NUMEC P-37

NUCLEAR MATERIALS AND EQUIPMENT CORPORATION
APOLLO, PENNSYLVANIA

February 5, 1962



Mr. Morris Goldberg, Director
Contracts Division
New York Operations Office
U. S. Atomic Energy Commission
376 Hudson Street
New York 14, New York

Attention: Mr. Seymour Zirin, Contracts Administrator

Subject: CONTRACT AT(30-1)-2389
"DEVELOPMENT OF PLUTONIUM-BEARING FUEL MATERIALS"
MONTHLY PROGRESS LETTER FOR MONTH OF JANUARY 1962

Gentlemen:

NUMEC herewith transmits the Monthly Progress Letter for January 1962 covering work performed under Contract AT(30-1)-2389.

## PROJECT AND FACILITY ADMINISTRATION

Since one of the objects of the initial in-pile tests is to determine the relative behavior of co-precipitated $UO_2$-$PuO_2$ and that prepared by mechanical blending of the individual oxide powders, during this period particular emphasis has been placed on powder blending trials, pellet sintering studies, and subsequent evaluation of pellets made with the blended material. Homogeneity studies on pellets indicate that the blending procedure currently utilized is unsatisfactory since particle build-up occurs during blending and these individual particles are not homogenized during subsequent sintering.

Powder preparation via the oxalate route and associated characterization has been continued in order to allow assessment of reproducibility prior to irradiation testing. Moisture pickup studies on $PuO_2$ powders have been continued using the thermobalance with different atmospheres. Results indicate that the moisture pickup rate and equilibrium content is essentially independent of gas atmosphere at 76% relative humidity.

## DISCLAIMER

The Sharples Micromerograph has been placed in operation to allow rapid determination of $PuO_2$ powder particle size distribution. Operation, including reproducibility of results and powder recovery, has been satisfactory.

Homogeneous precipitation studies on $UO_2$ have been continued to determine the feasibility of direct preparation of dense $UO_2$-$PuO_2$ feed material for swaging, plasma torch fusing, and mechanical packing. A glove box is being outfitted to allow extension of these studies to $PuO_2$ and $UO_2$-$PuO_2$ mixtures.

Various methods for the production of spherical $PuO_2$ particles are being tried in order to assess relative particle shapes, density, surface texture, and reproducibility. Plasma torch production of these particles has been successful using a number of different feed materials. These products are now being evaluated. Further coating effort has been deferred pending completion of these spheroidization studies.

Continuing effort is being placed on preparing the hot cell alpha boxes to allow post-irradiation examination as soon as possible. Form AEC-21, "Preliminary Request for Irradiation Services" covering the initial series of contemplated radiations has been submitted.

A fuel cycle economics program is being written for the RPC-4000 computer to allow ready assessment of the physics results obtained with the NUSURP program. The results will be used to provide guidelines for the materials development program.

## PREPARATION AND CHARACTERIZATION OF FUEL MATERIALS

To allow pellet fabrication and evaluation, four continuous co-precipitation runs yielding 1.6 kilograms of $UO_2$-5 w/o $PuO_2$ were completed. The preparation data are summarized in Table I.

In preparation for $UO_2$-$PuO_2$ homogeneous precipitation work, the following auxiliary studies have been made with $UO_2$:

a) Standard absorption spectra have been recorded for a number of pure uranium compounds in solution, including UNH, $UO_2SO_4$, UNH-6$MH_2SO_4$, and UNH-citrate.

b) The pH and absorption spectra changes occurring during a homogeneous ADU precipitation (Urea + UNH) run were recorded, and similar measurements were repeated when $NH_4OH$ was used as the precipitant in order to gain understanding of the terminal stage prior to precipitation.

c) Peroxide precipitation of uranium compounds has been initiated as a preliminary step to examining $U^{4+}$-$Pu^{4+}$ and $UO_2^{2+}$-$Pu^{4+}$ peroxide co-percipitation alternates to the ADU-$Pu(OH)_4$ process.

Table I

Summary of Preparation Data
Continuous Coprecipitation

| Product Identification | 871-A3A and A3B | 297-Pu-14A | 297-Pu-14B |
|---|---|---|---|
| Feed Composition | | | |
| gm U/liter | 100 | 95.06 | 95.06 |
| gm Pu/liter | 5.3 | 4.94 | 4.94 |
| $H^+$, molarity | 1.0 | 1.0 | 1.0 |
| Feed Flow Rate, liters/hr | 1.2 | 1.25 | 1.25 |
| Ammonia Concentration, molar | 14.3 | 14.3 | 14.3 |
| Ammonia Flow Rate, liters/hr | 0.26 | 0.25 | 0.25 |
| Holdup Time, minutes | 31 | 30 | 30 |
| Total Number Throughputs | 4.25 | 4.6 | 4.6 |
| Drying Temperature, °C | 200 | 100 | 100 |
| Reduction Temperature, °C | 740 | 740 | 740 |
| Reduction Time, minutes | 80 | 80 | 80 |
| Surface Area, $M^2/gm$ | - | 7.7 | 6.3 |

A glove box is now being outfitted to allow extension of these studies to $PuO_2$ and $UO_2$-$PuO_2$. Heat exchange and fume scrubbing equipment is being installed to allow a wide variety of small-scale chemical operations. Other associated equipment includes a 40 milliliter batch centrifuge and a 1000°C furnace suitable for calcination and reduction.

To supplement the long-term static moisture pickup studies carried out on $PuO_2$ powder, dynamic measurements, using different carrier gases, are being made using the Aminco Recording Thermobalance. These data provide information during the early stages of moisture pickup as equilibrium is approached. Investigations during this month were carried out at room temperature using material Sample 297-Pu-4-1 (surface area of 60 $M^2/gm$) exposed to 76% relative humidity atmospheres of air, nitrogen and carbon dioxide. The $PuO_2$ powder sample was dried to constant weight in the thermobalance at 115 to 120°C in a stream of dry nitrogen prior to and following each experiment. The rate of weight gain was found to be essentially independent of carrier gas composition; this suggests that carbon dioxide and oxygen play a relatively minor role in absorption effects on $PuO_2$. Under these conditions, 90% of the moisture pickup occurred during the first 6-7 hours of exposure. Similar measurements will be made at lower humidities and on samples with lower surface areas to provide information applicable to the full range of $PuO_2$ powders and ambient atmospheric conditions of interest. Also, to cover a broad range of powder surface areas, long-term static moisture pickup measurements are continuing on $PuO_2$ Samples 297-5-1 thru 5.

Installation of the Micromerograph glove box was completed during this month and several trial runs were made with $PuO_2$. Excellent reproducibility was obtained with duplicate samples and better than 95% recovery of dispersed solids was obtained despite the 2-3 micron average $PuO_2$ particle size. Initially, this measurement technique will be used to compare size distribution of the precursor oxalates and the final $PuO_2$ product. Further, because of the speed and simplicity of operation, it will ultimately be used for routine size control.

As a preliminary to the fabrication of irradiation specimens to allow comparison of performance between co-precipitated and mechanically-mixed materials, two lots of $UO_2$-$PuO_2$ were prepared by dry-mixing of the individual component powders in a pilot-scale twin-shell rotary blender. The component uranium dioxide and plutonium dioxide powders were hammer-milled and properties re-measured prior to being weighed and blended. These powders were closely matched as regards surface area (4.1-4.4 $M^2/gm$). (Previous work had shown that macro-uniformity was obtainable within ±3% when ½% $PuO_2$ having a surface area of 5.4 $M^2/gm$ was blended with $UO_2$ having a surface area of 3.2 $M^2/gm$.) In both blending lots, the minor component ($PuO_2$) was first mixed with an equal amount of the major component ($UO_2$),

then mechanically blended for two hours; subsequently, the remainder of the major component was added and the full charge was blended for an additional twelve hours. No intermediate attrition or deagglomeration was attempted even though some agglomeration was observed during blending. Process conditions and powder characteristics are summarized in Table II. The final product in both cases appeared to be composed of soft spherical particles. The effect of this type of agglomeration on final sintered pellet structure is discussed below. Other blending techniques, including the use of intermediate hammer-milling and wet ball-milling, are now being investigated as means for obtaining more uniform particle-to-particle mixing of the component powders.

## PREPARATION AND COATING OF SPHERICAL OXIDE PARTICLES

Alternate methods for agglomerating and shaping spherical particles are being investigated, and the end products are being evaluated. The resulting particles will be used directly for coating studies and also will be evaluated as possible feed for the plasma torch.

The plasma torch feed mechanism has now been modified to allow feeding material as large as 20 mesh. Successful torch runs using three different types of $PuO_2$ feed (crushed high-fired pellets, agglomerated and fired spheres, and high-fired granules) have yielded approximately 50% spherical particles. Microscopic examination of particle cross sections shows that a large central void is present in the majority of particles. Complete evaluation of the products from the three different feed materials is now under way.

## FABRICATION AND EVALUATION OF FUEL SHAPES

Sintering trials on coprecipitated and mechanically mixed $UO_2$-20 w/o $PuO_2$, $UO_2$-5 w/o $PuO_2$, and $UO_2$-0.5 w/o $PuO_2$ have been undertaken in preparation for the fabrication of irradiation test specimens. In general, the mechanically mixed powders press to a higher green density and sinter to a lower density than do the coprecipitated powders. A compacting pressure of 8-10 TSI appears optimum for all of these powders; compacting pressures of 12 TSI result in overpressing. Sintering at 1600°C for four hours is sufficient to achieve high densities with all coprecipitated material while significant density increase is realized for the mechanically mixed compositions by extending the sintering time (~93.5% T.D. after 4 hours and ~96% T.D. after 16 hours). These pellets are being evaluated for degree of homogeneity by (1) x-ray diffraction, (2) optical microscopy, and (3) autoradiography. The latter method is accomplished by transferring a polished metallographic section, after decontamination, out of the glove box into a special container having a double window of 0.00025" thick Mylar sheet. Exposure of the x-ray film by direct contact with the Mylar film for a suitable time (approximately 45 seconds) results in satisfactory radiographs.

Table II

Process Conditions and Characterization Data
Dry-Blending of $PuO_2$ and $UO_2$

| Sample Identification | 297-MB-R5 | 297-MB-R20 |
|---|---|---|
| $PuO_2$, w/o | 5 | 20 |
| $UO_2$, w/o | 95 | 80 |
| Powder Pretreatment | hammer-milling | hammer-milling |
| $PuO_2$ Surface Area, $M^2/gm$ | 4.4 | 4.4 |
| $UO_2$ Surface Area, $M^2/gm$ | 4.1 | 4.1 |
| Ambient Relative Humidity, % | 45-50 | 45-50 |
| Blender Type | P-K twin shell | P-K twin shell |
| Shell Size | 2 quart | 2 quart |
| Powder Charge, gm | 562 | 624 |
| First-Stage Blending Time, hr | 2 | 2 |
| Second Stage Blending Time, hr | 12 | 12 |
| Analytical Sampling | Composite +4 individual | Composite +4 individual |
| Physical Appearance after Blending | 75% soft 60-100 mesh spherical agglomerates remainder fines | 50% soft 10-100 mesh spherical agglomerates remainder fines |

All three analytical tools indicated a high degree of homogeneity of solid solution in the coprecipitated compositions; however, autoradiography showed the presence of a few small random regions of low or non-alpha emitting material in an otherwise almost fully homogeneous matrix in the coprecipitated $UO_2$-20 w/o $PuO_2$ composition. This is under further investigation to determine the extent and character of this material.

For the mechanically mixed compositions sintered 16 hours at 1600°C, x-ray diffraction showed complete solution of the $PuO_2$ and $UO_2$ but indicated that there was a range of composition of the solid solution in the pellet. Autoradiography showed a pronounced balling effect with multi-layered spheres of alternating $UO_2$-rich and $PuO_2$-rich layers. Optical microscopy confirmed these observations and showed regions of greater porosity between the spherical shaped agglomerates. It is believed that the balling effect occurs during the initial stages of blending of the very fine $UO_2$ and $PuO_2$ powders. It is to be noted that these spheres remain intact through both the pre-slugging at 6 TSI, the manual granulation, and the cold compaction at 8-10 TSI. As previously mentioned, work is under way to determine procedures for eliminating this balling effect.

Additional work has been performed on the decomposition of $PuO_2$ during sintering. $PuO_2$ green pellets having a carbon content of 0.27% were sintered at 1600°C in various atmospheres, namely, (1) 94% $N_2$-6% $H_2$, (2) 94% Ar-6% $H_2$, (3) Argon, and (4) vacua. In all cases, almost the entire amount of carbon was removed as a result of the firing. The results are being evaluated. It has been further shown by experiment that the surface area of the pellet available to the sintering atmosphere has an effect on the formation of $Pu_2O_3$; i.e., the densification rate on sintering is a factor in determining the amount of oxygen deficient $PuO_2$ that can be formed.

## IRRADIATION TESTING AND EVALUATION

Mock-up assembly of the irradiation capsules will be performed shortly. Remote disassembly will also be tried in order to check design details. Work is continuing on the assembly and outfitting of the alpha boxes required for post-irradiation, hot cell examination.

## REACTOR PHYSICS AND ENGINEERING PARAMETRIC STUDIES

A fuel cycle economics program is being written for the RPC-4000 computer, and this is being integrated with the NUSURP physics program. Physics results have indicated that long core life is an inherent feature of high Pu-240 content plutonium; the results being relatively insensitive to

cross section assumptions. Economic evaluation is, therefore, necessary to offer guidance to the materials development program; i.e., for closer specification of fuel composition and enrichments of interest in near-thermal plutonium fueled reactors.

Very truly yours,

Karl H. Puechl

Karl H. Puechl
Acting Director
Advanced Materials Center

KHP/lkp

## EXTERNAL DISTRIBUTION

U. S. Atomic Energy Commission, New York Operations Office
- M. Goldberg, Contracts Division
- S. Zirin, Contracts Division
- M. Balicki, Research and Development Division
- V. Siuta, Research and Development Division
- L. Topper, Research and Development Division
- H. S. Potter, Patent Group

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

U. S. Atomic Energy Commission, National Laboratories
- F. C. Moesel, Office of Technical Information - Washington (2)
- J. M. Simmons, Division of Reactor Development - Washington (5)
- M. Whitman, Division of Reactor Development - Washington
- T. O. Ziebold, Division of Reactor Development - Washington
- Reports and Statistics Branch - Washington
- F. Foote, Argonne National Laboratory
- H. Young, Argonne National Laboratory (4)
- A. Squire, Bettis Atomic Power Laboratory
- E. A. Eschbach, Hanford
- E. A. Evans, Hanford
- J. Musser, Hanford
- I. D. Thomas, Hanford
- O. J. Wick, Hanford
- W. K. Woods, Hanford
- W. Cashin, KAPL
- H. Rizzo, Lawrence Radiation Laboratory (3)
- R. D. Baker, Los Alamos Scientific Laboratory
- L. B. Jones, Mound Laboratory
- Office of Technical Information Extension, ORNL

U. S. Atomic Energy Commission, Contractors
- W. O'Leary, Allis Chalmers Manufacturing Company
- R. W. Dayton, Battelle
- W. Duckworth, Battelle
- R. H. Gale, Cumbustion Engineering
- L. H. Matheson, Dow Chemical Company
- G. Spaulding, Electric Autolite Company
- A. Strasser, Nuclear Development Corporation of America
- Olin Mathieson Chemical Corporation
- R. W. Hartwell, Power Reactor Development Company
- C. W. Kuhlman, United Nuclear Corporation

Document includes 9

## NUMEC DISTRIBUTION

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