caking tendencies in the powder. This is done by titrating water into the sample, shaking vigorously to distribute the water and to break prematurely formed agglomerates and simultaneously observing when the particles begin

---

(i) NUMEC P-60, Progress Report, "Development of Plutonium Bearing Fuel Materials", page 12.

(ii) W. B. Innes, Anal. Chem., 28, 332 (1956).

to adhere to the container walls. The method is based on the same principle as A.S.T.M. Test No. C128-57; i.e., the powder does not cake until the pores are filled and the additional water forms a layer around the particles. The method is fairly reproducible as seen in Table 2.4; an excess of one drop of water in several grams of sample is easily detected.

To obtain an independent check on the accuracy of the method, a drying curve of an amply wetted sample of UO_2 was obtained on the thermobalance. From a plot of the slope of the curve vs. time, the point at which the interparticulate water is completely evaporated and capillary water begins to evaporate can be determined. For two runs, this break in the curve yielded an average pore volume of .0895 cc/gm compared to a titration value of .097 cc/gm (Sample No. 1, Table 2.4).

This test method is now being adapted to routine glove box use. In conjunction with the apparent beneficial effects of employing water as a binder for PuO_2 pressing (see Fabrication and Evaluation of Fuel Shapes), this test might be used to determine the exact amount of water required to produce the desired lubricating properties. This would be superior to adding a fixed amount, on a weight basis, for all powders. Possibly, the method could be used with other liquid binders also.

Dry Solids Blending Trials

The selection of desirable ceramic powder properties often depends not only on fabricability and sinterability but also on blending characteristics. The tendency of certain fine oxide powders to agglomerate or segregate when agitated normally implies poor blendability. As an initial screening test, two 300 gram lots of UO_2-0.5% PuO_2 were prepared by twin-shell blending of the pure component oxide powders. In order to determine the relative ease of blending high and intermediate surface area PuO_2 powders with intermediate surface area UO_2 powder, two simultaneous blends were made using 360°C and 740°C calcined oxides. These blends were then sampled and analyzed for macro-scale homogeneity.

Although it is recognized that control of ambient humidity and powder moisture content are generally required for optimum precision blending, no moisture control was attempted in this trial. All materials had been stored under normal ambient temperature and humidity conditions prior to use. The UO_2 powder, obtained from a commercial source, was chosen for initial trials based on its satisfactory fabrication properties as shown by earlier sinterability tests(i). Characteristics of the starting materials are shown in Table 2.5. Blending was performed as follows: Precision weighed 1.5 gm quantities of as-received 297-Pu-9 Lot II and Lot III PuO_2

(i) NUMEC P-40, Progress Report, "Development of Plutonium Bearing Fuel Materials", page 20.

Table 2.4

Water Titration of Various UO_2 Powder Samples

Sample No.	Total Porosity - cc Absorbed per gram of Sample			
	Trial I	Trial II	Trial III	Trial IV
1	0.09962	0.09500	0.09731	0.09629
2	0.22736	0.21142	0.21939	0.22277
3	0.11485	0.11701	0.11382	0.11154
4	0.22122	0.22053	0.22455	0.23304
5	0.11417	0.10784	0.11145	0.11101
6	0.06863	0.07361	0.07657	0.07112

Table 2.5

Oxide Blend Makeup

Component	Surface Area M^2/gm	Bulk Density gm/cc	Blend I gm	Blend II gm
UO_2 Sample Ref.(i)	3.3	1.5	300.01	300.00
PuO_2 297-Pu-9-Lot II	5.4	1.8	-	1.5062
PuO_2 297-Pu-9-Lot III	43	1.3-1.4	1.5005	-

(i) NUMEC P-40, Progress Report, "Development of Plutonium Bearing Fuel Materials", p. 20.

powders were manually blended for several minutes with 100 gm quantities of as-received ceramic-grade UO_2 having a surface area of 3.3 M^2/gm and bulk density of 1.5 gm/cc. Each first-stage blend was then added to an additional 200 gm of UO_2 and mixed for 16 hours in a 1 pint Patterson-Kelley "twin-shell" blender.

Five samples (1.5-2.0 gm each) were taken from different portions of each blend and were further divided in half for the purpose of obtaining duplicate analyses of uranium and plutonium content. Each of the ten samples were weighed, dissolved, and analyzed using the amperometric method previously described(1). The results are presented in Table 2.6. It is to be noted that the 3% standard deviation based on duplicate analyses is of the same magnitude as the 2.3% sample-to-sample variation of plutonium content in Blend II; hence, the actual homogeneity may be better than indicated for this blend. The results show a strong difference between the blendability of the high and intermediate surface area PuO_2 samples. Although the lower average Pu/U ratio of the high surface area PuO_2 blend may be largely due to the presence of absorbed water and undecomposed carbonates in the 360°C calcined material, as weighed, the four-fold higher sample-to-sample variation between blends is clearly an indication of radically different segregation effects, as might be expected from the known difference in powder properties. These results, obtained by small-batch blending over a 16-hour time period, serve to emphasize the need for control of powder properties to obtain the type of blending required in large-scale production where blending is normally done on a shorter time cycle.

Additional blending trials with larger batches, different U/Pu ratios, and powder properties will be made during the next reporting period in order to determine scale-up effects and control procedures. In addition, smaller sample quantities will be examined to establish the scale of inhomogeneity.

Preparation of High-Density Granular Pu and Pu-U Oxides

Direct methods of preparing high-density coarse particle-size oxides for ultimate use in mechanical packing and swaging are being examined experimentally. In the case of PuO_2, the homogeneous oxalate method is being investigated first.

The homogeneous generation of oxalate ions is most easily carried out by hydrolysis of an oxalate ester

$$R_2(C_2O_4) + 2H_2O \longrightarrow ROH + H_2C_2O_4$$

(i) NUMEC P-70, Progress Report, "Development of Plutonium Bearing Fuel Materials", page 18.

Table 2.6

Comparative Analysis for Macro-Homogeneity in Dry Blends of Two Types of PuO_2 Powders with a Ceramic-Grade UO_2

Blend	I High Surface Area PuO_2 + Intermediate Surface Area UO_2			II Intermediate Surface Area PuO_2 + Intermediate Surface Area UO_2		
Sample	% U	% Pu	Pu/U x 10^3	% U	% Pu	Pu/U x 10^3
1	87.3 ± 0.4	0.316 ± 0.010	3.62	87.9 ± 0.4	.510 ± 0.015	5.80
2	87.2 ± 0.4	0.324 ± 0.010	3.72	87.2 ± 0.4	.535 ± 0.016	6.14
3	85.9 ± 0.4	0.384 ± 0.011	4.47	88.4 ± 0.4	.533 ± 0.016	6.03
4	87.9 ± 0.4	0.382 ± 0.011	4.35	87.9 ± 0.4	.510 ± 0.015	5.80
5	87.0 ± 0.4	0.418 ± 0.013	4.81	87.6 ± 0.4	.537 ± 0.016	6.13
Average	-	0.365 ± 0.011	4.19	-	0.525 ± 0.016	5.98
Std. Deviation	-	0.039	0.45	-	0.012	0.17
% Std. Deviation	-	10.7%	10.9%	-	2.3%	2.8%

and hence

$$M^{4+} + 2H_2C_2O_4 \longrightarrow M(C_2O_4)_2 + 4H^+$$

Dimethyl and diethyl esters are suitable and have been used at other installations with good success in the case of thorium and uranium. Preliminary experiments are now under way on the preparation of $Th(C_2O_4)_2$ and $U(C_2O_4)_2$. Information gained in these experiments will then be used for the preparation of $Pu(C_2O_4)_2$ and $Pu(C_2O_4)_3$.

For co-precipitated U-Pu oxide products, homogeneous precipitation using urea can be used to generate ammonium hydroxide as follows:

$$H_2NCONH_2 + 3H_2O \longrightarrow 2NH_4OH + CO_2$$

Several pilot batches of UO_2 have been prepared to gain experience applicable to the U-Pu system.

Prototype Preparation of UO_2 by Homogeneous Precipitation: The homogeneous precipitation process was initiated by dissolving uranyl nitrate hexahydrate (UNH) in water and heating the solution, while gently stirring, to about 60°C. A solution of urea in water was then added, and the heating and stirring was continued for several hours under reflux conditions. For four preparations, the conditions are given in Table 2.7.

After the reaction was completed, the ADU was filtered from the mother liquor and washed four times in 2% ammonium hydroxide by the slurry-filter method. The solid ADU was very granular, settled rapidly and was easily filtered. The washed material was dried under a number of different conditions as shown in Table 2.8.

The dried ADU materials were free-flowing yellow powders. When examined under low magnification, the powder appeared to be a mass of individual spheroidal particles of various sizes. It appeared that those materials (samples 1412 and 1414) dried at higher temperatures were composed of smaller particles than material that was identical except for its lower drying temperature (samples 1411 and 1413). The distinction is quite small, but it does illustrate the changes in external appearance that can be caused by rather minor variations in preparation technique.

The ADU material was further characterized by x-ray powder diffraction methods and surface area measurements. Preliminary results show that the ADU gives a fairly good diffraction pattern indicating a well crystallized material.

The dried ADU was reduced under a number of different conditions in a $6\%H_2$-$94\%N_2$ atmosphere. The samples were brought up to reduction temperature

Table 2.7

Reaction Conditions for Homogeneous Precipitation of ADU

Experiment No.	19-1-1	19-1-27	19-5-12	19-7-20
M $(UO_2)^{2+}$	0.25	0.25	0.71	0.71
M Urea	0.50	1.00	1.40	2.80
Reflux Time (hrs)	20	20.5	25	18
pH of Mother Liquor	6.5	7.2	3.4	7.1

Table 2.8

Drying Conditions for ADU

Experiment No.	19-1-1	19-1-27	19-5-12		19-7-20	
Drying Temperature, °C	25	25	25	65	25	95
Drying Time, Hours	24	24	24	24	24	24
Sample Number	1405	1406	1411	1412	1413	1414

over a three-hour period, were kept at temperature for approximately one hour, and then were slowly cooled. A portion of the reduced material was ignited in air to 900°C in order to determine O/U ratio. Currently available information is presented in Table 2.9. The general characteristics of the ADU and product particles may be judged from Figure 2.6. Future runs will be made under process conditions chosen to yield a more uniform grade of material, and the resulting techniques will be then applied to the preparation of UO_2-PuO_2.

Analytical Chemistry

During this quarter work was continued on the methods and analyses described previously(i). The study of the simultaneous determination of plutonium and uranium by differential spectrophotometry was completed and a topical report is in preparation. In addition, a procedure for the determination of carbon in plutonium compounds by means of a modified Leco gas evolution apparatus was established. Finally, the selection of the optimum carrier distillation procedure and buffer medium for the spectrographic determination of trace impurities in plutonium oxide was investigated.

The effect of variables on the simultaneous spectrophotometric determination of plutonium and uranium was ascertained and the precision of the method was statistically evaluated. It was found, as shown in Table 2.10, that at the two wavelengths of interest, 420 and 670 mμ the absorbance is not significantly affected by the variation of the sulfuric acid concentration from 3.5 to 5 M. The absorbance of these solutions was also stable over a period of 24 hours. The effect of varying the concentration of either of the major components is presented in Tables 2.11 and 2.12. Under the conditions described in these Tables the coefficient of variation for a size determination for uranium and plutonium was 0.6 and 0.2 per cent respectively. A series of synthetic mixtures was also prepared, and the quantitative recovery of each component was determined. The results are presented in Table 2.13. Finally, the precision of the determination of uranium in a series of unknown samples of mixed oxides based on duplicate analyses was estimated. The results shown in Table 2.14 indicate an error of less than 0.4 per cent.

For the determination of carbon in plutonium oxide preparations, a Leco carbon analyzer was modified to allow operation in a glove box. The precision and accuracy of the method was evaluated with a pure compound

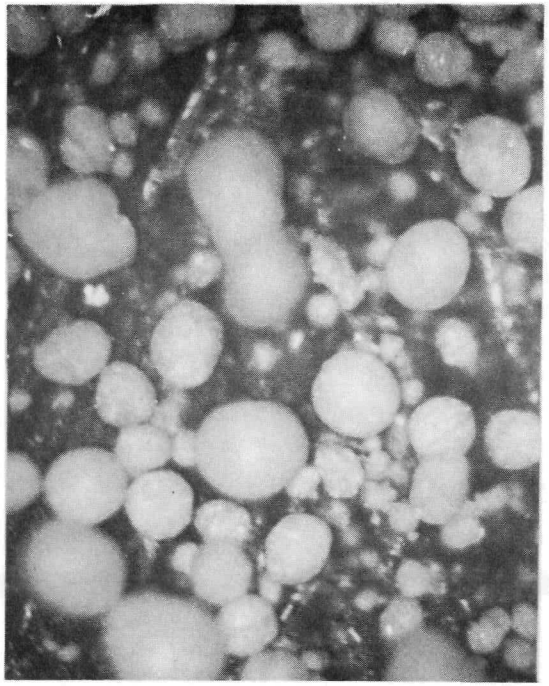
---

(i) NUMEC P-70, Progress Report, "Development of Plutonium Bearing Fuel Materials", page 18.

Table 2.9

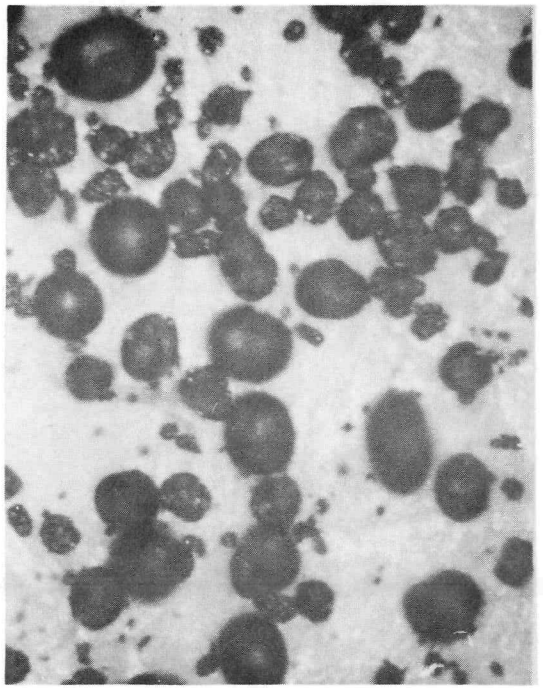
Properties of UO_2 Derived from Homogeneous Precipitation of ADU

Sample Number	1405	1405	1406	1406
Reduction Temperature, °C	540	740	540	740
O/U Ratio	-	-	2.16	2.10



ADU Spherical Particles

Sample 1405



Spherical UO_2 Formed by 740°C Reduction of ADU Shown at Left

Sample 1405

120X

Cross-Section of Spherical UO_2 Showing Internal Voids

Sample 1405

Figure 2.6

Characteristics of ADU and UO_2 Spherical Particles Produced by Homogeneous Precipitation with Urea from UNH Solution

Table 2.10

Effect of Acidity on the Absorbance of Plutonium Solutions

H_2SO_4, M	Absorbance	
	Wavelength 420 mμ	Center Wavelength 670 mμ
3.5	.140	.495
4.0	.147	.497
4.5	.148	.499
5.0	.146	.495

Table 2.11

Determination of Uranium
in Presence of Plutonium

Plutonium mg/ml	Uranium mg/ml	
	Introduced	Measured
0.066	13.30	13.33
0.132	13.30	13.31
0.66	13.30	13.33
0.99	13.30	13.28
1.98	13.30	13.23
2.64	13.30	13.13
3.30	13.30	13.21
	Average	13.26

$S = \pm 0.086$, $V(\%) = \pm 0.6$

Table 2.12

Determination of Plutonium in Presence of Uranium

Uranium mg/ml	Plutonium mg/ml	
	Present	Found
1.60	1.758	1.757
3.20	1.758	1.757
6.40	1.758	1.762
9.60	1.758	1.759
12.80	1.758	1.763
16.00	1.758	1.765
		Average 1.760

$S = \pm 0.033$, $V(\%) = \pm 0.2$

Table 2.13

Simultaneous Determination of Uranium and Plutonium by Differential Spectrophotometry

Plutonium		Difference		Uranium		Difference	
Taken	Found	mg	%	Taken	Found	mg	%
0.981	0.981	0	0	13.30	13.36	0.06	0.5
1.006	0.996	0.010	1.0	13.30	13.36	0.12	0.9
1.125	1.119	0.006	0.5	13.30	13.27	0.03	0.2
1.063	1.067	0.004	0.4	13.30	13.34	0.04	0.3
1.931	1.921	0.010	0.5	13.30	13.26	0.04	0.3
2.061	2.037	0.024	1.2	13.30	13.44	0.14	1.0

Table 2.14

Determination of Uranium in the Presence of Plutonium by Differential Spectrophotometry

Standard Deviation Between Duplicates

Uranium w/o (X)	Average w/o $(\bar{X})$	d	D	D^2
87.1 87.4	87.25	0.3	0.34	0.1156
87.2 87.1	87.15	0.1	0.11	0.0121
86.3 85.5	85.90	0.8	0.93	0.8649
88.1 87.6	87.85	0.5	0.56	0.3136
86.2 87.7	86.95	1.5	1.72	2.9584 D^2=4.2646

N = 10
P = 5
D.F. = N-P = 5
S = 0.653%

$\frac{t}{\sqrt{N}}$ = 0.716

$S.E._R$ = 0.5%

and a Bureau of Standards sample. The modification of the instrument involved the placing of the power supply to the induction coils (for the reaction tubes) outside of the glove box and passing the O_2 sweep gas and combustion products through an absolute filter into the conductivity measuring apparatus which was also located outside of the glove box. In this manner, only a part of the instrument is subject to contamination, and maintenance is thereby facilitated.

As shown in Table 2.15 the reproducibility of the estimation of carbon in a pure $CaC_2O_4 \cdot H_2O$ compound (carried out daily over a period of a week) was better than 3 per cent. The accuracy as tested with a Bureau of Standards sample was also good; the measured agreement was 0.775% in comparison with the certified value of 0.77%. Results on the determination of residual carbon as a function of calcination temperature of plutonium oxalate are presented elsewhere in this report.

Various procedures found in the literature for the estimation of trace impurities in plutonium materials[i][ii] are being evaluated. Initial work indicates that to allow selection of the best carrier, one requires a high purity material to serve as a matrix. For this purpose, plutonium metal will be purified by an anion resin separation and known quantities of impurities will then be incorporated therein.

The use of sodium fluoride as a spectrographic buffer to prevent the swamping of the spectrum of the trace element with the complex plutonium spectrum was also studied[iii]. While Johnson and Vejvoda reported that they could tolerate only 0.5 mg of plutonium, in a modified procedure as much as 5 mg of plutonium was found not to interfere. The modifications included the use of large flat graphite electrodes impregnated with Apiezon lubricant in place of copper electrodes, and the sodium fluoride salt concentration was increased by about an order of magnitude. Further studies to evaluate the limits of detection of trace elements are in progress.

(i) J. L. Daniel, "A Detailed Study of the Carrier Concentration Method of Spectrographic Analyses", HW64299, March 11, 1960.

(ii) R. J. KoFoed, Jr., "The Influence of the Matrix on the Carrier Distillation of Metallic Impurities from PuO_2 and U_3O_8", HW54032, April 10, 1958.

(iii) A. J. Johnson and E. Vejvoda, Anal. Chem. 31, 1643 (1959).

Table 2.15

Standard Deviation for Difference Between Duplicates
$CaC_2O_4 \cdot H_2O$ Daily Duplicate Runs

X gm/mho	$\bar{X}$	d	D%	D^2%
.02007 .02088	.02047	.00081	3.957	15.66
.02037 .02199	.02118	.00162	7.648	58.49
.02424 .02432	.02428	.00008	0.320	0.102
.01994 .01932	.01963	.00062	3.158	9.97
.01907 .01960	.01933	.00053	2.741	$\Sigma D^2 = 7.513$ 91.738

N = 10; P = 5; D.F. = N-P = 5 $\quad S = \sqrt{9.1738} = 3.028\%$

$S^2 = \frac{\Sigma D^2}{2P} = \frac{91.738}{10} = 9.1738 \quad \frac{t}{\sqrt{N}} = 1.031;$

$S.E._R = (1.031)(3.028) = 3\%$

FABRICATION AND EVALUATION OF FUEL SHAPES

Task 3.00
L. J. Jones

B. M. Cinai E. K. Halteman R. M. Horgos

PuO_2 Sintering Studies

Samples from two lots of PuO_2 made by continuous precipitation were calcined at 350, 420, 490, 560, and 760°C (see NUMEC P-70 and preceding sections of this report). Prior to cold pressing and sintering of these samples, they were vacuum dried at 70°C and stored 265 hours in relative humidity controlled between 45 and 50%. All samples (samples calcined at 760°C were not processed at this time) gained weight during the storage period, with weight gain decreasing with increasing calcining temperature. Upon sintering, all samples showed a decrease in weight considerably greater than the weight gain during storage. As shown in Table 3.1, this weight loss upon sintering decreased with increased calcining temperature. Not shown in Table 3.1 are data of weight losses during sintering for one hour at 1250°C and 1400°C. Together with the 1600°C data, a general increase in weight loss with increasing sintering temperature is indicated. It would appear that the weight changes are considerably more complex than a simple moisture pick-up since the differences noted during the various sintering runs would preclude simple moisture absorption.

To determine if the weight decreases on sintering could be partially attributed to vaporization of PuO_2 or residual PuO_3, samples are being sintered for longer time periods at 1600°C. To date, samples have been sintered at 1, 5, and $10\frac{1}{2}$ hours. The weight decrease appears to occur entirely within the first hour of sintering; thus, vaporization cannot be considered a significant factor. Longer sintering runs will be performed to verify these results.

Pressing of these powders was accomplished much in the same manner as described in previous quarterly reports(i)(ii). The powder was dry-slugged at 6500 psi in a 0.467 inch diameter die and hand granulated through a 20 mesh screen. The resultant granules were hand pressed, without the addition of organic binder, in hardened steel dies at pressures ranging

---

(i) NUMEC P-60, Progress Report, "Development of Plutonium Bearing Fuel Materials", p. 24.

(ii) NUMEC P-70, Progress Report, "Development of Plutonium Bearing Fuel Materials", p. 33.

Table 3.1

Effect of Calcining Temperature on Pressing and Sintering

Sample No.	Calcining Temp, °C	Weight Increase During Storage(1) (mg/gm)	Weight Decrease on Sintering(2) (mg/gm)	Avg. Green Density(3) (gm/cc)	Avg. Sintered Density(4) (gm/cc)	Avg. Shrinkage (%)
297-Pu-4-1	350	21.7	49.3	5.24	10.70	24.1
297-Pu-4-2	420	20.8	30.3	5.88	10.77	21.3
297-Pu-4-3	490	17.6	27.0	5.73	10.70	22.3
297-Pu-4-4	560	12.7	21.7	5.99	10.79	20.7
297-Pu-4-5	760	-	18.3	6.80	10.68*	13.2
297-Pu-5-1	350	21.2	88.2	4.64	10.82	27.1
297-Pu-5-2	420	21.6	33.8	5.77	11.04	21.6
297-Pu-5-3	490	19.2	31.2	5.60	10.81	23.3
297-Pu-5-4	560	15.0	22.0	5.68	10.83	23.4
297-Pu-5-5	760	-	19.1	7.11	10.53*	12.3

(1) Samples vacuum dried at 70°C followed by storage in a box atmosphere of 45 to 50% relative humidity for 265 hours.

(2) Sintered one hour at 1600°C in 94% N_2-6% H_2 atmosphere.

(3) Geometrical density - average of 3 or 4 pellets.

(4) Archimedean density - average of 3 or 4 pellets (* Pu-4-5 and Pu-5-5 pellet densities by geometry).

from 35 to 46 tsi. Sterotex was used as the die and punch lubricant and was applied as a saturated solution in trichlorethylene. All sintering runs consisted of a four-hour heat-up period to achieve maximum temperature, a one-hour period at temperature, and a four-hour cooling period. The furnace atmosphere through all stages was 6% H_2-94% N_2.

As shown in Table 3.1, PuO_2 calcined at temperatures from 350 to 560°C produced pellets with relatively low green densities which resulted in high shrinkage during sintering. The average green densities of pellets pressed from these powders ranged from 4.64 to 5.90 gm/cc. The average shrinkage in both diameter and length was about 22%. In contrast, powder calcined at 760°C resulted in pellets with average green densities of 6.80 to 7.11 gm/cc; average shrinkage ranged from 12.3 to 13.2%. In all cases, the final sintered densities were in the same range of 10.5 to 10.8 gm/cc.

Investigations of binder additives to the PuO_2 to improve the handling and pressing characteristics are being performed. No satisfactory procedure using Carbowax has been found. To date, water has been found to be the best additive to PuO_2 to improve pressing characteristics. For the low temperature calcined material, the moisture absorbed from the atmosphere has been sufficient. Powders calcined at 760°C and higher are less abosrbant, and additional water had to be added. Further work involving the addition of polyvinyl alcohol is under way.

Mixed Oxide Sintering Studies

Co-precipitated UO_2-0.5% PuO_2 (Lot No. 297-Pu-2) was pelletized at 20.5 to 35 tsi, yielding green densities of 5.44 to 6.04 gm/cc. All pellets were pressed from as-received, slug-pressed, and granulated powder without binder additives. These pellets were sintered for one hour at 1250, 1400, and 1600°C, resulting in average sintered densities of 9.84 (89.7% T.D.), 10.24 (93.4% T.D.), and 10.37 gm/cc (94.5% T.D.), respectively. These densities and the increase with sintering temperature are similar to those obtained for pure UO_2 of corresponding surface area.

Mechanically mixed and sintered samples of UO_2-50% PuO_2 and UO_2-75% PuO_2 (sintering data presented previously[i] have been subjected to metallographic examination and x-ray analysis. PuO_2 and UO_2 powders were mechanically mixed by Spex milling for three minutes. The powders were prepared and pressed, without binder, in the same manner as the PuO_2 pellets. The samples were sintered for one hour at 1600°C in a 94% N_2-6% H_2 atmosphere. Sintered densities were 10.44 (97.6% T.D.) and 10.48 gm/cc (92.4% T.D.) for the UO_2-50% PuO_2 and UO_2-75% PuO_2, respectively. Micro-examination

(i) NUMEC P-70, Progress Report, "Development of Plutonium Bearing Fuel Materials", p. 37.

of the sintered pellets revealed unabsorbed sintered conglomerates of UO_2 in a PuO_2 matrix as shown in Figure 3.1, which is a photomicrograph at 200X of the UO_2-50% PuO_2 sample. Examination at higher magnification revealed a fine grain structure in the UO_2 zones in both samples. In the UO_2-75% PuO_2 sample, the PuO_2 could also be distinguished as unabsorbed islands within the UO_2 zones as shown in Figure 3.2. No other phase could be detected in either sample.

The incomplete interabsorption of the PuO_2 and UO_2 suggested by metallographic examination was confirmed by x-ray diffraction examination. Separate but broad diffraction patterns were obtained for both PuO_2 and UO_2. A greater than usual breadth of the lines was attributed to the partial solution of one oxide in the other resulting in a range of solid solutions and corresponding range of lattice parameters, and hence in line broadening. In addition to the PuO_2 and UO_2 patterns, the UO_2-75% PuO_2 sample also showed at least three unidentifiable extra lines. The UO_2-50% PuO_2 sample showed only PuO_2 and UO_2 lines.

It is apparent from the above description that blending and mixing procedures were unsatisfactory and that the time at temperature was insufficient to yield complete solid solution of the mixed oxides. Studies on both of these facets of the problem will be undertaken during the next quarter. In addition, it is highly desirable that an inexpensive screening test for determining degree of solid solution be developed. It is expected that dissolution of the sintered compacts in acid and gravimetric determination of the undissolved PuO_2 will suffice. However, such a method must be calibrated and tested as to its adequacy. For example, the dissolution rates of known solid solutions of PuO_2-UO_2 having varied PuO_2 contents must be determined. This will be undertaken during this next quarter.

Eutectoid-Like Structure in Sintered PuO_2

Considerable research effort to elucidate the conditions and mode of formation of the eutectoid-like structure first observed in PuO_2 pellets sintered at 1600°C in an atmosphere of 94% N_2-6% H_2 has been undertaken. The typical microstructure at a magnification of 200X is shown in Figure 3.3. The eutectoid structure is shown at higher magnification in Figure 3.4.

It was suspected that an impurity either present in the calcined powder or absorbed during sintering was responsible for the second phase formation. To determine if the extra phase detected after sintering PuO_2 pellets was originally present in the PuO_2 powders as calcined, a sample of the original powder, 297-Pu-1, was examined by x-ray diffraction utilizing the glancing angle technique. Broad lines from only one face-centered-cubic phase of lattice parameter 5.394Å, i.e., very close to that for stoichiometric PuO_2 (5.396Å), were detected. The breadth of the lines is due primarily to the very fine crystallite size. Since this powder had been calcined at only 360°C, a similar examination was carried out on 297-Pu-5-5 powder, which

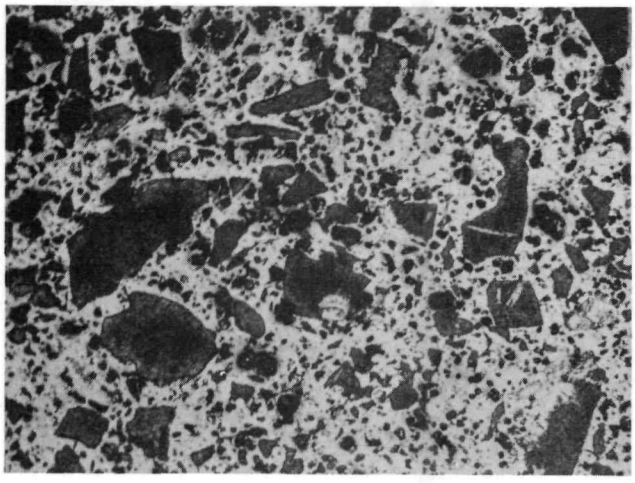


Figure 3.1
UO_2-50% PuO_2 Sintered 1 Hour at 1600°C
in 94% N_2-6% H_2 Atmosphere

200X

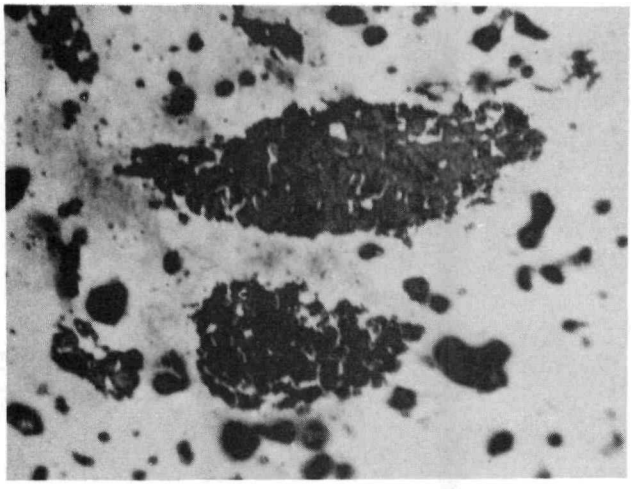


Figure 3.2
UO_2-75% PuO_2 Sintered 1 Hour at 1600°C
in 94% N_2-6% H_2 Atmosphere

800X

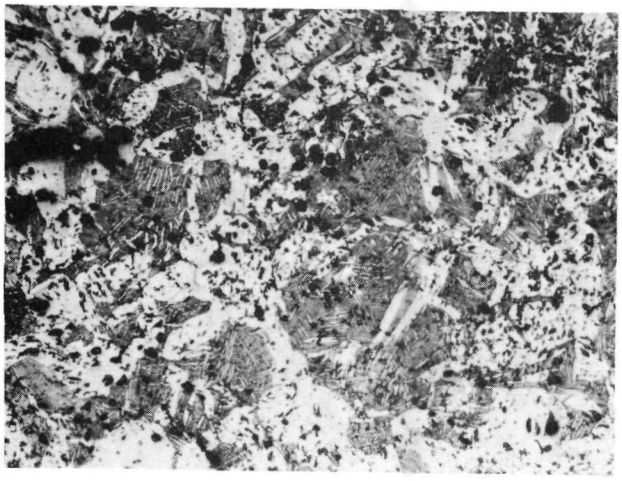


Figure 3.3

PuO_2 Pellet Sintered for 1 Hour at 1600°C
in 94% N_2-6% H_2 Atmosphere

200X

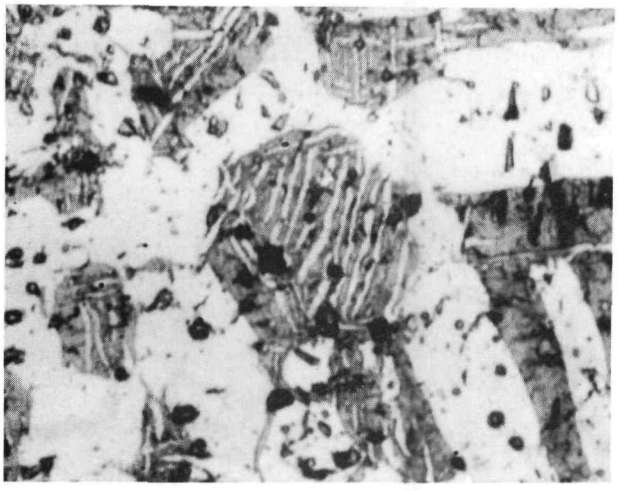


Figure 3.4

PuO_2 Pellet Sintered for 1 Hour at 1600°C
in 94% N_2-6% H_2 Atmosphere

800X

had been calcined at 740°C. Again only one face-centered-cubic phase was detected. The diffraction lines were now somewhat sharper indicating an increase in crystallite size due to the higher calcination temperature.

Pellets were sintered for one hour at 1600°C in 94% argon-6% hydrogen and in vacuo and for one hour at 900, 1200, and 1400°C in 94% nitrogen-6% hydrogen. No eutectoid-like microstructure has been observed in samples of PuO_2 sintered at 900, 1200, or 1400°C. The sample sintered in vacuo at 1600°C had the same eutectoid structure as that sintered in nitrogen-hydrogen. The sample sintered in argon-hydrogen also resulted in the same two phases as were found in pellets sintered at 1600°C in vacuo or in the nitrogen-hydrogen atmosphere; however, the second phase appeared as platelets in a matrix of PuO_2 grains, not in the eutectoid-like form.

X-ray diffraction examination has shown the eutectoid structure to consist of a face-centered cubic phase of lattice parameter 5.402Å (presumably PuO_2) and, as yet, an unidentified phase. An x-ray diffraction photograph of the sample sintered one hour at 1600°C in vacuo is shown in Figure 3.5.

Chemical analysis of PuO_2 pellets after sintering at 1600°C in the nitrogen-hydrogen atmosphere revealed total metallic impurities of less than 0.02% and zero carbon content. It would seem that the eutectoid-like microstructure is not due to the presence of such impurities. Since the eutectoid structure has been found in pellets sintered in various atmospheres, it would appear that gas impurities and resultant compound formation would not be the cause. Therefore, it has been hypothesized that a reduction of the PuO_2 is occurring resulting in a highly oxygen deficient phase.

Cooling a PuO_2 pellet, sintered in nitrogen-hydrogen atmosphere, from 1600°C to room temperature in only two minutes compared with the standard four hour cooling period still resulted in a eutectoid-like microstructure; however, x-ray diffraction examination showed only one face-centered cubic phase having a lattice parameter close to that for stoichiometric PuO_2.

Sintering at 1700°C in nitrogen-hydrogen atmosphere resulted in partial fusion in the pellet as shown in Figure 3.6. However, x-ray diffraction examination still detected the same two phases as were found in the eutectoid-like microstructure.

In keeping with the hypothesis of a eutectoid transformation occurring on cooling in PuO_2 pellets sintered at 1600°C in vacuo or in the nitrogen-hydrogen atmosphere, differential thermal analysis carried out on such material has revealed a transformation on heating between about 625 and 700°C, and on cooling between about 650 and 605°C. However, not only was the latter transformation less certain than that on heating, but repeated cycling of the sample between room temperature and 800°C resulted in the apparent cessation of transformation in either direction.

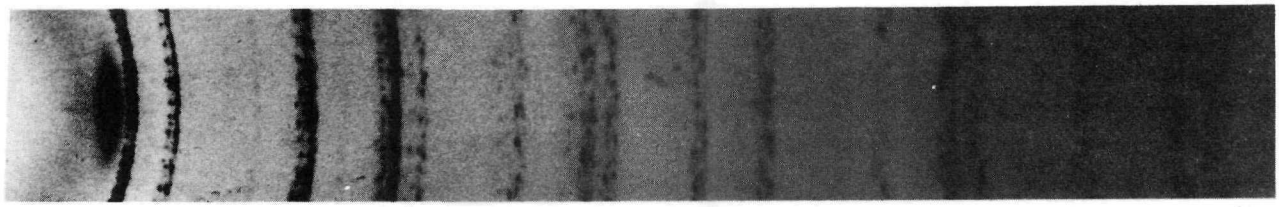


Figure 3.5

X-ray Diffraction Photograph of PuO_2 Pellet Sintered for 1 Hour at 1600°C in Vacuo

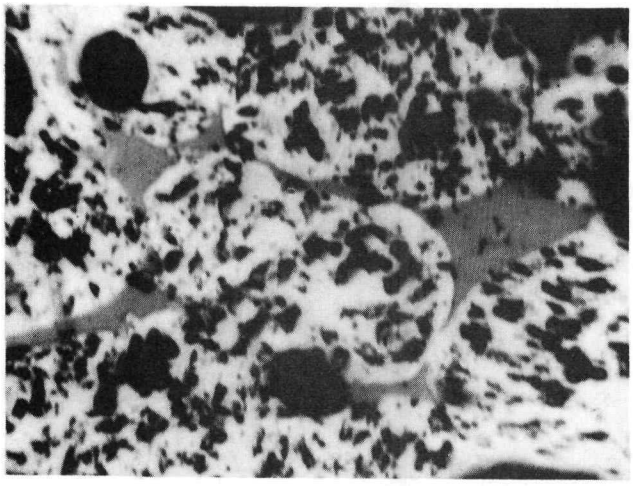


Figure 3.6

PuO_2 Pellet Sintered 1 Hour at 1700°C in 94% N_2-6% H_2 Atmosphere Showing Evidence of Fusion

As Polished

800X

Again in keeping with the tentative identification of one of the phases of the eutectoid-like microstructure being highly oxygen-deficient PuO_2, gains in weight were measured on twice heating a sample, containing a eutectoid-like microstructure, in air at 1000°C. These heatings are now being continued at higher temperatures.

From the foregoing experiments, it is tentatively concluded that the eutectoid-like microstructure observed in PuO_2 pellets forms on cooling as a result of loss of oxygen at the sintering temperature. The latter oxygen-deficient PuO_2 is conceived as disproportionating into a near stoichiometric and a highly oxygen-deficient PuO_2 (possibly Pu_2O_3) on cooling, possibly between about 650 and 600°C. Further work is required to fully explain all the observed effects.

Fuel Particle Preparation--Plasma Torch

Emphasis has been placed upon completing the glove box housing for the plasma torch in order to commit this box to the plutonium line at the earliest possible date. All work on this box in the past has been directed towards operation of the plasma torch and its related equipment with very little actually being done to the glove box proper. Within this quarter, the glove box construction has been completed, and the box has passed the final leak test. Prior to final commitment of this box, an extensive program of plasma torch operation will be performed to determine if the heat generated or if the large quantities of gas required for the torch operation will have any adverse effect on the glove box operation. In addition to the construction work on the box, an analytical balance and equipment required to classify the plasma torch products by size and shape have been installed in the box. Also, an apparatus has been designed and is under construction to allow determination of the crushing strength of the produced particles. It is expected that plutonium will be processed through this box within the first few weeks of the coming quarter.

Thermal Conductivity and Melting Point Apparati

The assembly of an apparatus for the measurement of the thermal conductivity of poor conductors at high temperature by the use of point and plane sources is currently in progress. The major pieces have been assembled, and the various sliding vacuum joints tested. It was found impossible to make a vacuum tight quartz to metal seal using a modified Housekeeper seal. A Kovar to quartz seal using titanium hydride as a binder has, therefore, been ordered. This will be a complete assembly and will be soft soldered directly to the top and bottom susceptor blocks of the apparatus. The RF generator has been modified by removing the step down transformer in its tank circuit and placing it inside the glove box a minimal distance from the apparatus. Thus, the line losses will be reduced by the use of lower current. Testing of the high voltage filter sections and controls for the electron gun will be started soon after delivery of the high voltage power supply.

The apparatus for melting point determination using a tungsten strip heater has been assembled and made vacuum tight. A 300 ampere power supply has been constructed using "Variac" cores for the primary winding and 3/8 inch water cooled copper tubing for the secondary winding and lead lines. Standardization runs are in progress using a standard lamp to calibrate the optical pyrometer and to determine the absorption error in the quartz windows. The equipment is being checked by comparing the melting point of Al_2O_3, MgO, and UO_2 with those found in the literature.

FUEL ELEMENT FABRICATION AND EVALUATION

Task 4.00
L. J. Jones

R. M. Horgos

Mechanical Packing

Further experimentation in this area has been deferred pending the preparation and characterization of suitable feed materials. As described previously in this report, particular emphasis has been placed on readying the plasma torch and its box for commitment the plutonium line, and, in addition, work has been initiated to produce spheres by other techniques.

Box and Equipment Installation

The decontamination box has been modified to include a stainless steel tank welded into the base of the box for use in ultrasonic cleaning of fuel elements. Shelving and other auxiliary equipment have been installed in preparation for closing the box, leak testing and commitment to the plutonium line. The welding box which attaches to the powerboard port of the decontamination box requires a number of major changes prior to its commitment to the line. However, this will not delay commitment of the decontamination box.

The corrosion test box has been completed during this period and is presently being given its final leak test. All problems involving excessive heat absorption by the glove box components from the operation of the autoclaves have been resolved. In this box the vacuum evaporator which is to be used for replication of samples in preparation for electron microscopy has been modified to allow coating plutonium particles with various metallic elements. This glove box will be committed to the plutonium line during the second week of October.

The NaK canning box has been completed, helium leak tested, and operationally checked out. Capsules have been welded in this box in an inert atmosphere at a maximum current of 175 amps without adversely affecting the glove box operation.

The three special glove boxes for housing the swager and associated equipment have been delivered together with the feed mechanism box supports. Installations of equipment will be scheduled to permit operation when suitable feed materials have been developed.

RADIATION TESTING AND EVALUATION

Task 5.00
L. J. Jones

R. M. Horgos

Since irradiation tests in the final analysis determine the suitability or lack of suitability of a material for reactor application, in-pile testing will be started as soon as possible. The radiation program, although comprehensive, is a minimal one to determine the relative merits of fuels prepared via different fabrication routes. For example, the relative behavior of fuel prepared by co-precipitation and that prepared by mechanical mixing of the oxide components will be determined. Also, the relative behavior of fuel elements prepared by the sintered pellet route, mechanical packing, and swaging will be investigated. In general, short duration rabbit tests to determine thermal behavior and long duration high burnup tests to determine radiation damage resistance characteristics will be carried out. In all instances, the fuel material and elements will be completely characterized prior to irradiation in order to make the tests meaningful.

Rabbit Tests

Analyses of short-term irradiations in hydraulic rabbit facilities can determine the relative merits of the various preparation and fabrication procedures. In particular, thermal performance, that is, the maximum heat capable of being produced without resulting in fuel melting or phase change will be determined. These capsules will be kept in-pile sufficiently long (approximately one hour) to achieve a build-up of fission products that will permit determination of fission gas release rates. In addition, fission product analysis of sectioned samples will yield information relative to the radial flux depression, which is important information desired for physics studies.

Since there are a number of variables present in any irradiation experiment such as vertical flux distribution, reactor power level, heat transfer, etc., a pure UO_2 sample will be used as a control in each rabbit capsule. Two plutonia-bearing samples will be included in each capsule. Utilizing an 0.250 inch diameter fuel pellet and a 1-3/4 inch active fuel length, thermal equilibrium longitudinally is reached over the central 1 inch length. A sketch of the proposed sample arrangement and rabbit capsule is shown in Figure 5.1.

The initial series of rabbit irradiations are scheduled for pile insertion during the next period. Since the irradiations are for one hour only, hot

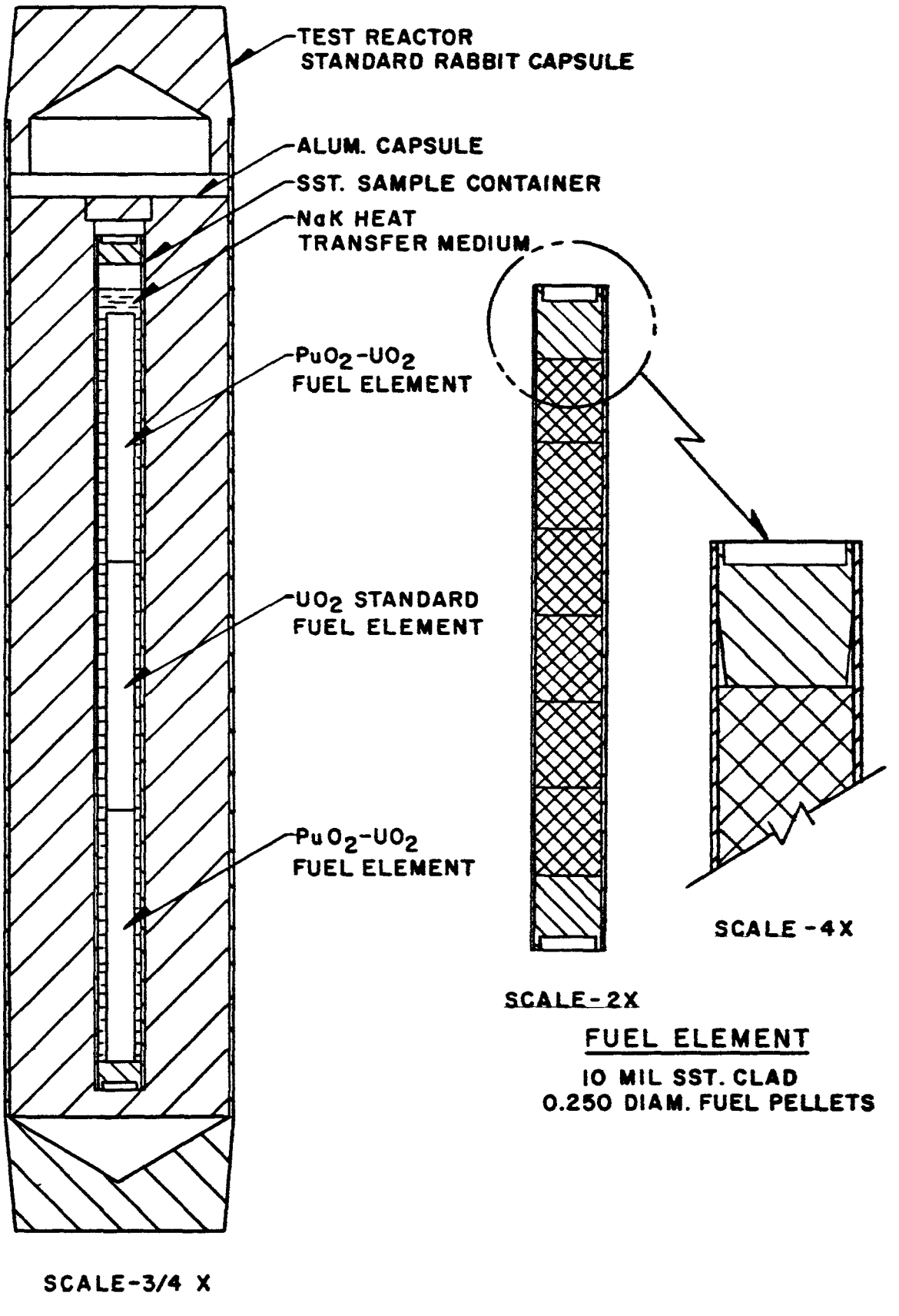


Figure 5.1

PROPOSED RABBIT TEST FUEL ELEMENT & CAPSULE

laboratory examination will commence shortly thereafter. Approximately a four-day cooling period after irradiation will be required to permit decay of high energy short half-life fission products and sodium-24 present in the NaK heat transfer medium.

High Burnup Tests

In order to assess the effect of continued burnup on the properties of plutonia-bearing fuel materials, long exposure tests are required. For example, it is known that the fission gas release rate in other ceramic fuels remains relatively constant up to a high burnup at which time there is a sharp increase in the fission gas release rate, presumably due to breakdown of the crystal lattice of the oxide. Such information on plutonia-bearing fuels can only be determined by prolonged exposure to a relatively high neutron flux. In addition, the effects of the fission product atoms on fuel dissolution characteristics and on microstructure can be obtained from such irradiations. Above all, high burnup tests are necessary as engineering proof tests of the ability of plutonium fuels to achieve a high total power generation.

To achieve these high burnups, long duration tests are required. Consequently, it is necessary that these samples be inserted in-pile as soon as possible commensurate with establishment of optimum fabrication procedures. The rabbit tests will be used to establish some confidence in the fabrication procedure to be utilized for the high burnup samples.

Hot Laboratory Equipment Fabrication

Five alpha boxes for hot laboratory work are on order, and delivery is expected in October. Equipment for capsule opening, fuel element dimensioning, and fuel element sectioning has been procured.

Design of an alpha box for the metallographic cell has been completed, and procurement is expected before the end of the next quarter.

REACTOR PHYSICS AND ENGINEERING PARAMETRIC STUDIES

Task 8.00
K. H. Puechl

W. Ross J. Ruzbacki

During this period, two papers were accepted for publication in Nuclear Science and Engineering, and one other paper was published in the September 1961 issue. The published paper[i] compares NUSURP calculated resonance escape probabilities for water lattices to values calculated using more standard theory and further discusses the discrepancy between measured and calculated values for the effective resonance integrals. Since this paper was submitted, further effort has been expended in an attempt to resolve this discrepancy. Specifically, recent experimental data obtained by the Bettis group[ii] on 0.387 inch fuel rods has been analyzed. These data show that the effective resonance integral of a UO_2 rod is 1.30 times the value obtained for a metallic uranium rod having the same dimensions. This result differs appreciably from the 1.41 factor obtained by Hellstrand[iii] and used in the original development of the NUSURP procedure. When the 1.30 factor is used in the NUSURP procedure, it has been found that experiment and theory are in essential agreement for this one point. This result gives confidence that the NUSURP procedure can be modified to yield general agreement between theory and experiment provided that correct values for the isolated rod effective resonance integrals are used as input.

The two papers just recently accepted deal with the potential of plutonium as a fuel in near-thermal converter and burner reactors. Under the assumptions used to determine resonance self-shielding in plutonium, the results to be reported show that with sufficient Pu-240 content there generally exists a region of fuel loading, for most lattices of interest, where further addition of fuel decreases the reactivity of the lattice. This region, wherein reactivity decreases with further fuel addition, has

---

(i) K. H. Puechl, "An Approach to Reactor Physics Using Results of Integral Experiments--Part II", Nuclear Sci. and Eng. 11, 61 (1961).

(ii) G. G. Smith, J. Hardy, D. Klein and J. A. Mitchell, "Experimental Studies of U-238 Resonance Capture in UO_2 Fuel Rods", Nuclear Sci. and Eng. 9, 421 (1961).

(iii) E. Hellstrand, "Measurements of the Effective Resonance Integral in Uranium Metal and Oxide in Different Geometries", J. Appl. Phys. 28, 1493 (1957).

been designated as the region of "negative resistance". This behavior is primarily due to the fact that the spectral hardening associated with fuel addition increases the effective Pu-240 cross section relative to other isotopes present. More recent work in this area has shown that this behavior is exhibited over a broad range of assumptions regarding resonance self-shielding in the plutonium isotopes. The "negative resistance" effect is certainly an attainable phenomenon with plutonium; however, determination of the exact magnitude requires experimental investigation. Because of this behavior, plutonium fueled systems of the general type studied are characterized by a relatively long core life with an associated small reactivity variation; i.e., the tendency for the reactivity to increase with fuel removal is counteracted by fission product buildup and fissionable isotope conversion.

NUMEC P-80

PREPARATION AND COATING OF SPHERICAL OXIDE PARTICLES

Task 11.00
C. S. Caldwell - L. J. Jones

F. Shipko R. M. Horgos
B. Vondra J. Miles

During this period, work was initiated on a new task. The task objective is to develop suitable techniques for coating spherical PuO_2 and PuO_2-UO_2 particles and to evaluate the products for use in reactor applications. Initial work will be performed with PuO_2 as the substrate and Ni and Cu coatings. This choice of materials was made to gain experience with general procedures and techniques. As techniques are developed, other coatings will be considered.

Several small lots of PuO_2 (297-Pu-9-Lot II) were prepressed, granulated, and reduced in size to yield regular spherical (-70+80 mesh) fuel particles having a green density of about 5 gm/cc. After pre-firing at 1000°C for one hour in air, followed by screening, the particles were sintered at 1350, 1475, and 1600°C for four hours in air to yield spherical granules falling within the range -80+100 mesh (U. S. Sieve Series). In accordance with earlier results reported in NUMEC P-34 on dry-pressed and sintered cylindrical pellets, the optimum density (estimated by metallographic examination of pellet cross-sections) was not obtained at the highest sintering temperature, but rather at an intermediate level, in this case, 1475°C. Subsequent to sintering, these particles were coated with nickel. "Electroless" nickel coating rates appeared to be faster than obtained previously with similar UO_2 fuel particles. A cross section of a resultant nickel-coated PuO_2 particle is shown in Figure 11.1. In this example, the coating thickness built up more rapidly than expected, hence the coating is quite irregular. Process conditions have now been altered to reduce the rate of buildup, hence to produce more uniform coatings. No difficulty has been experienced in obtaining a good oxide-to-nickel bond.

Other coatings will be applied to PuO_2 and PuO_2-UO_2 material produced directly by this route and to plasma flame polished material of higher density and improved uniformity. Evaluation methods for particle density, structure, and mechanical strength will be used to aid in guiding conditions required for the practical production of suitable fuel materials.

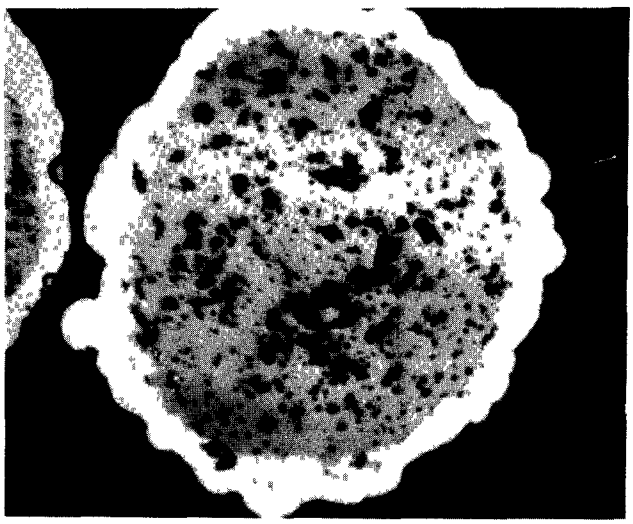


Figure 11.1

Nickel Coated PuO_2 Spherical Particle

400X