Progress Report
DEVELOPMENT OF PLUTONIUM-BEARING FUEL MATERIALS

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NUMEC P-103	December 31, 1962
NUMEC P-104	March 31, 1963

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PROJECT AND FACILITY ADMINISTRATION

Task 1.00

K. H. Puechl

UO_2-PuO_2 coprecipitation runs made with modified equipment have yielded powders having improved sinterability. UO_2-35 w/o PuO_2 that can be readily sintered to above 93% of theoretical density has now been consistently produced. With this modified equipment, sinterability appears to be much less sensitive to PuO_2/UO_2 composition.

Sintering studies with PuO_2 compacts have also been continued and extended to include the effects of impurities. The sintering data indicate that air sintering of PuO_2 results in higher density than reduction (N_2-6% H_2) sintering; reduction sintering tends to convert an appreciable amount of PuO_2 to Pu_2O_3. Further, it has been shown that the addition of 0.5 w/o strontium carbonate tends to enhance the sinterability of PuO_2.

In preparation for the fabrication of high burnup irradiation specimens, various blending techniques as well as larger scale equipment are being evaluated. Previous laboratory trials had indicated that satisfactory homogenization of component UO_2 and PuO_2 powders could be achieved by wet ball milling. Since this and the subsequent drying operation are time-consuming process steps, these procedures are being optimized, and alternate dry blending methods are also being reassessed. Preliminary results with UO_2-ThO_2 and UO_2-PuO_2 give indication that simplification may be possible.

Oxidation kinetics data on UO_2-PuO_2 is now being generated by thermogravimetric analysis. Preliminary interpretation of the data indicates that there is no simple correlation between the oxygen diffusion rate and the PuO_2/UO_2 composition.

Samples of UO_2-PuO_2 covering the complete composition range have been exposed to 680°F water for 1000 hours, and the results indicate that over the entire range corrosion is comparable to that exhibited by UO_2. Vacuum sintering of such pellets for 1 hour at 1000°C in contact with 304 and 316 stainless steels as major constituents have also been carried out, and metallographic and x-ray diffraction examination indicate no reaction between ceramic and metals.

The short-term irradiation capsules are now at the reactor site awaiting insertion. Some difficulty had been encountered due to the propogation of cracks in the Type 6061-S aluminum capsule weld zones. This difficulty has been overcome, and the capsules have been accepted for insertion by the reactor operator.

The high burnup test program has now been finalized, and the preliminary design of the test capsule has been completed. Both thermal and fast reactor fuels will be irradiated to obtain performance comparison among various fabrication procedures.

PREPARATION AND CHARACTERIZATION OF FUEL MATERIALS

Task 2.00

C. S. Caldwell O. Menis

Preparation and Characterization of Plutonium Oxide

(J. Goodman, J. Limpert)

Plutonium dioxide for use in homogenization and sintering studies has been prepared by oxalate, hydroxide, and peroxide precipitation and air calcination. The oxalate and peroxide products were made as in runs 297Pu27A[i] and 297Pu29[ii], and the hydroxide was precipitated by a continuous method using gaseous ammonia. Preparation and powder characterization data are summarized in Tables 2.1-2.4. The high tap density obtained by calcination of plutonium hydroxide at 840°C suggests that further calcination at elevated temperatures may yield a high-density feed suitable for vibratory compaction or swaging.

Preparation and Characterization of Mixed Plutonium-Uranium Oxides

(J. Goodman, H. Krake, T. Potter)

Four continuous UO_2-35 w/o PuO_2 coprecipitation runs have been carried out to further test the improved methods of process control instituted during the last reporting period. Both aqueous and gaseous ammonia were used as precipitants and duplicate runs were made in each case.

Powder characterization data from these and previous runs indicate that the improved process has four major advantages over previous techniques; namely,

1) The UO_2-PuO_2 powder surface area is relatively insensitive to plutonium content;

2) The UO_2-PuO_2 powder surface area remains high (4-6 M^2/gm) following high temperature (840°C) reduction. (It is pointed out that such reduction is desirable when N_2-6% H_2 non-explosive gas is utilized since the reduction can thereby be accomplished more rapidly.)

(i) NUMEC P-103, Progress Report, "Development of Plutonium-Bearing Fuel Materials"

(ii) NUMEC P-104, Progress Report, "Development of Plutonium-Bearing Fuel Materials"

Table 2.1

Plutonium Oxalate Preparation Route

Sample Identification	297Pu38
Precipitation Conditions	
Method	Continuous
Temperature, °C	35
Feed Composition	
gm Pu/l	200
H^+, molarity	3
Strike Solution Composition	(25% excess)
$H_2C_2O_4$, molarity	1.0
H_2O_2, molarity	0.8
Precipitation Average Holdup, hours	0.5
Total Number Throughputs	8
Drying Temperature, °C	100
Drying Time, hours	24
Furnace Conversion Conditions	
Temperature, °C	760
Time, minutes	30

Table 2.2

Plutonium Hydroxide Preparation Route

Sample Identification	297Pu239
Precipitation Conditions	
Method	Continuous
Temperature, °C	55
Feed Composition	
gm Pu/l	100
H+, molarity	1.0
Nominal Feed Flow Rate, l/hr	1.2
Precipitant	
Composition	NH_3 gas
Flow Rate	780 cc/min @ 34.7 psia
Average Holdup, minutes	30
Total Number of Throughputs	2.8
Drying Conditions	
Temperature, °C	100
Time, hr	26
Conversion Conditions	
Gas Atmosphere	N_2-6% H_2
Gas Flow Rate, SCFH	5.0
Rate of Temperature Climb, °C/min	12
Temperature, °C	840
Time at Temperature, minutes	80
Furnace Charge, gm	80.0

Table 2.3

Batch Plutonium Peroxide Route

Sample Identification	297Pu40
Plutonium Feed Solution	
Batch Size, gm Pu	99.7
Plutonium Concentration, gm/l	100.0
H+ Concentration, M	3.0
Precipitant	
H_2O_2 Reagent Strength, v/o	30.0
H+ Concentration, M	3.0
Volume H_2O_2 Added Slowly, l	0.320
Total Volume H_2O_2 Added, l	0.580
Addition Rate During Slow Addition, ml/min	25
Agitator Speed (2.5 in. dia. flat turbine impeller), rpm	700
Precipitation Temperature, °C	18
Digestion Conditions	
Temperature, °C	12
Time, hr	1.0
Filtration Time, minutes	4
Drying Conditions	
Temperature, °C	55
Time, hr	48
Calcination Conditions	
Temperature, °C	490
Time, hr	0.5

Table 2.4

PuO_2 Powder Characterization Data

Run Identification	Origin	Surface Area M^2/gm	Bulk Density gm/cc	Tap Density gm/cc	Subsieve Size microns	Total Metallic Impurity ppm
297Pu38	Oxalate	4.88	1.53	2.70	1.4	460
297Pu39	Hydroxide	2.65	3.25	5.19	4.4	2400
297Pu40	Peroxide	24.1	2.77	4.45	2.3	2271

3) The particle sizes are considerably smaller than obtained previously, and this characteristic does not appear to be sensitive to the choice of precipitant (see Figure 2.1).

4) The UO_2-35 w/o PuO_2 powder exhibits greatly improved sinterability. Whereas previously produced powders of this composition could be sintered to only 90% of theoretical density, the improved product was readily sintered to 95-96% of theoretical density at 1600°C.

Preparation and characterization data and the results of spectrographic analyses are summarized in Tables 2.5-2.8. Plutonium filtrate losses during these runs were limited to 0.03-0.3 mg/ml.

Preparation of UO_2-PuO_2 by Component Powder Blending
(R. Swain)

Previously obtained laboratory-scale tests[1] indicated that satisfactory blending of component powders could be achieved by wet ball milling. Autoradiography of sintered pellets indicated that the degree of homogeneity achieved by such blending is comparable to that attainable by coprecipitation. Studies have now been initiated to evaluate larger scale equipment and to optimize the blending procedures. Other blending techniques that may result in satisfactory blending without the need for subsequent drying are also being investigated. Finally, chemical analysis of small blended samples are being made in order to develop correlations between the results of such analyses and the results of autoradiography. If definitive correlations are possible, quality control procedures could be greatly simplified.

To establish optimum conditions for wet ball milling, four multi-kilogram blends have been made using UO_2 powders plus 1% ThO_2 as a stand-in for PuO_2. Four different cylinder charges were used ranging from 25 to 40% of the cylinder volume. Powder samples from various locations within the jar were removed after 30, 60, 90, and 120 minutes of milling, and 50 mg fractions from these samples are being analyzed for thorium by x-ray fluorescence.

Simultaneously, a sub-kilogram blend of UO_2 and PuO_2 has also been prepared by wet ball milling using a 40% cylinder charge. Twenty-two 500 milligram samples were removed for amperometric and alpha counting analysis after 2 hours of blending. Pellets are now being fabricated, and these will be analyzed by autoradiography to allow comparison with the chemical and counting data.

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(1) NUMEC P-100, Progress Report, "Development of Plutonium-Bearing Fuel Materials", page 46.

Table 2.5

Process Conditions
for Coprecipitation of UO_2-35 w/o PuO_2
(Aqueous Ammonia Precipitant)

Run Identification	297Pu35 and 297Pu36				
Composition	UO_2-35 w/o PuO_2				
Precipitation Conditions Method Temperature, °C	Continuous 55	Continuous 55	Continuous 55	Continuous 55	Continuous 55
Feed Composition gm Pu/liter gm U/liter H^+, molarity	 35.0 65.0 1.0	 35.0 65.0 1.0	 35.0 65.0 1.0	 35.0 65.0 1.0	 35.0 65.0 1.0
Nominal Feed Flow Rate, l/hr	1.2	1.2	1.2	1.2	1.2
Precipitant Composition NH_4OH, molarity	14.5	14.5	14.5	14.5	14.5
Precipitant Flow Rate, liters/hr	0.3	0.3	0.3	0.3	0.3
Precipitant Average Holdup, min	30	30	30	30	30
Total Number Throughputs	3	2	2	2	1
Run Period	Startup	Steady State	Steady State	Steady State	Shut Down
Oxide Sample Identification	TS80-740	SS80-640	SS80-740	SS80-840	RS80-740
Drying Temperature, °C	180	180	180	180	180
Gas Atmosphere	N_2-6% H_2	N_2-6% H_2	N_2-6% H_2	N_2-6% H_2	N_2-6% H_2
Gas Flow Rate, SCFH	5.0	5.0	5.0	5.0	5.0
Rate of Temperature Climb, °C/min	12	12	12	12	12
Conversion Temperature, °C	740	640	740	840	740
Time at Conversion Temperature, minutes	80	80	80	80	80
Pu-35 Furnace Charge, gm	80.8	180	180	180	80.3
Pu-36 Furnace Charge, gm	80.3	163.8	163.9	165.7	80.5

Table 2.6

Process Conditions
for Coprecipitation of UO_2-35 w/o PuO_2
(Gaseous Ammonia Precipitant)

Run Identification	297Pu37				
Composition	UO_2-35 w/o PuO_2				
Precipitation Conditions Method Temperature, °C	Continuous 55	Continuous 55	Continuous 55	Continuous 55	Continuous 55
Feed Composition gm Pu/liter gm U/liter H^+, molarity	 35.0 65.0 1.0	 35.0 65.0 1.0	 35.0 65.0 1.0	 35.0 65.0 1.0	 35.0 65.0 1.0
Nominal Feed Flow Rate, l/hr	1.2	1.2	1.2	1.2	1.2
Precipitant Composition, NH_3	Gas	Gas	Gas	Gas	Gas
Precipitant Flow Rate, cc/min	180 cc/min 24.7 psia	180 cc/min 24.7 psia	180 cc/min 24.7 psia	180 c/min 24.7 psia	180 c/min 24.7 psia
Precipitant Average Holdup, min	30	30	30	30	30
Total Number Throughputs	3	2	2	2	1
Run Period	Startup	Steady State	Steady State	Steady State	Shutdown
Oxide Sample Identification	TS80-740	SS80-640	SS80-740	SS80-840	RS80-740
Drying Temperature, °C	180	180	180	180	180
Gas Atmosphere	N_2-6% H_2	N_2-6% H_2	N_2-6% H_2	N_2-6% H_2	N_2-6% H_2
Gas Flow Rate, SCFH	5.0	5.0	5.0	5.0	5.0
Rate of Temperature Climb, °C/min	12	12	12	12	12
Conversion Temperature, °C	740	640	740	840	740
Time at Conversion Temperature, minutes	80	80	80	80	80
Furnace Charge, gm	80.0	176.3	176.3	176.5	79.8

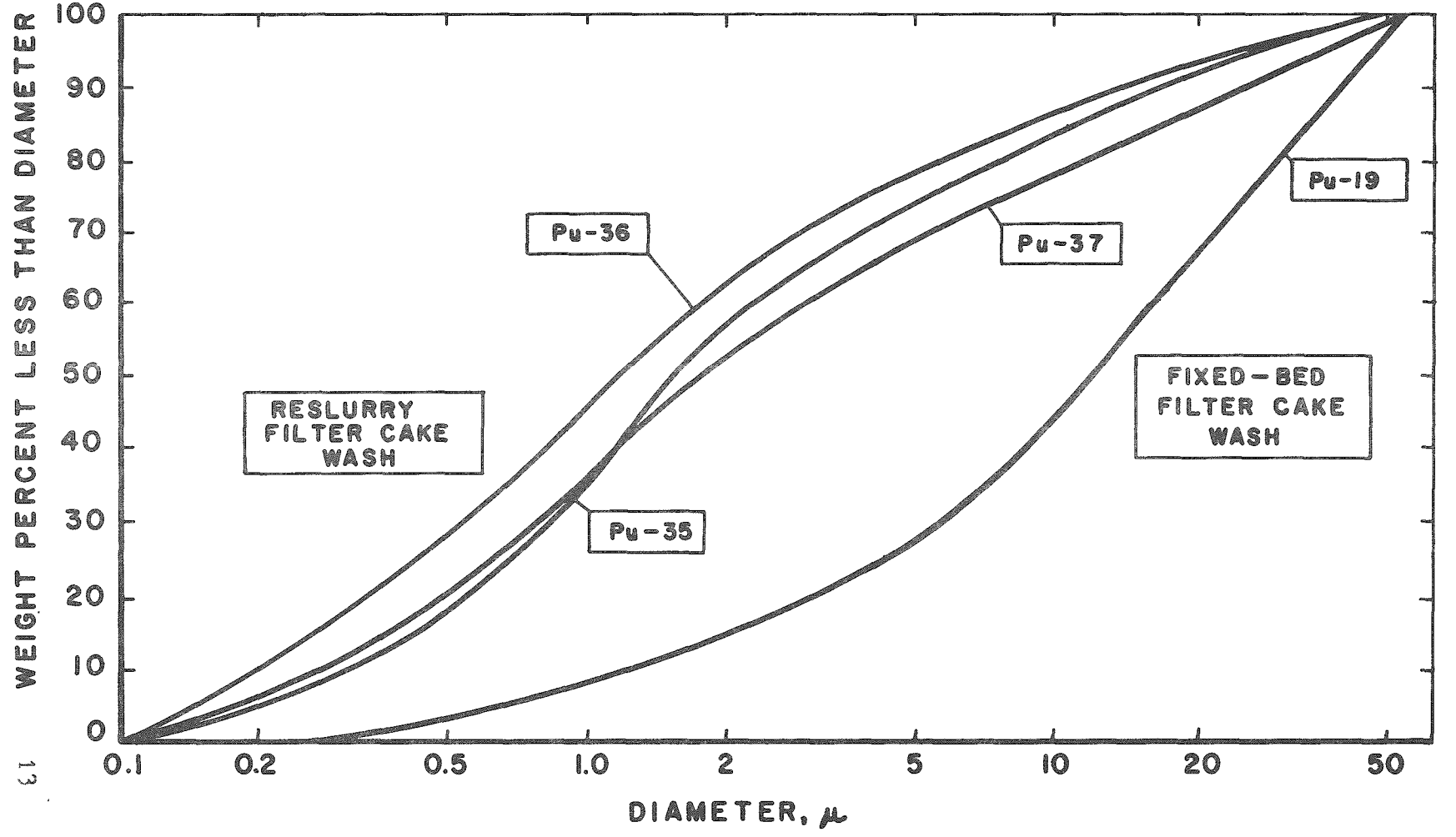
Table 3.7

Summary of Powder Characteristics for Coprecipitated UO_2-PuO_2 Materials

Sample Number	PuO_2 Content w/o	Milling*	Oxygen/Metal Ratio in Uranium Fraction	B.E.T. Surface Area M^2/gm	Bulk Density gm/cc	Tap Density gm/cc	Air Permeability Particle Size microns	Average MSA Particle Size for -200 mesh Fraction microns
Pu34TS80-740	5	NM	2.66	10.46				
Pu34SS80-640	5	HM	2.66	16.76	0.52	1.14	0.21	0.8
Pu34SS80-840	5	HM	2.29	6.42	0.73	1.72	0.33	1.3
Pu34RS80-740	5	NM	2.66	10.81				
Pu35TS80-740	35	HM	2.31	8.45	1.36	2.91	0.60	2.7
Pu35SS80-640	35	HM	2.36	10.90	1.37	2.75	0.53	2.0
Pu35SS80-740	35	HM	2.28	7.68	1.33	2.62	0.56	2.1
Pu35SS80-840	35	HM	2.18	6.20	1.35	2.69	0.60	1.6
Pu35RS80-740	35	HM	2.44	9.94	1.16	2.94	0.51	1.5
Pu36TS80-740	35	HM	2.31	6.84	1.57	2.94	0.72	1.5
Pu36SS80-640	35	HM	2.48	9.72	1.46	2.82	0.68	1.4
Pu36SS80-740	35	HM	2.30	6.64	1.54	2.78	0.64	2.3
Pu36SS80-840	35	HM	2.19	4.41	1.47	2.74	0.67	1.2
Pu36RS80-740	35	HM	2.32	8.23	1.31	2.47	0.55	1.3
Pu37TS80-740	35	HM	2.29					0.74
Pu37SS80-640	35	HM	2.40	10.93	1.37	2.68	0.59	3.5
Pu37SS80-740	35	HM	2.27	6.87	1.44	2.63	0.60	1.7
Pu37SS80-840	35	HM	2.18	4.52	1.51	2.89	0.68	1.7
Pu37RS80-740	35	HM	2.28					1.0
Pu38					1.53	2.69	1.44	

* HM - Hammermilled
NM - Non-Milled

RUN NO.	AMMONIA PRECIPITANT	PRECIPITATOR CONTROL
Pu-19	AQUEOUS (14.5M)	PROTOTYPE
Pu-35	"	IMPROVED DESIGN
Pu-36	"	"
Pu-37	GAS	"



PARTICLE SIZE DISTRIBUTION OF UO_2-35 w/o PuO_2

FIG. 2.1

In addition, UO_2-1% PuO_2 and UO_2-10% PuO_2 blends have been prepared using UO_2-35 w/o PuO_2 coprecipitated material as one of the powder components. Samples have been taken after two hours of milling and chemical, counting, and autoradiographic analyses will be compared.

Four dry ball mill blends of UO_2-0.5 w/o PuO_2 have also been prepared. The effects of blending time, charge size and moisture content are being evaluated Preliminary chemical analysis data indicate plutonium content coefficients of variation of 1.1 and 1.4% using 0.5 gram samples subsequent to 1 and 4 hour milling, resp. The effects of such blending on particle size distribution and impurity content are now being ascertained.

While twin-shell blending was used previously to demonstrate the adverse effects (agglomerate formation and segregation) of prolonged blending[1], studies are now being made to determine optimum blending time required for the production of maximum achievable homogenization. Using 544 grams of UO_2 and 2.5 grams of PuO_2, a UO_2-0.5% PuO_2 blend has been prepared in a 1 quart blender. Samples were withdrawn from various locations after 5, 10, 15, 20 and 25 minutes of blending, and 200 mg fractions have been analyzed for plutonium content by amperometric titration. The results presented in Table 2.9 show that optimum blending time is approximately 10 minutes.

A Lödige blender is also being evaluated using ThO_2 as the minor component. Mixtures containing from 6 to 13 kg of UO_2 with 1% ThO_2 have been blended and sampled to determine the effects of charge size and blending time. Microscopic examination of powder and fabricated pellets show no gross agglomerate formation. Preliminary ThO_2 analysis using 50 mg samples indicate coefficients of deviation of 5 to 7% as compared with 1% to 6% obtained by wet ball milling. Equipment modifications are now being made to obtain further improvement.

Analytical Chemistry

(O. Menis, B. Conroy, J. Limpert)

During this period, the capability for chemical analysis has been increased by the construction and checkout of two apparati. Specifically, a thermogravimetric balance has been modified to allow determination of the oxygen-to-metal ratio in UO_2-PuO_2 mixtures, and a special coulometry cell has been constructed to allow determination of trace quantities to hexavalent uranium in UO_2-PuO_2.

(i) NUMEC P-100, Progress Report, "Development of Plutonium-Bearing Fuel Materials", pages 46-47.

Table 2.9

Efficiency of Dry Twin-Shell Blending
UO_2 Plus $\frac{1}{4}$ w/o PuO_2 in 200 mg Samples

Blend Time (minutes)	Sample Number 1	2	3	4	5	Average	Coefficient of Deviation (%)
5	.454	.407	.529	.512	.50	.482	10.5
10	.521	.493	.518	.519	.521	.514	2.3
15	.515	.511	.534	.447	.444	.490	8.5
20	.511	.522	.492	.503	.524	.510	2.6
25	.501	.513	.515	.484	.490	.501	2.7
					Average	.499	

For the determination of the oxygen-to-metal ratio, an apparatus similar to that described by Sinclair[i] was constructed. A picture of this apparatus prior to introduction into a glove box is shown in Figure 2.2. The apparatus consists of a thermobalance wherein a sample can be weighed in a sample tube under controlled atmospheres. The quartz tube is protected by an Inconel thimble which is heated by a platinum winding. Trial runs have been carried out with Bureau of Standards U_3O_8 and utilizing a nitrogen-6% hydrogen atmosphere to minimize the hydrogen handling problem. The data obtained from these runs are presented in Table 2.10. It is seen that the results agree within 0.01 mg of the theoretical value. The apparatus is now being installed in a glove box to allow operation with plutonium.

For the determination of U(VI), a special coulometry cell based on the work of Booman[ii] has been assembled as shown in Figure 2.3. This apparatus will also be used for the determination of the concentration of fertile material in irradiated samples.

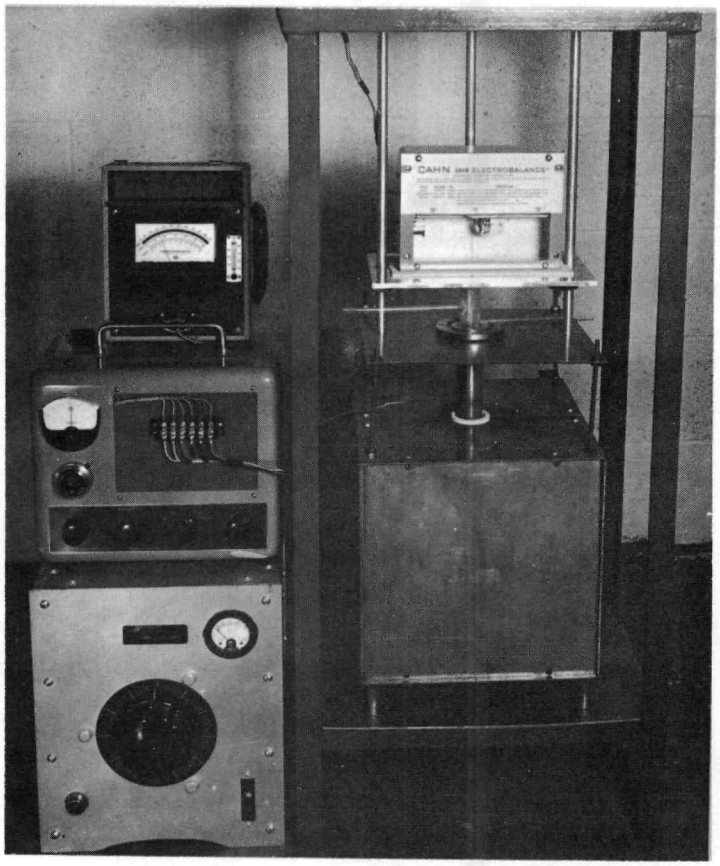
(i) J. L. Drummond and V. M. Sinclair, "Some Aspects of the Measurement of Oxygen-to-Metal Ratio in Solid Solution of Uranium and Plutonium Dioxides", presented at Sixth Conference on Analytical Chemistry in Nuclear Reactor Technology, Gatlinburg, Tennessee, October 1962.

(i) G. L. Booman and W. B. Holbrook, "An Extraction, Controlled-Potential Coulometric Method Specific for Uranium (VI)", Anal. Chem. 31, 10-16 (1959).

Table 2.10

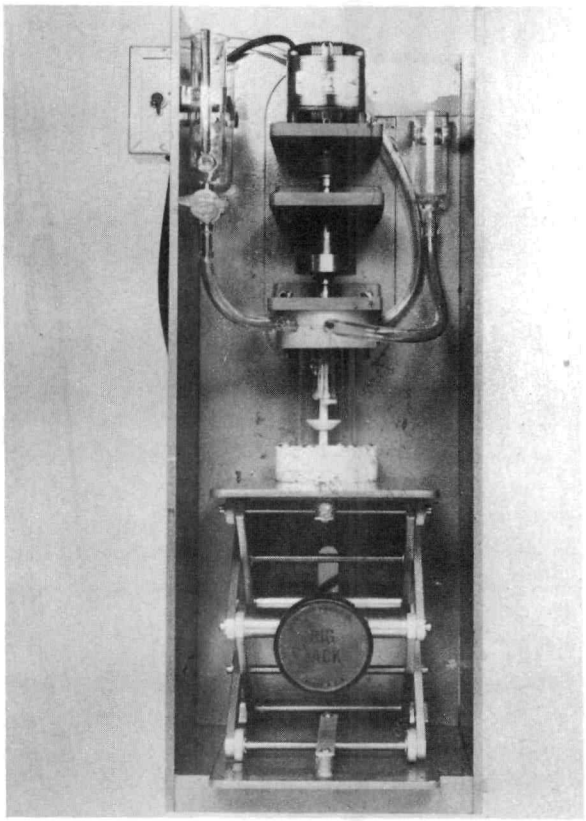
Determination of Oxygen-to-Metal Ratio

	1		2	
	U_3O_8	UO_2	U_3O_8	UO_2
Weight in Argon, gm	0.22276		0.23312	
Theoretical		0.21429		0.22426
Reduced		0.21420		0.22426
Oxidized	0.22277		0.23312	
Reduced		0.21430		0.22425
Difference	0.00001	0.0001	0.00000	0.00001



A Mock-Up of a Thermogravimetric Apparatus

Figure 2.2



Controlled Potential Coulometry Cell

Figure 2.3

FABRICATION AND EVALUATION OF FUEL SHAPES

Task 3.00

E. K. Halteman I. D. Thomas

PuO_2 Sintering Studies

(M. D. Houston)

Sintering evaluation of PuO_2 powders produced by various process routes has been continued and the effects of additives are being explored.

Pellets of three material batches, 297Pu29 (oxalate route), 297Pu30 (peroxide route), and 297Pu31 (peroxide route), were sintered at 1600°C for 1 hour in N_2-6% H_2 as well as in air. The characteristics of the powders utilized were tabulated previously(i). The sintering data are presented in Table 3.1. The results show that higher sintered densities are attainable in an oxidizing atmosphere and that the oxalate-derived powder tends to sinter to a higher density than the peroxide-derived material. This latter result was not anticipated since the surface areas of the peroxide-derived PuO_2 were 26.0 and 19.5 M^2/gm, resp. The relatively low sintered densities may be due to the presence of appreciable amounts of unconverted compounds as indicated by the relatively high weight losses observed during both oxidation and reduction sintering. Weight change observations following reoxidation indicate that sintering in N_2-6% H_2 reduces approximately 20% of the PuO_2 to Pu_2O_3.

The sintering studies were also extended to ascertain the effect of controlled impurity additions on the sintering behavior in an oxidizing atmosphere. While some enhancement in sinterability is anticipated under these conditions due to the effect of lattice defects on material diffusion, such additions may also tend to stabilize PuO_2 and inhibit Pu_2O_3 formation under reduction sintering. The ions Ca^{+2} and Sr^{+2} were selected on the basis of ionic size and valance. In addition, the effect of Mg^{+2} impurity was also investigated because of its relatively small ionic radius. Powder lot 297Pu29 derived from the peroxide was used, and the impurity additions (0.5 w/o) were introduced as carbonates and calcium fluoride. The PuO_2 and impurities were intimately mixed by paste blending in an agate mortar. A total of 5 compacts from each powder blend and from pure PuO_2 were pressed at 20 tsi and fired for 1 hour in flowing oxygen at 1600°C. As shown in

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(i) NUMEC P-103, Progress Report, "Development of Plutonium-Bearing Fuel Materials", pages 4-6, and NUMEC P-104, Progress Report, "Development of Plutonium-Bearing Fuel Materials", pages 3-7.

Table 3.1

Sintering Characteristics of Various PuO_2 Preparations
(Sintered at 1600°C for 1 hour)

Composition Designation	Compaction Pressure TSI	Green Density gm/cc	Sintering Atmosphere	Firing Weight Loss %	Linear Shrinkage %	Fired Density gm/cc	Percent Theoretical Density	Weight Gain on Reoxidation %
297Pu29 (Oxalate Route)	10	6.53	N_2-6% H_2	1.3	13.4	10.01	87.3	0.54
	20	7.10	N_2-6% H_2	1.3	11.8	10.21	89.1	0.55
	40	7.57	N_2-6% H_2	1.3	9.2	10.12	88.3	0.71
	20	7.16	Air	0.6	12.4	10.49	91.5	-
	40	7.57	Air	0.6	10.8	10.71	93.4	-
297Pu29 (Peroxide Route)	20	6.60	N_2-6% H_2	2.3	11.1	9.24	80.6	0.71
	40	7.04	N_2-6% H_2	2.3	10.3	9.26	83.9	0.56
	20	6.60	Air	1.7	11.7	9.45	82.5	-
	40	7.04	Air	1.7	10.9	9.87	86.1	-
297Pu30 (Peroxide Route)	20	6.20	N_2-6% H_2	2.7	14.5	9.75	85.1	-
	40	6.73	N_2-6% H_2	2.7	13.5	10.28	89.7	-
	20	6.20	Air	2.4	15.0	10.07	87.9	-
	40	6.73	Air	2.4	14.5	10.51	91.7	-

Table 3.2, only the strontium addition enhanced the sinterability; the addition of calcium as the carbonate or fluoride had little effect. On the basis of color change, both strontium and calcium appeared to form solid solutions with the PuO_2. During subsequent reduction firing, all compacts lost weight (0.5-0.7 w/o), hence it can be concluded that none of the additives tended to stabilize the PuO_2.

Mixed Oxide Sintering Studies
(M. D. Houston)

Sintering trials on various coprecipitated UO_2-PuO_2 materials have been continued. During this period, the compositions which were evaluated included three pure UO_2 batches, UO_2-20% PuO_2, three UO_2-35% PuO_2 preparations, and UO_2-80% PuO_2.

Three batches of UO_2 designated as 297Pu21, Pu22, and Pu23 were prepared by the ADU method to check out certain equipment modifications. These modifications and the complete history and characterization data of these powders had been previously reported(i). All three batches exhibited similar compaction and sintering behavior as indicated by the data presented in Table 3.3. Densities in the range 93-96% theoretical were generally observed. The low densities observed with Pu23SS5 and Pu23SS6 result from the high content of volatile material that remains after the low temperature or short-time conversion, resp. These data, therefore, are proof that reproducible product can be precipitated in the modified equipment.

The material prepared in run 297Pu25 (UO_2-20 w/o PuO_2) as described in a previous report(ii) was also compacted and sintered. As shown in Table 3.4, all batches (converted at various temperatures in the range 640-840°C) sintered to above 93% of theoretical density. With increasing conversion temperature, the green densities at equivalent compaction pressure and the sintered densities increased. Final densities appeared to be more dependent on the conversion temperature than on the pressure utilized for compaction. In general, the sintered densities for various preparation runs of UO_2-20 w/o PuO_2, that is, 297Pu13 (batch method), 297Pu17 (batch method), and 297Pu25 (continuous method), appear to be similar. Again, reprodicibility of product appears to be satisfactory.

(i) NUMEC P-102, Progress Report, "Development of Plutonium-Bearing Fuel Materials", pages 11-16.

(ii) NUMEC P-103, Progress Report, "Development of Plutonium-Bearing Fuel Materials", pages 14-17.

Table 3.2

Effect of Impurities on Sintering Characteristics of PuO_2

Sintered at 1600°C for 1 Hour in O_2
297Pu29 (Peroxide-Derived)
Controlled Impurity Content - 0.5 w/o
Compacted - 20 TSI

Controlled Impurity	Green Density gm/cc	Weight Loss on Firing (%)	Linear Shrinkage (%)	Fired Density gm/cc	Percent Theoretical Density	Refired Density (N_2-6% H_2) % TD
None	6.58	1.7	11.8	9.54	83.2	87.9
SrO	6.57	1.9	15.2	10.62	92.7	89.9
CaO	6.55	2.1	10.1	8.97	78.3	76.9
MgO	6.49	2.3	11.3	9.18	80.1	82.2
CaF_2	6.59	1.8	10.1	9.03	78.8	-

Table 3.3

Sintering Data for UO_2 Preparations
(Sintered at 1600°C for 1 Hour in N_2-6% H_2)

Composition	Compaction Pressure TSI	Green Density gm/cc	Weight Loss on Firing %	Linear Shrinkage %	Fired Density gm/cc	Percent Theoretical Density
Pu21-TS-0	10	5.19	1.3	20.9	10.32	94.2
	20	5.56	1.3	19.3	10.41	95.0
Pu21-SS-0	10	4.97	1.4	22.3	10.42	95.1
	20	5.55	1.4	19.7	10.50	95.8
Pu21-SS-2	10	5.03	1.3	21.5	10.24	93.4
	20	5.56	1.3	19.1	10.37	94.6
Pu21-SS-6	10	4.99	1.8	21.9	10.39	94.8
	20	5.52	1.8	19.6	10.42	95.1
Pu21-SS-X	10	4.72	1.8	22.8	10.14	92.5
	20	5.30	1.8	19.3	9.92	90.5
Pu21-RS-0	10	5.06	1.9	21.8	10.48	95.6
	20	5.76	1.9	18.5	10.43	95.2
Pu22-TS-0	10	5.02	1.8	22.1	10.41	95.0
	20	5.72	1.8	18.3	10.43	95.2
Pu22-SS-1	10	5.17	1.7	20.7	10.25	93.5
	20	5.77	1.8	18.3	10.35	94.4
Pu22-SS-2	10	5.24	1.7	21.2	10.37	94.6
	20	5.85	1.8	17.9	10.39	94.8
Pu22-SS-3	10	5.27	1.5	21.0	10.45	95.3
	20	5.85	1.5	18.2	10.50	95.8
Pu22-SS-4	10	5.15	1.6	21.5	10.44	95.2
	20	5.73	1.7	18.8	10.53	96.1
Pu22-RS-0	10	5.03	1.6	21.8	10.44	95.2
Pu23-TS-0	10	5.17	1.7	21.6	10.48	95.6
	20	5.78	1.7	18.6	10.53	96.1
Pu23-SS-1	10	5.16	1.6	20.8	10.31	94.1
	20	5.72	1.6	18.4	10.34	94.3
Pu23-SS-2	10	5.30	1.4	20.8	10.44	95.2
	20	5.86	1.4	18.2	10.52	96.0
Pu23-SS-3	10	5.21	1.5	20.6	10.42	95.1
	20	5.83	1.5	17.7	10.30	94.0
Pu23-SS-5	10	4.77	2.4	22.1	9.86	90.0
	20	5.52	2.4	18.3	9.98	91.1
Pu23-SS-6	10	4.33	4.4	24.0	-	-
	20	4.88	4.4	21.1	-	-
Pu23-RS-0	10	5.11	1.8	21.5	10.40	94.9
	20	5.75	1.8	18.4	10.48	95.6

Table 3.4

Sintering Characteristics
of Coprecipitated UO_2-20 w/o PuO_2
(Sintered at 1600°C for 1 Hour in N_2-6% H_2)

Composition	Compaction Pressure TSI	Green Density gm/cc	Weight Loss on Firing %	Linear Shrinkage %	Fired Density gm/cc	Percent Theoretical Density
Pu25TS80-740	10	5.02	1.6	22.7	10.66	96.4
	20	5.73	1.6	19.2	10.61	95.9
Pu25SS80-640	10	4.64	2.5	24.4	10.33	93.4
	20	5.36	2.5	20.6	10.38	93.8
Pu25SS80-740	10	5.04	1.7	22.2	10.52	95.1
	20	5.77	1.7	18.4	10.52	95.1
Pu25SS80-840	10	5.43	1.2	20.8	10.73	97.0
	20	6.01	1.2	18.1	10.76	97.3
Pu25RS80-740	10	5.10	2.1	22.1	10.69	96.6
	20	5.74	2.1	19.2	10.58	95.7
Pu13	8.2	4.91	1.8	23.1	10.70	96.7
Pu17 (17.8%)	11.7	5.25	1.5	21.2	10.62	96.0

Since poor sintering characteristics had been previously observed for coprecipitated UO_2-35 w/o PuO_2 (297Pu19)[1], three additional batches of this composition were prepared using the modified equipment. It was found that this recently produced material (297Pu35, 297Pu36, 297Pu37) exhibited far better sintering characteristics than 297Pu19. Densities in the range of 95 to 98% of theoretical were readily obtained. The sintering data are presented in Table 3.5. In general, the green densities are lower than for 297Pu19 and the weight losses on firing, higher. These sintering results indicate that the equipment modifications allow production of more sinterable product, and further that the product characteristics are reproducible.

A batch of UO_2-80 w/o PuO_2 (297Pu28) was also prepared by coprecipitation to ultimately provide a coprecipitated blend for mixing with UO_2. Powder characteristics for this material[ii] indicated a relatively high bulk density (3.43 gm/cc) and tap density (6.07 gm/cc); hence, relatively poor sintering characteristics were anticipated. A relatively high pressure (27 tsi) was necessary to compact the pellets, and the density increase due to compaction was quite small; 7.56 gm/cc compacted as compared to 6.07 gm/cc tap density. The sintering data presented in Table 3.6 confirm poor sinterability. It is interesting to note that the highest densities were obtained by sintering in an oxidizing atmosphere. Apparently, with the small amount of UO_2 present, the material behaves more like PuO_2 than UO_2. Subsequently, ball milling was utilized to condition this powder, however, some impurity was obviously introduced during the milling operation, since a rather porous clinker resulted on sintering. On the basis of preliminary analysis, it is suspected that the harmful impurity is silica, which comes from the grinding media. This is being investigated in detail.

Oxidation Kinetics of UO_2-PuO_2
(R. Gerrish)

Oxidation kinetic studies by means of thermogravimetric analysis are continuing on mixed oxide sintered pellets in ordered to aid in the interpretation of sintering data and to help assess the extent of solid

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(i) NUMEC P-102, Progress Report, "Development of Plutonium-Bearing Fuel Materials", pages 29-30; NUMEC P-103, Progress Report, "Development of Plutonium Bearing Fuel Materials", pages 22-27; and NUMEC P-104, Progress Report, "Development of Plutonium-Bearing Fuel Materials", pages 32-35.

(ii) NUMEC P-104, Progress Report, "Development of Plutonium-Bearing Fuel Materials", page 12.

Table 3.5

Sintering Characteristics
of Coprecipitated UO_2-35 w/o PuO_2
(Sintered at 1600°C for 1 Hour in N_2-6% H_2)

Composition	Compaction Pressure TSI	Green Density gm/cc	Weight Loss on Firing %	Linear Shrinkage %	Fired Density gm/cc	Percent Theoretical Density
Pu35SS80-640	20	5.57	2.1	18.3	9.83	88.2
	40	6.36	2.1	13.6	10.12	90.8
Pu35SS80-840	11.7	5.63	1.2	19.5	10.73	96.3
	20	6.05	1.0	18.0	10.95	98.3
	40	6.80	1.0	14.5	10.90	97.8
Pu36SS80-840	11.7	5.62	1.2	19.7	10.72	96.2
Pu37SS80-840	10	5.54	1.1	19.9	10.65	95.6
	20	6.06	1.1	17.4	10.69	96.0
Pu19SS80-840	11.7	6.58	0.6	13.1	10.06	90.3

Table 3.6

Sintering Characteristics
of Coprecipitated UO_2-80 w/o PuO_2

Material (Pu28)	Green Density gm/cc	Firing Atmosphere	Firing Time hours	Weight Loss on Firing %	Linear Shrinkage %	Fired Density gm/cc	Percent Theoretical Density
As Prepared	7.56	N_2-6% H_2	1	2.0	8.4	9.43	83.0
	7.56	N_2-6% H_2	16	1.7	8.7	9.60	84.5
	7.56	Air	1	1.0	8.7	9.67	85.1
Ball Milled	6.75	N_2-6% H_2	16	2.7	-	6.69	58.9
	6.75	Air	1	0.6	11.5	9.78	86.1

solution formation. Preliminary runs have been made with various UO_2-PuO_2 compositions at different temperature intervals in order to determine the basic rate of oxidation as a function of temperature and composition. The materials utilized and the temperature intervals are tabulated in Table 3.7.

A typical oxidation curve as a function of time is shown in Figure 3.1 for UO_2-5 w/o PuO_2 powder (Pu14B) which was oxidized at 402°C. These results show the two-step oxidation typical of pure UO_2. For contrast, a typical oxidation curve for the UO_2-12.5 w/o PuO_2 sintered pellets is shown in Figure 3.2.

Using the characteristics of the powder from which the pellets were sintered, a pseudo particle size was used to calculate diffusion coefficients of oxygen in the pellets relative to one another. The diffusion equations resulting from least squares fitting to Arrhenius plots for the UO_2-5 w/o PuO_2, UO_2-12.5 w/o PuO_2, and the UO_2-20 w/o PuO_2 sintered pellets are presented in Table 3.8.

These observed diffusion coefficients are orders of magnitude lower than observed for pure urania. This is due primarily to the use of sintered pellets; however, the dilution of the cations with plutonium, which is in its highest state of oxidation, is also a contributing factor. Using the exact surface area of the sintered pellets will change D_o by an order of magnitude, however, the activation energy (slope of the diffusion curve) will remain basically unchanged. These diffusion equations will be rederived using pellet surface areas measured by the B.E.T. method so that absolute diffusion coefficients, rather than relative values, can be obtained. The relative results, however, do indicate that there is no simple relationship between the oxidation rate and the percentage of contained plutonia.

Physical Property Measurements

(E. K. Halteman, R. Gerrish, J. Roth)

The high temperature thermal expansion apparatus has been checked out, and the glove box is being closed up prior to commitment of the apparatus to plutonium.

Prior to commitment to plutonium, trial operation of the high temperature x-ray diffractometer is also continuing using ThO_2 and UO_2. Based on the measured variation of the lattice constant with temperature over the range 0 to 750°C, the thermal coefficient of expansion of ThO_2 has been estimated to be 10.5×10^{-6} cm/cm-°C. This is in close agreement with the literature value of $10.0 \times 10^{-6} \pm 0.5 \times 10^{-6}$ cm/cm-°C. Similar measurements have also been made with UO_2 over the temperature range 0 to 1000°C. These date are currently being analyzed. The apparatus appears to be performing satisfactorily and will be committed to plutonium during the next reporting period.

Table 3.7

Tabulation of Thermogravimetric Oxidation Runs

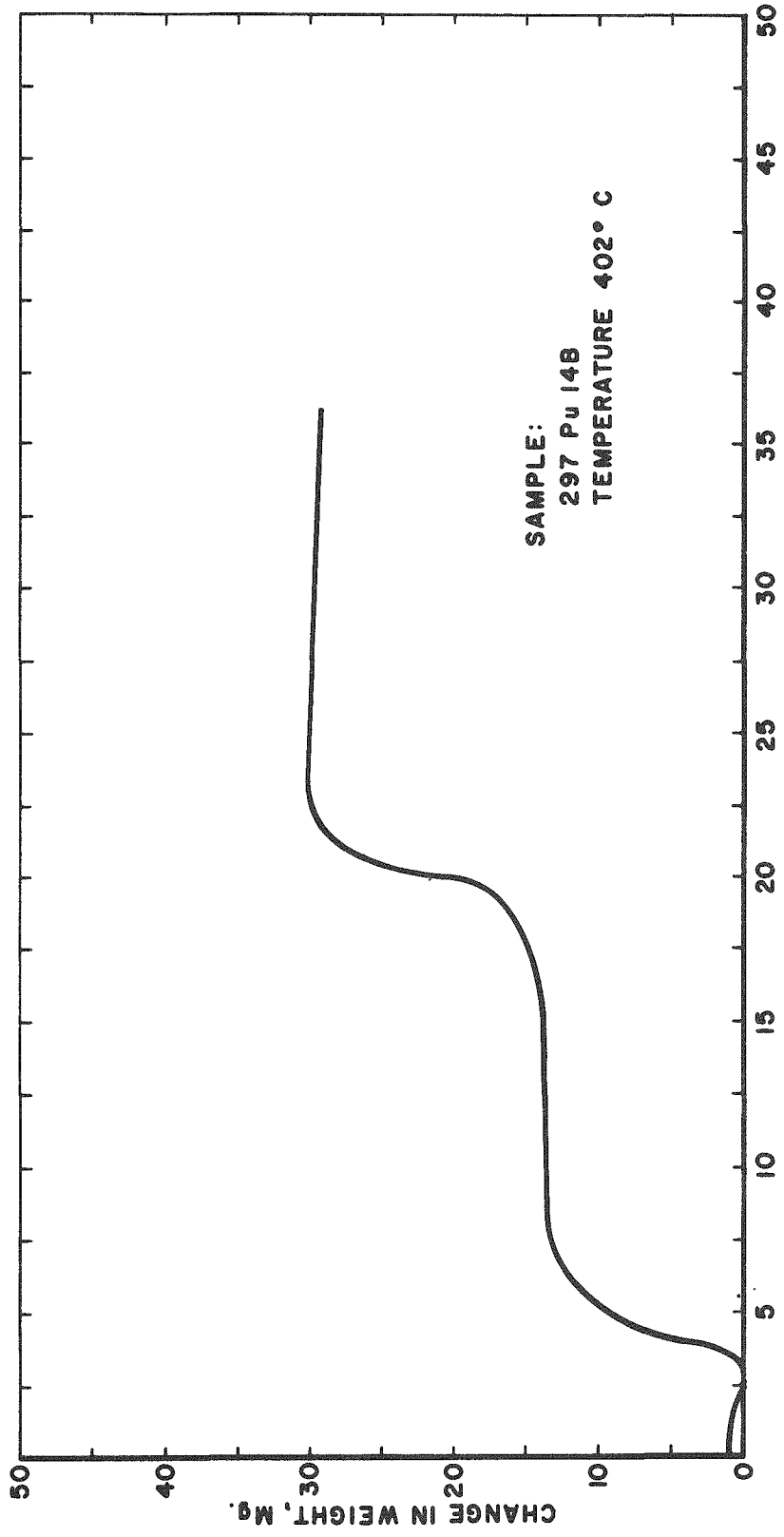
Material	w/o PuO_2	Oxidation Run Temperatures °C
297Pu14A	5.0	215, 320, 405, 500, 502
297Pu14B*	5.0	241, 355, 402
297Pu20SS80-840 NM	12.5	440, 461, 480, 500
297Pu20SS80-840 HM	12.5	430, 450, 470
CP20 (297Pu13)	20.0	400, 420, 480
297Pu19	35.0	480, 500

* Powder instead of sintered pellets

Table 3.8

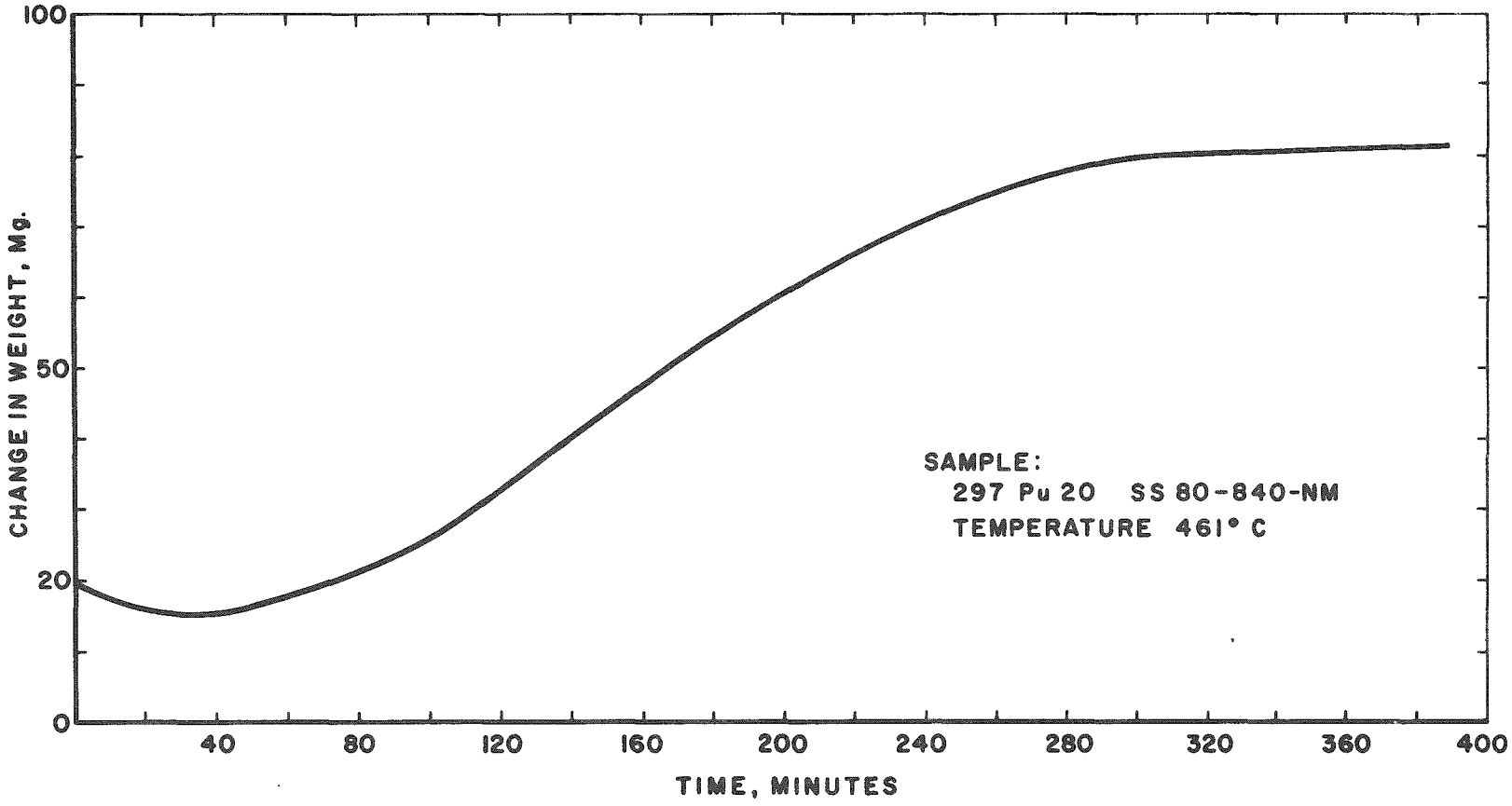
Relative Oxygen Diffusion Equations for UO_2-PuO_2 Pellets

Material	w/o PuO_2	Diffusion Equation
297Pu14A	5.0	$D = (1.95 \times 10^{-3}) \text{ Exp } (-45{,}150/RT) \text{ cm}^2/\text{sec}$
297Pu20	12.5	$D = (.64 \times 10^{-9}) \text{ Exp } (-21{,}900/RT) \text{ cm}^2/\text{sec}$
297Pu13	20.0	$D = (.89 \times 10^{-4}) \text{ Exp } (-38{,}300/RT) \text{ cm}^2/\text{sec}$



OXIDATION CURVE

FIG. 3.1



OXIDATION CURVE

FIG. 3.2

FUEL ELEMENT FABRICATION AND EVALUATION

Task 4.00

I. D. Thomas

Compatibility Study
(M. Zambernard)

Metallographic and x-ray diffraction examination of UO_2-PuO_2 pellets sintered in vacuum for 1 hour at 1000°C in contact with iron, nickel, chromium and 304 and 316 stainless steels indicate no ceramic-metal interaction at the interface for UO_2-PuO_2 compositions of 0.5, 5, 12.5, 17.8 and 35 w/o PuO_2.

Corrosion Tests
(M. Zambernard)

The 100, 500, and 1000 hour corrosion tests in 680°F water for seven coprecipitated UO_2-PuO_2 compositions in the range 0.5 to 100 w/o PuO_2 have been completed. Weight gain data and visual inspection indicate corrosion behavior comparable to UO_2. The drying time has been increased to 48 hours since weight decreases were still significant after 8 and 16 hour drying periods.

The pellets used in the water test are currently being subjected to 750°F-2200 psi steam.

RADIATION TESTING AND EVALUATION

Task 5.00

L. J. Jones

Short-Term Irradiation Tests
(L. J. Jones, R. M. Horgos)

The fourteen short-term irradiation capsules are now at the reactor site awaiting insertion into the reactor. Insertion had been previously scheduled for the April-May cycle, however, leak testing at the reactor site indicated that 5 of the 28 outer cap welds had developed leaks during transit. All elements were, therefore, returned for repair. This was satisfactorily accomplished, and all elements have now passed leak testing at the reactor site, as well as at NUMEC.

Upon return of the capsules, they were again leak tested with verifying results. Subsequent sectioning and microscopic examination of the faulty weld areas showed cracks emanating into the fused zone from the jointure, and in some cases these cracks had progressed through the gas voids and shrink cavities to the surface. The Aluminum Company of America was thereupon consulted, and they indicated that such cracks could propogate in the Type 6061-S aluminum fusion weld due to small temperature changes or rough handling. They further indicated that this condition could be overcome by employing a filler rod welding technique. Mock-up joints were therefore machined and welded using the recommended procedures. The joints were satisfactorily leak-tested and micro-examination showed that the weld zones were entirely free of cracks even following thermal cycling and quenching from 100°C. All capsules were therefore dedesigned accordingly and welded. Leak testing was performed both prior to and after thermal cycling to insure against the previous in-transit failure. The elements were shipped and subsequent leak testing at the reactor indicated that all capsules were satisfactory.

High Burnup Irradiation Tests
(R. M. Horgos)

The preliminary design of the instrumented capsules for the high burnup irradiation program has been completed, and the fuel materials have been designated. The irradiation program will utilize five capsules, each containing five two-inch long fuel specimens. Two of the capsules will contain thermal reactor fuels, and three will contain fast reactor fuels; irradiation will be to 20,000 and 100,000 MWD/Tonne, resp. The heat flux from each capsule will be continuously monitored during irradiation by the utilization of four pairs of thermocouples.

The chief objectives of the program will be (1) to observe relative performance between coprecipitated UO_2-PuO_2 and composite powders prepared by mechanically mixing component powders, (2) to determine the effect on performance of relatively gross inhomogeneities that may result from poor powder blending, and (3) to observe differences in performance that may arise due to differences in powder stoichiometry or Pu_2O_3 content.

REACTOR PHYSICS AND ENGINEERING PARAMETRIC STUDIES

Task 8.00
J. D. Clement

Assessment of Plutonium in Near-Thermal Reactors
(W. J. Ross, J. Ruzbacki)

Recent experimental data on UO_2 water latticeshave been analyzed to allow updating of the NUSURP code. The later data appears to be in closer agreement with MUFT, REPETITIOUS, and SOFOCATE calculated results, and as such is also in better agreement with NUSURP calculated results. While deviations are still noted for tight or highly-loaded lattices, there is insufficient experimental data in this range to warrant adjustment of NUSURP parameters.