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Progress Report
DEVELOPMENT
OF
PLUTONIUM-BEARING FUEL MATERIALS
January 1 through March 31, 1963
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PROJECT AND FACILITY ADMINISTRATION

Task 1.00
K. H. Puechl

Summary of Development Activities

Three batches of PuO_2 were prepared via the plutonium peroxide route to allow assessment of this process relative to the standard oxalate procedure. Except for the high tap density, it was found that the powder characteristics of PuO_2 prepared in this manner are similar to the characteristics of PuO_2 prepared by the oxalate route.

Because of the increased demand for mixed oxides for irradiation specimens and other studies, certain equipment modifications were made to achieve better reproducibility and to minimize operator time. Trial preparation runs were performed using the modified equipment. In one of these runs, ammonia gas was evaluated as the precipitant relative to the previously used ammonium hydroxide solution.

A study has been initiated to assess the feasibility of utilizing gamma spectrometry for rapid in-process determination of plutonium in solutions that also contain uranium. For the initial investigations, the gamma radiation around the 60 Kev plutonium and americium peaks was analyzed. The results indicated that plutonium can be determined to within 1% provided that the uranium concentration is known to better than 2 mg/ml.

In preparation for burnup analysis of irradiated specimens, plutonium separation studies using TTA extraction have been continued, and the determination of cesium and strontium fission products by flame photometry has been investigated. For the extraction studies the effect of trichloroacetic acid is being investigated. For the determination of cesium and strontium by flame photometry, it was found that the relatively high background, especially in the case of strontium, could be significantly reduced by the use of perchloric acid. From these studies, it is concluded that interferences can be minimized or eliminated and that strontium and cesium can be determined with a relative standard deviation of 5-6%.

Since previously performed sintering studies with PuO_2 have yielded some as yet unexplained data, further studies were performed. Specifically, the effect of carbon content on the weight loss during sintering was determined. From these data, it is concluded that residual carbon is not the cause of the extraneous results but that the erratic sintering behavior is probably due to residual moisture in the N_2 -6% H_2 sintering atmosphere.

Mixed oxide sintering studies were also continued. Metallographic examination of UO_2 -35 w/o PuO_2 pellets indicates that the low densities obtained

may be due to grain growth and broadening of grain boundaries during sintering.

As an alternate to the production of spherical particles for dispersion-type fuel elements, powder agglomeration studies have been initiated. Green spheres were formed in a small mill jar, and the particle size distributions of both the formable and non-formable powder fractions were determined by centrifugal sedimentation size analysis. The results indicate that the finer particles in the powder are selectively "snowballed" into the spherical shape and the coarser particles are left behind in the residue.

To aid in the interpretation of sintering data as well as to assess the effects of oxidizing environments, a study has been initiated to determine the oxidation kinetics of UO_2 - PuO_2 by means of thermogravimetric analysis. To check out glove box procedures, preliminary runs were performed by oxidizing UO_2 powder to U_3O_7 ; satisfactory results were obtained.

Preparation of duplex pellets for determining the reaction between UO_2 - PuO_2 and possible cladding and diluent metals is continuing, as is the associated metallographic and x-ray diffraction examination.

Pellets of pure PuO_2 and six compositions of coprecipitated PuO_2 - UO_2 have been fabricated for corrosion testing in water and steam under a variety of water chemistry conditions. Preliminary tests performed in 750°F-2200 psi steam for 10 hours showed no visual evidence of corrosion.

All 80 fuel elements for the short-term irradiation program have now been fabricated and representative pellets of the various compositions and density ranges are undergoing detailed chemical, metallographic, and x-ray diffraction examination. The 14 fuel capsules have been loaded and shipped to the reactor site.

The NUSURP code has been modified to allow calculation of undermoderated systems. Experimental data on uranium lattice measurements as well as analytically derived data from MUFT, REPETITIOUS, and SOFOCATE codes are now being analyzed to check the validity of the NUSURP code modification prior to analysis of plutonium behavior in such systems.

General Plant and Project Aspects

In preparation for the return of the short-term irradiation specimens, effort is continuing on equipment installation within the alpha boxes. Such installation in the main hot cell alpha boxes and in the metallography cell alpha box is nearing completion. The Junior Cave itself is being modified prior to the installation of the alpha box which will house radiochemistry equipment for burnup analysis.

The installation of the HRC high temperature camera on a diffractometer within an alpha box has been completed, and this equipment is now ready for commitment to plutonium.

PREPARATION AND CHARACTERIZATION OF FUEL MATERIALS

Task 2.00

C. S. Caldwell

O. Menis

Preparation and Characterization of Plutonium Oxide
(G. Ehrlich, J. Goodman, J. Limpert, J. Roth)

Continued effort has been placed on screening runs to allow assessment of various PuO_2 preparation routes relative to the standard oxalate procedure. During this period, the plutonium peroxide route was investigated by the preparation of three batches with each being prepared under slightly different process conditions.

Plutonium Peroxide Preparation Route

Three batches of plutonium peroxide were precipitated by the addition of hydrogen peroxide strike solution to stirred, acidified plutonium nitrate solution. Following oven drying, the peroxide was converted to PuO_2 by air calcination at 490°C . The process conditions utilized (listed in Table 2.1) were modifications of those used by Leary, et al⁽ⁱ⁾ and Orth, et al⁽ⁱⁱ⁾.

The plutonium peroxides, in general, are not compounds of well-defined stoichiometry; the ratio of oxygen to plutonium are non-integral with greater or lesser amounts of anions incorporated into the crystal lattice. The cubic or hexagonal form can be obtained depending upon process conditions, with the hexagonal form being preferred because of its granular nature and good filtration/washing properties. For stabilization or enhancement of the hexagonal form relative to the cubic, Leary recommended the incorporation of sulfate in the feed. In addition, both Leary and Orth stressed the need for "proper" agitation to minimize the regions of low acidity that tend to develop locally at the strike solution entry point since the cubic form is precipitated under low acid conditions.

For Run 297Pu29 the procedure recommended by Leary was followed except that sulfate was not used since the sulfate ion is not readily removed. In short, the run was made in this manner to allow assessment of possible filtration difficulties in combination with a short calcination cycle relative to good filtration and longer higher temperature calcination. The wet precipitate was collected in 5 micron porous stainless steel filter cannisters previously

(1) J. A. Leary, et al, LA-1913.

(ii) D. A. Orth, et al, Industrial and Engineering Chemistry, Vol. 53, 9, p. 685, September 1961.

Table 2.1

PuO₂ Preparation Conditions
(Batch Plutonium Peroxide Route)

<u>Run Number</u>	<u>297Pu29</u>	<u>297Pu30</u>	<u>297Pu31</u>
<u>Plutonium Feed Solution</u>			
Batch Size, gm Pu	119.0	64.5	74.0
Plutonium Concentration, gm/l	20.7	65.0	85.8
H ⁺ Concentration, <u>M</u>	3.0	4.5	3.6
Sulfamic Acid Concentration, <u>M</u>	-	0.3	0.3
<u>Precipitant</u>			
H ₂ O ₂ Reagent Strength, v/o	30.0	50.0	30.0
H ⁺ Concentration, <u>M</u>	-	-	3.0
Volume H ₂ O ₂ Used for Plutonium Valence Adjustment, l	0.07	-	-
Volume H ₂ O ₂ Added Slowly, l	0.342	0.240	0.260
Total Volume H ₂ O ₂ Added, l	0.707	0.500	0.482
Addition Rate During Slow Addition, ml/min	18	7.1	4.3
Agitator Speed (2.5 in. dia flat turbine impeller), rpm	760	700	700
<u>Precipitation Temperature, °C</u>	20	15	20
<u>Digestion Conditions</u>			
Temperature, °C	15	6	12
Time, hr	0.5	2.5	1.0
<u>Filtration Time, min</u>	7	4	9
<u>Drying Conditions</u>			
Temperature, °C	55	55	55
Time, hr	48	48	48
<u>Calcination Conditions</u>			
Temperature, °C	490	490	490
Time, hr	0.5	0.5	0.5

described.⁽ⁱ⁾ X-ray diffraction of the precipitate indicated the presence of both the cubical and hexagonal forms. Powder patterns of oven-dried material (dried at 55°C for 48 hours) were essentially amorphous with the presence of a faint broad PuO_2 pattern. Filtration was very rapid, and the filtrate was a deep red color but was free of sediment. While standing for several days, the red color changed to a weak straw color, and some sediment formed. The excess hydrogen peroxide was subsequently "killed" by the addition of NaOH solution, and the "killed" filtrate was clarified by further filtration. Alpha counting indicated that the plutonium concentration in the waste liquid was about 4 mg/liter. From the point of view of filtration alone, it was therefore concluded that the addition of sulfate into the feed is not necessary.

For Runs 297Pu30 and 297Pu31 sulfamic acid was added to the plutonium solution as suggested by Orth. The major difference between these two runs was the addition of 3M HNO_3 to the hydrogen peroxide strike solution in the case of Run 297Pu31. For both these runs, the filtration characteristics were similar to that of Run 297Pu29.

In all instances the dried filter cakes consisted of hard rigid lumps which could, however, be readily crushed to granular powder. The dried cakes were calcined in lump form in flowing air at 490°C for 30 minutes. The converted materials had the same hard aggregate structure as the precursors; final comminution was by hammermilling using 10 mil herringbone screens.

The powder characteristics for all runs are tabulated in Table 2.2. It is seen that the characteristics of the product PuO_2 are similar for all materials produced; however, the surface area of the precursor for Run 297Pu29 is extremely low in comparison to the other two runs. Except for the high tap density, the characteristics of the PuO_2 are similar to those of PuO_2 prepared by the standard oxalate route.

For Run 297Pu29, the particle size distribution of PuO_2 is shown in Figure 2.1 along with previous results obtained with oxalate and hydroxide derived material. It is seen that the distribution is nearly identical to that of hydroxide derived PuO_2 and that these distributions lie midway between those obtained on PuO_2 from batch and continuous oxalate routes.

The hammermilled products were analyzed for trace impurities; the results are presented in Table 2.3. The high levels of iron, manganese, chromium, and nickel are probably due to stainless steel corrosion during processing; however, the high carbon levels cannot be explained at this time.

(i) NUMEC P-60, Progress Report, "Development of Plutonium-Bearing Fuel Materials", page 10.

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(i) NUMEC P-60, Progress Report, "Development of Plutonium-Bearing Fuel Materials", page 10.

Table 2.3

Trace Impurities in Hammermilled PuO₂
Produced via the Peroxide Route
(parts per million)

<u>Sample Number</u>	<u>Fe</u>	<u>B</u>	<u>Cd</u>	<u>Mn</u>	<u>W</u>	<u>Mg</u>	<u>Sn</u>	<u>Cu</u>	<u>Pb</u>	<u>Cn</u>	<u>Si</u>	<u>Ni</u>	<u>Mo</u>	<u>V</u>	<u>C</u>
297Pu29	800	1	2	50	0	70	10	10	15	60	5	60	5	0	800
297Pu30	400	1	1	50	0	10	5	10	10	300	1	50	10	0	320
297Pu31	500	1	1	80	0	40	5	10	10	300	1	80	10	0	310

FIGURE 2.1
COMPARISON OF PLUTONIUM DIOXIDE PARTICLE SIZE DISTRIBUTIONS
PREPARED BY BATCH AND CONTINUOUS OXALATE PRECIPITATION
(MSA LIQUID SEDIMENTATION METHOD)

Investigation of this preparation route will be extended to continuous precipitation only if sintering studies on the batch materials indicate significant improvement over oxalate derived product.

Preparation and Characterization of Mixed Plutonium-Uranium Oxides
(G. Ehrlich, J. Goodman)

With the increased demand for mixed oxides for sintering studies, compatibility studies and irradiation specimens considerable effort during this period has been placed on the modification of equipment to achieve better reproducibility and to minimize operator time. In addition to these equipment modifications, three continuous coprecipitation runs were carried out.

Initially, U/Pu nitrate feed and aqueous ammonium hydroxide solutions were metered into the precipitator from constant head reservoirs using valves and rotameters; to maintain constant flow rates with this system required constant operator attention. This situation had been improved, to some extent, by the installation and use of pulsating diaphragm constant displacement (IAPP) metering pumps. Experience has shown that these pumps can be operated for U/Pu nitrate feed service over extended periods of time without drift of feed rate and thereby without operator attention. However, similar experience has indicated difficulty when these pumps were used for metering concentrated ammonium hydroxide solutions; specifically, the dissolved ammonia gas volatilizes and causes vapor locking in the pump cavity, and this produced erratic or, at times, complete stoppage of flow. This situation has been somewhat improved by the installation of spring-loaded pressure check valves into the pump discharge line. However, because of this difficulty, the system was further modified to allow the use of anhydrous ammonia gas. Ammonia gas can now be metered into the bottom of the precipitator directly from a liquified ammonia cylinder through a regulator valve and rotameter equipped with a flow controller.

A new precipitator has also been designed and installed. This unit contains a series of 4 vertical baffles to reduce the vortex of the stirred slurry and thereby to increase turbulence and promote better mixing. In addition, a conductivity probe was also installed to allow automatic control of the slurry level through activation of a solenoid valve installed at the withdrawal port. This unit is shown in Figure 2.2.

The three preparation runs were carried out to obtain UO_2 -80 w/o PuO_2 material for compatibility studies, to determine the effect of using concentrated aqueous ammonia as precipitant for UO_2 -12.5 w/o PuO_2 and to check out the equipment on UO_2 -5 w/o PuO_2 using gaseous ammonia as precipitant. For the latter two runs, the precipitates produced during start-up and shut-down were segregated from the steady-state material as was done previously. The preparation conditions for the three runs are presented in Table 2.4. Powder property data are tabulated in Table 2.5.

Table 2.4

Summary of Preparation Data
for Coprecipitated UO₂-PuO₂ Materials

Run Identification	297Pu28	297Pu33			
Composition	UO ₂ -80 w/o PuO ₂	UO ₂ -12.5 w/o PuO ₂			
Precipitation Conditions					
Method	Continuous	Continuous	Continuous	Continuous	Continuous
Temperature, °C	55	55	55	55	55
Feed Composition					
gm Pu/liter	77.8	12.5	12.5	12.5	12.5
gm U/liter	20.0	87.5	87.5	87.5	87.5
H ⁺ , molarity	1.0	1.0	1.0	1.0	1.0
Feed Flow Rate, liters/hr	1.2	1.2	1.2	1.2	1.2
Precipitant Composition					
NH ₄ OH, molarity	14.5	14.5	14.5	14.5	14.5
Precipitant Flow Rate					
liters/hr	0.43	0.23	0.23	0.23	0.23
Precipitation Average Holdup,					
minutes	28.4	32.0	32.0	32.0	32.0
Total Number Throughputs	2.9	3.0	5.5	1.0	1.0
Run Period	Total	Start Up	Steady State	Shut Down	
Oxide Sample Identification	297Pu28	TS80-740	SS80-640	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, SCFH	4.5	4.5	4.5	4.5	4.5
Rate of Temperature Climb,					
°C/min	12	12	12	12	12
Conversion Temperature, °C	840	740	640	840	740
Time at Conversion Temperature,					
min	80	80	80	80	80
Furnace Charge, gm	175.9	171.9	218.0	224.6	156.9

(Continued)

Table 2.4 (Continued)

Summary of Preparation Data
for Coprecipitated UO₂-PuO₂ Materials

Run Identification	297Pu34			
Composition	UO ₂ -5 w/o PuO ₂			
Precipitation Conditions Method Temperature, °C	Continuous 55			
Feed Composition gm Pu/liter gm U/liter H ⁺ , molarity	5.0 95.0 1.0			
Feed Flow Rate, liters/hr	1.1			
Precipitant	Anhydrous Gaseous Ammonia			
Precipitant Flow Rate, SCFH	0.034			
Precipitation Average Holdup, min	60			
Total Number Throughputs	3	5.4	5.4	1
Run Period	Start Up	Steady State		Shut Down
Oxide Sample Identification	TS80-740	SS80-640	SS80-840	RS80-740
Drying Temperature, °C	180	180	180	180
Conversion Gas Atmosphere	N ₂ -6% H ₂	N ₂ -6% H ₂	N ₂ -6% H ₂	N ₂ -6% H ₂
Conversion Gas Flow Rate, SCFH	4.5	4.5	4.5	4.5
Rate of Temperature Climb, °C/min	12	12	12	12
Conversion Temperature, °C	740	640	840	740
Time at Conversion Temperature, min	80	80	80	80
Furnace Charge, gm	207.4	490.0	490.1	90.0

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Table 2.5

Summary of Powder Characteristics
for Coprecipitated UO₂-PuO₂ Materials*

Sample Number	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	w/o Greater Than 74 microns (200 mesh)
297Pu28	-	5.2	3.43	6.07	3.9	5.8	< 2
Pu33TS80-740	-	9.6	-	-	-	-	-
Pu33SS80-640	2.27	12.5	0.71	1.55	0.82	4.2	45
Pu33SS80-840	2.15	9.0	0.70	1.84	0.37	1.2	< 2
Pu33RS80-740	-	-	-	-	-	-	-

* Powder properties measured for hammermilled powders.

Figure 2.2
Four-Liter Continuous Precipitator

The UO_2 -80 w/o PuO_2 (Run 297Pu28) precipitate was dried overnight at 180°C and converted to oxide powder by calcining for 30 minutes at 840°C in an N_2 -6% H_2 atmosphere. Final powder comminution was performed by hammer-milling using 10 mil herringbone screens. The extraordinarily high tap density (6.8 gm/cc) and large Fisher subsieve particle size (3.9 microns) suggested poor sinterability, and this was verified. Sintered pellet densities were low, generally approximately 84% of theoretical.

Run 297Pu33 (UO_2 -12.5 w/o PuO_2) was made prior to the previously described equipment modifications and was intended to be a repetition of Run 297Pu20 in order to clarify seemingly abnormal behavior. However, early in the run, the pump in the ammonium hydroxide feed system became vapor locked and thereby the flow rate was drastically reduced. Unreacted U/Pu nitrate was carried into the filtrate as indicated by the presence of post-precipitated material in the waste receiver tanks. The continuous run was promptly terminated, and excess ammonium hydroxide was added to the remaining precipitator slurry. In order to assess the effects of such a major process upset, the precipitate was carried through the standard drying, calcination and reduction cycles, and the powder properties were compared to those obtained under the standard conditions in Run 297Pu20. This comparison is shown in Table 2.6. With the exception of the large agglomerate size of 297Pu33 powder calcined at 640°C and the high surface area ($9.0 \text{ M}^2/\text{gm}$) of the powder calcined at 840°C , comparable powder specimens from the two runs have similar characteristics. It is therefore concluded that the final powder characteristics are not very sensitive to this type of process upset; as indicated by previous investigations, the powder characteristics are determined primarily by the dry conversion conditions.

In Run 297Pu34, UO_2 -5 w/o PuO_2 was prepared by using gaseous ammonia as precipitant in order to check out the equipment and to demonstrate process control. The precursor was air-dried at 180°C for 16 hours and was converted in N_2 -6% H_2 at temperatures of 640, 740, and 840°C . These materials are presently being characterized.

Analytical Chemistry

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

A study has been initiated to assess the feasibility of utilizing gamma spectrometry for rapid in-process determination of plutonium in solutions that also contain uranium. Further, in preparation for burnup analysis of irradiated specimens, plutonium separation studies using TTA extraction have been continued, and determination of cesium and strontium fission products by flame photometry has been investigated.

Determination of Plutonium in Plutonium-Uranium Solutions by Gamma Spectrometry

Analyzing for plutonium by gamma spectrometry is complicated by the variability of plutonium isotopic composition and variability in higher isotope (primarily

Table 2.6

Comparison of Powder Characteristics
of Specimens of UO₂-12.5 w/o PuO₂*

Sample Number	Oxygen/Metal Ratio in Uranium Fraction	B.E.T. Surface Area M ² /gm	Bulk Density gm/cc	Tap Density gm/cc	Fisher Sub-Sieve Particle Size microns	MSA 50% Particle Size microns	Greater Than 74 microns (200 mesh)
297Pu20SS80-640	2.28	11.7	0.68	1.91	0.30	2.5	3
297Pu33SS80-640	2.27	12.5	0.71	1.55	0.82	4.2	45
297Pu20SS80-840	2.17	6.8	0.74	2.08	0.40	1.0	< 2
297Pu33SS80-840	2.15	9.0	0.70	1.84	0.37	1.4	< 2

* Powder properties measured for hammermilled powders.

americium) content. This difficulty, however, can be overcome by preparing standard samples from stock solution and first analyzing these for plutonium content by amperometric titration.

Further difficulties are encountered in the presence of uranium or other heavy or radioactive elements due to gamma background and/or self-shielding within the medium. The presence of such elements must therefore be known or must be ascertained prior to interpretation of gamma spectrometry results.

For the initial investigations, the gamma radiation around the 60 kev plutonium and americium peaks was analyzed. The results are presented in Table 2.7 for solutions containing 4 mg/ml of uranium. It is seen that there is a slight increase in self-shielding over the range of plutonium concentration investigated (5.4 to 54.0 μ g/ml). For in-process control, this small self-shielding effect can be neglected.

To determine the self-shielding effect of larger concentrations of uranium (as might be present in PuO_2/UO_2 fuel mixtures), measurements were repeated with a uranium concentration of 50 mg/ml. These data indicate a 23% reduction in activity, or that a 2 mg/ml change in uranium concentration results in a 1% change in the counting rate. In practice then, for 1% accuracy in the determination of plutonium, the uranium concentration must be known to better than 2 mg/ml.

Development of Analytical Procedures for the Determination of Fuel Burnup

For evaluation of both the short-term and high-burnup test specimens, the integrated fission energy must be determined. Normally, two methods are used; namely, mass spectrometric determination of fissionable nuclides and radiochemical determination of isolated fission products.⁽¹⁾ For the short-term tests, the amount of fissile material depletion is small; therefore, essentially complete reliance must be placed on fission product analysis. Further, for $\text{UO}_2\text{-PuO}_2$ fuels, the interpretation of all data is

(i) B. F. Rider, et al, "The Determination of Uranium Burnup in MWD/Ton", GEAP-3373.

C. E. Crouthamel, R. Heimmich, and C. Gatrousis, "The Quantitative Determination of Fission and Nuclear Reactor Products", Talanta 1, 346-407 (1958).

D. N. Sunderman, "The Radiochemical Determination of Uranium Burnup", Paper Presented at ASTM Meeting at San Francisco, October 11-16, 1959.

Table 2.7

Determination of Plutonium by Gamma Spectrometry

Energy Analyzed: 60 kev

Uranium Concentration: 4 mg/ml

Plutonium μ g/ml	Counts per Minute	Counts per Minute/ μ g Pu ⁽ⁱ⁾
5.4	10,984	203.4
13.5	27,072	200.5
27.0	54,333	201.3
54.0	106,408	197.0
Average		200.5
Relative Standard Deviation, %		1.5

(i) Corrected for uranium background.

difficult since more than one fissile nuclide is present, since fissile nuclides are being formed as well as destroyed, and since fission product yields from the various nuclides are not well-known.

For the short-term tests, we plan to rely primarily on the radiochemical determination of Cs-137. Although this fission product forms a volatile compound and therefore tends to diffuse away from the point of formation, this is not serious in the short-term tests since high temperatures will not be maintained for extended periods of time. However, because of this volatility, Sr-90 will also be determined in the high burnup samples since this fission product forms a refractory oxide. Unfortunately, the half-life of Sr-90 is not accurately known⁽ⁱ⁾ and the yield from Pu-239 fissioning has not yet been established.

In general terms, the procedure will be to sample the fuel specimen, dissolve it in nitric acid, and separate out the plutonium in hot cell alpha boxes. Aliquots from the plutonium-free specimens can then be analyzed for Cs-137 and Sr-90 by flame photometry in a chemical hood.

Separation of Plutonium: Plutonium separation studies have been continued⁽ⁱⁱ⁾ using thenoyltrifluoroacetone (TTA). In particular, the effect of trichloroacetic acid on the extraction rate is being investigated. The results presented in Table 2.3 show that equilibrium is reached very rapidly with vigorous shaking but that a reversal occurs after prolonged shaking. This reversal may be due to a side reaction, such as reduction of Pu-IV to Pu-III. These observations are similar to the experiences of other investigators who worked with different systems. In particular, Heisig and Hicks⁽ⁱⁱⁱ⁾ working with the secondary butyl benzene-TTA-nitric acid system, noted the strong effect of phase mixing on the extraction rate; and Cunninghame and Miles^(iv) working with carbon tetrachloride as the solvent, noted reversal after prolonged shaking.

(i) J. E. Rein and B. F. Rider, TID-17385, 1963, p. 18.

(ii) NUMEC P-102, Progress Report, "Development of Plutonium-Bearing Fuel Materials", page 24

(iii) D. L. Heisig and T. F. Hicks, UCRL-1169, 1952.

(iv) J. G. Cunninghame and G. L. Miles, J. Inorg. Chem., 3, 154 (1956).

Table 2.8

Rate of Extraction of Pu-TTA Chelate
from Trichloroacetic Acid Medium

Organic, o: Xylene

Aqueous, a: 1M Trichloroacetic Acid

a/o = 1

Time, min	Percent Extracted	
	Equilibration ⁽ⁱ⁾ Rocking Motion	Equilibration ⁽ⁱⁱ⁾ Hand Shaking
1	-	99.995
2	94.8	-
3	95.6	99.995
5	98.1	98.1
7	98.1	-
10	97.7	-
60	97.1	-

(i) Rocking Motion - Slow rocking motion (2 inversions/min)
on an electrically driven rocker.

(ii) Hand Shaking - Vigorous shaking to produce unstable
evolution.

Determination of Cs and Sr by Flame Photometry: Following the procedures used in the other laboratories to analyze for impurities in plutonium⁽ⁱ⁾, flame photometry has been investigated as a means for determining cesium and strontium content. For this purpose, the experimental apparatus was installed in a chemical hood as shown in Figure 2.3. Equipment used was a Beckman DU spectrophotometer with a flame attachment, spectral energy recording attachment and power supply and a Sargent Model MR recorder having a one-second response. Rotameters were used to control the flow of oxygen and hydrogen. To collect traces of plutonium aspirated into the flame, a three-section chimney was constructed above the burner; absolute filters were contained in the center section, and the chimney was connected to a high speed blower to provide positive air movement through the filters.

In general, samples for analysis were prepared from 10 gram lots of $\text{UO}_2\text{-PuO}_2$. The mixed oxide was first dissolved in dilute (1-1) nitric acid by one hour exposure over a steam bath. The liquid was then filtered, and the plutonium was extracted with TTA. From the aqueous phase, 10 ml aliquots were then transferred to beakers containing 3-5 ml perchloric acid, and the solutions were fumed to near dryness. Upon cooling, the residues crystallized, and these crystals were dissolved in 0.2 N HNO_3 and diluted to 25 ml samples. In those cases when the standard addition technique was used, additions were made prior to dilution.

These solutions were atomized into the flame, and the emissions at 460.7 $\text{m}\mu$ and 852 $\text{m}\mu$ were measured. The optimum instrumental conditions are shown in Table 2.9. While a slit width as large as 0.15 mm can be tolerated for cesium analysis at 852 $\text{m}\mu$, the slit width for strontium analysis at 460.7 $\text{m}\mu$ must be reduced to 0.03 mm due to spectral interferences.

Table 2.9

Instrumental Conditions for Determination
of Strontium and Cesium by Flame Photometry

	<u>Strontium</u>	<u>Cesium</u>
Beckman DU Wavelength	460.7 $\text{m}\mu$	852 $\text{m}\mu$
Slit Width	0.03 mm	0.15 mm
Sensitivity	70%	-
Phototube Resistor	22 megohms	10,000 megohms
Phototube, volts per dynode	60	-
Oxygen-to-Hydrogen Ratio*	0.210	0.210

* Kontes rotameters were used to control gas flow rate.

(i) R. F. Buchanan, J. P. Faris, K. A. Orlandini, and J. P. Hughes, TID-7650, pp. 179-188, June 1958.

Figure 2.3

Recording Flame Spectrophotometer Installation

Calibration data were obtained for both strontium and cesium in the presence of 40 mg/ml of uranium. These data are presented in Tables 2.10 and 2.11. Over the strontium and cesium concentration ranges covered, 0 to 30 μ g/ml, there is a slight upward curvature caused by auto-repression of ionization. Assuming linearity over the range, the standard deviation obtained was 0.10 for strontium and 0.07 for cesium.

Table 2.10

Strontium Calibration Data
(Flame Photometry Determination)

Strontium Concentration (μ g/ml)	Response (mv)	Factor (μ g/ml/mv)
5	2.78	1.798
10	6.08	1.644
15	9.22	1.627
20	12.70	1.575
25	16.23	1.540
30	19.75	1.518

Mean = 1.617

Standard Deviation = 0.10

Table 2.11

Cesium Calibration Data
(Flame Photometry Determination)

Cesium Concentration (μ g/ml)	Response (mv)	Factor (μ g/ml/mv)
5	3.45	1.449
10	7.48	1.337
15	11.50	1.304
20	15.45	1.294
25	19.90	1.256
30	23.93	1.254

Mean = 1.315

Standard Deviation = 0.07

Variations of $\pm 20\%$ in uranium concentration produced a negligible effect on response for both cases.

The effects of various acid media were also investigated. The results for both strontium and cesium are presented in Figures 2.4 and 2.5. In the case of strontium, it is seen that the background is relatively high in both HCl and HNO₃ but that this background is significantly reduced and that the emission line intensity is somewhat increased when HClO₄ is present in the sample medium. In the case of cesium, perchloric acid does not have this pronounced effect. While several investigators have reported an enhancement of about 10% in the strontium line intensity in the presence of HClO₄, the increased sensitivity observed here in the presence of uranium is due primarily to reduction in the uranium interference, i.e., reduction in the nonquantized radiation emitted by uranyl ions in oxide fog or smoke. Similar suppressing of nonquantized radiation by HClO₄ has previously been observed in the presence of thorium.

In order to determine the optimum concentration of HClO₄ required, both cesium and strontium were analyzed over a range of HClO₄ concentrations. The results are presented in Figure 2.6. It is seen that the cesium response is independent of HClO₄ concentration, while the strontium response improves up to an HClO₄ concentration of 0.4 N. This was therefore taken to be the optimum concentration for analysis of these two components.

Interferences from various cations and anions were also investigated under optimum perchloric acid conditions. The cation results are presented in Table 2.12; the anion results in Figure 2.7. It is seen that yttrium, zirconium, and molybdenum interfere with strontium emission. While zirconium presents no problem in our application since it will not be carried over in the dissolution steps, the yttrium and molybdenum interferences, if any, will be taken into account by the standard addition technique. The lanthanum interference with cesium is not expected to be troublesome since a relatively high concentration (5 gm/25 ml) is required. Chloride and acetate anions produce little interference with strontium, however, sulfate decreases the response by about 50%. Assessment of cation interference was also carried out without using perchloric acid. These data showed that most of the rare earth elements interfered with the strontium response at concentrations above 1 gm/ml.

From these investigations, it is concluded that interferences can be minimized or eliminated and thereby that Sr and Cs can be determined with a relative standard deviation of 5 and 6%, resp., as indicated by the calibration data.

Table 2.12

Assessment of Cation Interferences
(Sr and Cs Determination by Flame Photometry)

Cation	Concentration (mg/25 ml)	Percent Deviation	
		Sr (460.7 m μ)	Cs (852 m μ)
Yttrium	100	0	0
	1,000	+9.5	0
	5,000	+15.2	0
Zirconium	100	0	0
	1,000	-14.2	0
	5,000	-14.5	0
Rhodium	100	0	0
	1,000	0	0
	5,000	0	0
Palladium	100	0	0
	1,000	0	0
	5,000	0	0
Ruthenium	100	0	0
	1,000	0	0
	5,000	0	0
Lanthanum	100	0	0
	1,000	0	0
	5,000	0	-1.6
Barium	100	0	0
	1,000	0	0
	5,000	0	0
Cadmium	100	0	0
	1,000	0	0
	5,000	0	0
Cerium	100	0	0
	1,000	0	0
	5,000	0	0

(Continued)

Table 2.12 (Continued)

Assessment of Cation Interferences
(Sr and Cs Determination by Flame Photometry)

Cation	Concentration (mg/25 ml)	Percent Deviation	
		Sr (460.7 m μ)	Cs (852 m μ)
Praseodymium	100	0	0
	1,000	0	0
	5,000	0	0
Neodymium	100	0	0
	1,000	0	0
	5,000	0	0
Samarium	100	0	0
	1,000	0	0
	5,000	0	0
Europium	100	0	0
	500	0	0
	1,000	0	0
Gadolinium	100	0	0
	500	0	0
	1,000	0	0
Molybdenum	100	-15.0	0
	1,000	-29.2	0
	5,000	-21.7	0
Indium	100	0	0
	1,000	0	0
	5,000	0	0

THE EFFECT OF ACID MEDIA ON STRONTIUM EMISSION IN THE PRESENCE OF URANIUM

Figure 2.4

THE EFFECT OF ACID MEDIA ON CESIUM EMISSION IN THE PRESENCE OF URANIUM

Figure 5

Figure 2.6

Figure 1.7

FABRICATION AND EVALUATION OF FUEL SHAPES

Task 3.00

E. K. Halteman, L. J. Jones, I. D. Thomas

PuO₂ Sintering Studies
(M. D. Houston)

Previously performed sintering studies⁽ⁱ⁾ with PuO₂ prepared by both the oxalate and hydroxide precipitation routes have yielded some, as yet unexplained, data. While attainment of high density has not been a problem, weight loss during sintering has been more erratic, and microstructure variability has been more pronounced than was anticipated based on the uniformity of the measured physical characteristics of the starting powders. In particular, for some preparations, it was observed that the weight loss during air sintering was greater than observed during sintering in an N₂-6% H₂ reducing atmosphere. This is contrary to the anticipated result since PuO₂ tends to reduce to Pu₂O₃. It appears that these erratic results may be due to sintering atmosphere impurities, i.e., oxygen or moisture in the reducing atmosphere, or to residual carbon content in the PuO₂. During this reporting period, the effects of carbon addition have been investigated.

For these studies oxalate derived PuO₂ was utilized; the calcination temperature was 1100°C. Samples containing 1, 2, and 5 w/o carbon were prepared by mixing the powders in a mortar as a damp slush containing alcohol.

Powder samples, including those containing no carbon additions, were exposed to the N₂-6% H₂ sintering atmosphere for various periods of time, and following observation of weight changes, they were then ignited in flowing oxygen at 1100°C and reweighed.

For reference, it is pointed out that complete reduction of PuO₂ to Pu₂O₃ constitutes a loss of oxygen amounting to 2.95% of the initial weight of PuO₂. Weight losses for carbon-free materials up to this maximum are therefore anticipated, and reversible weight gains on oxidation are also to be expected. The measured results on PuO₂ without carbon addition are presented in Table 3.1. It is seen that these data are erratic. While most samples lost weight during reduction and gained weight during oxidation, only a few samples gave indication that these processes are reversible. It is quite obvious that further experimentation is warranted with stricter control of all parameters, especially atmosphere purity control.

(i) NUMEC P-90, P-100, P-101, P-102, P-103, Progress Reports, "Development of Plutonium-Bearing Fuel Materials"

Table 3.1

Reduction-Oxidation Data for PuO_2

Reduced at 1600°C in N_2 -6% H_2
 Oxidized at 1100°C in O_2

Sample Number	Reduction Time hours	Weight Loss on Reduction %	Weight Gain on Oxidation %
1	1	-0.05	0.10
2	1	-0.20	-0.13
3	16	-0.11	0.92
4	1	0.72	0.85
5	1	0.80	0.83
6	1	1.60	0.76
7	1	0.72	0.41
8	16	1.40	0.31
9	16	4.20	-1.30
10	16	3.50	0.24
11	16	2.20	0.11
12	40	-0.10	0.63
13	40	-0.18	0.51
14	40	0.02	0.17
15	70	-0.40	0.39
16	70	-0.30	0.30
17	70	0.10	0.21
18	70	-0.25	0.28
19	17	0.05	-
20	17	0.11	-
21	17	0.25	-
22	17	0.25	-

For the samples containing carbon additions, the results are presented in Table 3.2. It is pointed out that if PuO_2 were to contain 2.2 w/o carbon it can be entirely reduced to Pu_2O_3 with the concomitant release of CO; the total weight loss on reduction under these conditions would be 5.05% of the initial sample weight. The data show an initial high weight loss and subsequent weight increase with time, with the net weight loss appearing to approach the amount of the carbon addition. These results strongly suggest that the N_2 -6% H_2 atmosphere contains sufficient moisture to cause reoxidation of Pu_2O_3 to PuO_2 during the extended reduction cycles.

Mixed Oxide Sintering Studies (N. D. Houston)

Sintering trials on coprecipitated UO_2 - PuO_2 have been continued. During this reporting period, pellets were fabricated from two batches of UO_2 -12.5 w/o PuO_2 and a batch of UO_2 -35 w/o PuO_2 .

The two batches of UO_2 -12.5 w/o PuO_2 utilized were processed by the "standard" coprecipitation procedure except that batch 297Pu20 was precipitated with 14.5 M ammonia while for batch 297Pu24, 3.5 M ammonia was used. As reported previously,⁽ⁱ⁾ the powder characteristics were not appreciably influenced by this change in ammonia concentration.

The results of the sintering trials are presented in Table 3.3. It is seen that for both batches of material (except for lot Pu24-SSO-740 which was essentially unconverted, O/H ratio of 2.66) the sintered densities ranged between 93.5 and 97.2% of theoretical.

UO_2 -35 w/o PuO_2 pellets were also sintered for 1, 16, and 24 hours in an N_2 -6% H_2 atmosphere in order to further investigate the reasons for the previously obtained low densities. Metallographic examination of these compacts, as shown in Figure 3.1, shows grain growth and broadening of grain boundaries with sintering time. Presumably this latter phenomenon is due to formation of a second phase which is anticipated in high plutonia content compacts in the presence of a reducing atmosphere. X-ray diffraction will be utilized to identify this phase, if a sufficient amount is present.

Production of Spherical Particles by Plasma Torch (E. M. Benson)

Further trial runs have been made to produce high density UO_2 -20 w/o PuO_2 spheres using the F-40 Thermal Dynamics plasma torch. Over the complete

(i) NUMEC P-103, Progress Report, "Development of Plutonium-Bearing Fuel Materials", page 18.

Table 3.2

Reduction Data for $\text{PuO}_2 + \text{C}$
Reduced at 1600°C in N_2 -6% H_2

Composition	Reduction Time hours	Weight Loss %
PuO_2 -2 w/o C	1	3.4
	4	2.8
	16	2.6
PuO_2 -5 w/o C	1	8.2
	4	7.3
	16	5.9
	18	5.3

Table 3.3

Sintering Data
for Coprecipitated $\text{UO}_2\text{-12.5\% PuO}_2$
(Sintered at 1600°C in $\text{N}_2\text{-6\% H}_2$)

Composition	Compaction Pressure TSI	Green Density g/cc	Linear Shrinkage %	Weight Loss on Firing %	Fired Density g/cc	Percent Theoretical Density
Pu20-TS80-740*	10	5.04	21.0	1.4	10.45	94.5
	20	5.65	19.0	1.4	10.54	95.5
Pu20-SS80-640	10	4.68	23.0	2.1	10.37	93.7
	20	5.40	20.0	2.0	10.43	94.5
Pu20-SS80-740	10	5.01	22.0	1.4	10.51	95.1
	20	5.67	19.0	1.4	10.57	95.6
Pu20-SS160-740	10	5.10	22.0	1.3	10.44	94.5
	20	5.74	19.0	1.3	10.55	95.5
Pu20-SS80-840	10	5.28	22.0	1.2	10.57	95.6
	20	5.90	18.0	1.3	10.59	95.7
Pu20-RS80-740*	10	4.97	23.0	2.0	10.46	94.6
	20	5.70	19.0	2.0	10.44	94.5
Pu24-TS80-740	10	5.08	22.0	1.7	10.71	96.9
	20	5.80	18.0	1.7	10.55	95.5
Pu24-SS80-640	10	4.71	23.0	2.4	10.34	93.6
	20	5.50	19.0	2.4	10.37	93.7
Pu24-SS0-740	10	4.14	-	3.8	Fracture	-
	20	4.87	-	4.2	Fracture	-
Pu24-SS80-740	10	4.99	22.0	1.6	10.56	95.6
	20	5.71	18.0	1.6	10.49	94.9
Pu24-SS120-740	10	5.10	22.0	1.8	10.58	95.7
	20	5.74	19.0	1.8	10.72	97.0
Pu24-SS160-740	10	5.12	22.0	1.6	10.56	95.6
	20	5.82	18.0	1.7	10.51	95.1
Pu24-SS80-840	10	5.47	20.0	1.2	10.55	96.4
	20	6.06	18.0	1.3	10.75	97.2
Pu24-RS80-740	10	5.04	21.9	2.1	10.53	95.4
	20	5.76	18.2	2.1	10.45	94.5

* Non-milled

Sintering Time - 1 hour

Neg. 450

400X

Sintering Time - 16 hours

Neg. 459

400X

Sintering Time - 24 hours

Neg. 452

400X

Figure 3.1

Photomicrographs of UO_2 -35% PuO_2

Compaction Pressure - 11.7 TSI

Sintered in N_2 -6% H_2 at 1600°C

range of torch conditions and gas compositions and flow rates, no better material has been produced than that described previously.⁽¹⁾ Torch modifications are now being designed to improve the particle residence time within the flame.

Production of Spherical Particles by Agglomeration (C. S. Caldwell)

For dispersion-type fuel elements, spherical particles having high crushing strength are required in order to minimize particle breakage and deformation during subsequent fabrication processes. Since it may not be possible to produce such high strength particles by plasma torch fusion, an investigation has been initiated to form spherical particles of PuO_2 by agglomeration.

For these initial studies, PuO_2 agglomerates were formed in a small mill jar, and the particle size distribution of both formable and non-formable powder fractions were determined by centrifugal sedimentation size analysis; B.E.T. surface areas were also determined. 297Pu9-Lot 4 material produced by "standard" oxalate precipitation was used as feed.

The results indicate that the finer particles in the powder are selectively "snowballed" into spherical shape, thereby leaving behind a residue of course particles. The surface areas of the particles in the formed particulates, however, were not significantly different from the surface areas of the particles in the residues. The particle size distributions for particles in the green spheres are compared to the size distributions of particles in the residues in Figures 3.2-3.4. For two of the samples, B₁ and P₃, further rolling of the residues after sphere removal resulted in no further yield of spheres; for Sample B-3-15, such additional treatment yielded agglomeration of 8% of the residual powder into +120 mesh particles, however, these particles had extremely poor green strength. These results indicate that sphere forming efficiency is dependent upon the particle size distribution of the feed powders. Strict control of feed particle size is therefore required; this can be attained to some degree by the control of powder preparation variables, however, various milling procedures must also be evaluated.

Oxidation Kinetics of $\text{UO}_2\text{-PuO}_2$ (R. Gerrish)

To aid in the interpretation of sintering data as well as to assess the effects of oxidizing environments, a program has been initiated to determine the oxidation kinetics of $\text{UO}_2\text{-PuO}_2$ by means of thermogravimetric analysis.

(i) NUMEC P-103, Progress Report, "Development of Plutonium-Bearing Fuel Materials", page 29.

FIGURE 3.2

COMPARISON OF PARTICLE SIZE DISTRIBUTION
OF SPHERICAL POWDER WITH RESIDUE POWDER
(MSA METHOD)

FIGURE 3.3
COMPARISON OF PARTICLE SIZE DISTRIBUTION
OF SPHERICAL POWDER WITH RESIDUE POWDER
(MSA METHOD)

FIGURE 3.4

**COMPARISON OF PARTICLE SIZE DISTRIBUTION
OF SPHERICAL POWDER WITH RESIDUE POWDER
(MSA METHOD)**

As a preliminary, the glove box procedures involved in the use of the thermogravimetric balance were evaluated by oxidizing characterized UO_2 powder to U_3O_7 . These kinetic data were then used to determine the diffusion coefficient of oxygen in UO_2 using a program written for the RPC-4000 computer. The result of a least squares fit to an Arrhenius plot for values of the diffusion coefficient against $1/T$ indicated that in the temperature range of 200 to 300°C the diffusion of oxygen in urania can be represented by the equation

$$D = 1.1 \times 10^{-2} \exp(-27,100/RT) \text{ cm}^2/\text{sec}.$$

Over the measured temperature range, this result agrees well with that obtained by Aronson, et al⁽¹⁾, who represented their data by the equation

$$D = 5.5 \times 10^{-3} \exp(-26,300 \pm 1500/RT) \text{ cm}^2/\text{sec}.$$

Preliminary oxidation runs using UO_2 - PuO_2 sintered pellets indicate a considerable reduction in the oxidation rate. The observed diffusion coefficient is 3 to 4 orders of magnitude smaller than for pure urania, due mainly to the use of sintered pellets and to the dilution of the cations with plutonium which is in its highest state of oxidation. The pellets used in these initial oxidation kinetic studies were prepared from batch 297Pu14 material having a composition of UO_2 -5 w/o PuO_2 .

Physical Property Measurements
(E. K. Halteman, R. Gerrish, J. Roth)

In preparation for glove box close-up, all modifications to the thermal conductivity apparatus have been completed, and the equipment is again operating. Samples of Al_2O_3 and MgO have been fabricated, and their thermal conductivities will be determined as a final check on the equipment prior to commitment to plutonium.

The stepless programmed temperature controller for the high temperature dilatometer has been modified to give better impedance matching to the low resistance heating element. In addition, current limiters are being incorporated in the unit by the manufacturer. The tungsten/tungsten-26% rhenium thermocouple used to provide the input to the temperature controller has been calibrated by using the freezing points of pure metals as standard temperature points. Quartz supports and pusher rods have also been procured in order to increase the sensitivity of the dilatometer in the low temperature range below 1000°C .

(i) S. Aronson, R. Roof, Jr., and J. Belle, J. Chem. Phys., 27, 137 (1957).

The installation of an MRC high temperature x-ray camera on a diffractometer has been completed. The glove box with all the necessary electrical lead-throughs has been installed and made leak-tight. The diffractometer has been aligned, and preliminary runs have been made using reduced UO_2 . The lattice parameters were calculated using standard procedures, i.e., Nelson and Riley extrapolation to $\theta = 0$, using a program written for the RPC-4000 computer. This equipment is now ready for commitment to plutonium.

FUEL ELEMENT FABRICATION AND EVALUATION

Task 4.00

L. J. Jones

I. D. Thomas

Compatibility Study

(M. Zambernard)

Preparation of duplex pellets for determining reaction between UO_2 - PuO_2 of various compositions and possible cladding and diluent metals is continuing. Metallography and x-ray diffraction examination of samples containing PuO_2/UO_2 ratios of 0.5, 5, 12.5, 17.8, and 35 w/o PuO_2 and the metals, 304 and 316 stainless, iron, nickel and chromium have been initiated. These data will be presented in the next progress report.

Corrosion Tests

(M. Zambernard)

Pellets of pure PuO_2 and six compositions of coprecipitated UO_2 - PuO_2 have been fabricated to allow initiation of corrosion tests in 650°F water and 750°F steam. All pellets were sintered in an N_2 -6% H_2 atmosphere for one hour at 1600°F . The ranges of densities attained are shown in Table 4.1. The UO_2 -80 w/o PuO_2 pellet densities were low, hence, these were refired for 16 hours at 1600°C ; however, the increase in density was only approximately 1.5%. Indication of poor sinterability of this material was given by the extraordinarily high (6.8 gm/cm^3) tap density of the starting powder.

All pellets, including the UO_2 -80 w/o PuO_2 composition, will be corrosion tested. For the low density pellets it will be difficult to determine the actual area in contact with the corrosive media; however, if there is little or no attack (as expected), the results will, nevertheless, provide positive information.

As a preliminary to the extended time corrosion test, i.e., 100, 500, and 1000 hours, several sintered pellets of UO_2 - PuO_2 in the composition range 0.5 to 10 w/o PuO_2 were exposed to 750°F -2200 psi steam for ten hours. Controls consisting of UO_2 pellets previously corrosion tested and found acceptable were also run simultaneously. All pellets showed no visual evidence of corrosion.

Short-Term Irradiation Test Fuel Fabrication

(M. D. Houston, M. Zambernard)

During this quarter, fuel element fabrication and testing for the short-term irradiation specimens was completed (see Task 5.00). In all, a total

Table 4.1

Density of Sintered Pellets for Corrosion Studies

<u>Composition</u>	<u>Density (gm/cm³)</u>	<u>Percent Theoretical</u>
PuO ₂	10.30-10.44	90.0-91.1
UO ₂ -80 w/o PuO ₂	9.44-9.60	83.1-84.5
UO ₂ -35 w/o PuO ₂	10.13-10.24	91.0-91.9
UO ₂ -17.8 w/o PuO ₂	10.60-10.81	96.0-97.8
UO ₂ -12.5 w/o PuO ₂	10.47-10.59	94.8-95.9
UO ₂ -5 w/o PuO ₂	10.30-10.45	93.7-95.2
UO ₂ -0.5 w/o PuO ₂	10.26-10.53	93.5-96.0

of eighty fuel elements have been prepared for both in-reactor and library samples. Representative pellets of the various compositions and density ranges, seventeen variables in all, are undergoing chemical, metallographic, and x-ray diffraction examination to provide complete pre-irradiation characterization.

RADIATION TESTING AND EVALUATION

Task 5.00
L. J. Jones

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

Fourteen aluminum capsules have been loaded with three stainless clad $\text{PuO}_2\text{-UO}_2$ fuel elements each together with the appropriate amount of NaK; further, all capsules have been welded, satisfactorily leak-tested, and shipped to the reactor site.

Hot Laboratory Equipment Fabrication
(R. M. Horgos)

The Junior Cave is being modified to permit relatively easy installation of the specially designed alpha box that will house the equipment required for chemical separations and burnup analysis. The irradiated bulk fuel will be sampled, dissolved, and aliquoted in the alpha boxes within the high level cell and transferred to the Junior Cave facility as relatively low level liquid samples. In particular, the front shield of the Junior Cave has been redesigned to open to the side, completely out of the way, to permit insertion and removal of the alpha box mounted on a stand which rolls on casters. The Junior Cave has been positioned in its proper location in the hot handling area, and installation of the door mechanism will be started as soon as the necessary structures and hardware are received. Central Research Laboratories Model 7 Master Slave manipulators are being installed for use in this facility.

Design of the alpha enclosure for the Junior Cave has been completed and includes such general features as a 14-inch diameter bag out port, cylindrical exhaust and inlet plenums for enclosure of high efficiency filters, a shielded storage cave, a scrap disposal tube, a centrifuge pod, and a sphincter valve. Fabrication of this box together with the support stand has been started. The shielded transfers to this box will be performed with special transfer casks designed for use with the sphincter valve.

All general modifications to the shielded steel metallographic cell required for incorporation of the alpha enclosure have been completed. The metallographic mounting press, automatic polishing wheels, electrolytic cell for etching, and miscellaneous shelving and hand tools have been installed in the alpha box. Facilities for later installation of a cathodic vacuum etcher have been incorporated. Entrance to this box will be by a sphincter valve, air lock, or bag-in. The latter can only be accomplished when the

alpha box is removed from the shielded cell and therefore is not applicable for transfer of irradiated material. A specially designed cask to transfer sphincter cans from the high level cells to the metallographic cell has been designed.

Shielding panels (4" thick lead) and a shielded access door for the Bausch and Lomb Metallograph have been designed and fabrication started. Support stands for the metallograph and for the lead shielding also are being fabricated.

All required modifications to the hot cell alpha boxes have been completed. The box ventilation system has been modified to minimize the pressure drop through the system since tests on the original system resulted in low air flow through the individual box exhaust fans and insufficient cooling of the in-line fan motors. Optical viewing ports for examination and photography of irradiated samples utilizing a thru-wall periscope were also added in the top of each box.

Design of the gamma scan equipment has been completed and fabrication started. Installation of this equipment will complete Alpha Box #1, which contains, in addition, the capsule opening equipment, a tubing cutter for specimen sectioning, and a diamond cut-off wheel.

Construction of the fission gas system is continuing. The out-of-cell collection system is being constructed and will be protected from alpha contamination by a micrometallic filter at the alpha box connection. Initially, the only in-box equipment required to perform the post-irradiation annealing studies are a furnace and a vacuum-tight furnace tube. However, provisions in the box for later installation of a puncturing device to puncture the cladding of high burnup oxide fuel elements under a closed vacuum system are being made. This puncturing device has been designed but has not as yet been fabricated.

A major concern in the utilization of the alpha boxes had been the plastic boots for the manipulators. The first models that were obtained were poorly constructed at the point where the manipulator jaw attached to the main arm of the manipulator. This resulted in gross tearing at this point, increasing the possibility of releasing contamination to the room. Other models of booting, utilizing new fabrication techniques, have been obtained, and these are now being tested.

REACTOR PHYSICS AND ENGINEERING PARAMETRIC STUDIES

Task 8.00
J. D. Clement

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

Modification of the NUSURP code to allow calculation of undermoderated systems has been completed. The modification involved the extension of Amster's compilation of cross sections averaged over the Wigner-Wilkins spectrum (SOFOCATE code), WAPD-185, to include larger values of plutonium-to-hydrogen ratios and higher temperatures and the programming of these values into the NUSURP code.

Experimental data on uranium lattice measurements as well as analytical data derived from MUFT, REPETITIOUS and SOFOCATE codes are now being analyzed to check the validity of the NUSURP code in the undermoderated region, prior to analysis of plutonium behavior in such systems.

Fast Reactor Survey
(J. D. Clement, J. Ruzbacki)

To allow rapid assessment of fuel behavior in fast reactors, a program has been initiated to develop a simplified model for describing the nuclear behavior of fast reactors. For performing general parametric studies, as contrasted with detailed design work, it is desirable to use a simplified model that will exhibit the salient nuclear behavior without requiring long and expensive computational time. In other words, a neutronics model is needed for fast reactors comparable to the NUSURP description developed for thermal reactors. As presently conceived, the simplified fast reactor model will have the following subroutines:

- 1) Calculate infinite medium spectrum. The input will consist of atom densities for a homogenized region. A library of energy dependent cross sections will be required.
- 2) Obtain spectrum averaged "fast group" cross sections from results of the first subroutine.
- 3) Solve multi-region, few group diffusion equation for reactivity and flux shapes. Each region will be represented by diffusion theory constants obtained from results of the second subroutine.

Presently, programming of the first subroutine for the RPC-4000 computer is nearing completion.