Thoria Development Activities Annual Report

Fiscal Year 1978

P. E. Hart

February 1979

**Prepared for the U.S. Department of Energy
under Contract EY-76-C-06-1830**

**Pacific Northwest Laboratory
Operated for the U.S. Department of Energy
by Battelle Memorial Institute**

NOTICE

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

The views, opinions and conclusions contained in this report are those of the contractor and do not necessarily represent those of the United States Government or the United States Department of Energy.

PACIFIC NORTHWEST LABORATORY
operated by
BATTELLE
for the
UNITED STATES DEPARTMENT OF ENERGY
Under Contract EY-76-C-06-1830

Printed in the United States of America
Available from
National Technical Information Service
United States Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22151

Price: Printed Copy \$ ____*; Microfiche \$3.00

*Pages	NTIS Selling Price
001-025	\$4.00
026-050	\$4.50
051-075	\$5.25
076-100	\$6.00
101-125	\$6.50
126-150	\$7.25
151-175	\$8.00
176-200	\$9.00
201-225	\$9.25
226-250	\$9.50
251-275	\$10.75
276-300	\$11.00

3 3679 00053 1949

THORIA DEVELOPMENT ACTIVITIES
ANNUAL REPORT
FISCAL YEAR 1978

P. E. Hart

February 1979

Prepared for the U.S. Department of Energy
under Contract EY-76-C-06-1830

Pacific Northwest Laboratory
Operated for the U.S. Department of Energy
by Battelle Memorial Institute

SUMMARY

In this report, PNL's ThO₂ development activities for FY-1978 are reviewed. These activities are in support of the FRAD (Fuels Refabrication and Development) program's goal of developing proliferation resistant fuel cycles. Included in this report are results for the five ThO₂ fuel related elements that are assigned to PNL. During FY-1978, work on these elements has been directed primarily toward establishing the TOFDL (Thorium Oxide Fuel Development Laboratory) facility where unit operations for ThO₂-based fuels will be defined and fuels for test irradiations fabricated. Additional activities include evaluation of ThO₂ powders derived by various oxalate precipitation conditions, the fabricability of commercially available ThO₂ powders, hybrid pellet fuel fabrication and definition of an irradiation test plan.

ThO₂ Powder Evaluation

A study was initiated of the effect of thorium oxalate precipitation parameters on the properties and fabricability of derived thorium oxide powder. High precipitation temperature was found to produce oxalate-derived oxide particles with either a square, platy or rod-like morphology; whereas, low precipitation temperature produced powder particles in the shape of nodules or near-cubes. Both mechanical stirring and long digestion time, when compared with ultrasonic stirring and short digestion time, favored the formation of precipitate particles with better crystalline shapes; precipitates formed under these conditions also required shorter filtration times. All ultrasonically stirred precipitations produced precipitates which required longer filtration times than the corresponding mechanically stirred precipitation.

ThO₂ Pellet Development

Facility requirements for thorium oxide development activities have been identified, specifications for required process equipment and analytical apparatus have been written, and purchase orders have been placed for the necessary capital equipment. Delivery of most of this equipment will coincide with completion of the laboratory.

Initial sintering tests showed that 16 hr ball milling is necessary to enhance the activity of commercially available ThO₂ powder to achieve sintered ThO₂ pellets with densities greater than 97% TD (% of theoretical density). Both green and sintered densities decreased with increasing UO₂ content in mechanical mixtures of UO₂ and ThO₂. The sintered density for the ThO₂-30wt%UO₂ mixture was 88% TD. Microstructures of sintered pellets showed non-homogeneous two-phase structures consisting primarily of high density ThO₂ particles and porous UO₂ particles. Work has been initiated to improve the homogeneity of the mixed powders and increase the density of the sintered pellets.

Hybrid Fuel Development

Hybrid fuels are defined as those produced by a combination of the sol-gel process and the conventional pelleting process. The sol-gel-derived particles are used as feed for producing green pellets which are then sintered to yield a product similar to that derived from the conventional process. A preliminary evaluation of the pressing and sintering characteristics of UO₂ microspheres made by an internal gelation technique at ORNL was completed. Sound pellets of 93% TD have been produced from less than 53 μ m diameter spheres. Results suggest that pressing pressure and die lubricant addition influence green pellet density and crack behavior. Sphere size appears to be the dominant factor affecting pellet green density and integrity. Cracking during sintering also seems to be related to off-gassing of excess oxygen from partially calcined spheres.

Irradiation Test Plan

An irradiation test plan for $\text{ThO}_2\text{-UO}_2$ fuels has been prepared. The plan includes steady-state, safety-related, and ramp testing and lead-rod and rod-assembly demonstrations.

Thorium Oxide Fuel Development Laboratory

Approximately 7200 square feet of laboratory space in the North Bay of PNL's 306W Building is being modified to provide thorium oxide pellet fuel process development capability on a near term basis. Site preparation included removal of large pieces of primary metal working equipment like rolling mills and old services and duct work. A functional design criteria for the laboratory has been approved and an environmental impact assessment is currently in the approval process. Due to the immediate need for this facility, the project is being handled in an accelerated, "fast track" mode. All major procurements, i.e., HVAC system and fume hoods, have been delivered or are under contract. Construction was initiated as soon as an appropriate segment of Title II Design was approved. Completion of the project is scheduled for May.

TABLE OF CONTENTS

SUMMARY.	ii
LIST OF FIGURES.	vi
1.0 ThO ₂ POWDER EVALUATION.	1
2.0 ThO ₂ PELLET DEVELOPMENT	11
3.0 HYBRID FUEL DEVELOPMENT	20
4.0 IRRADIATION TEST PLAN	26
5.0 THORIUM OXIDE FUEL DEVELOPMENT LABORATORY	27
ACKNOWLEDGMENTS.	30

LIST OF FIGURES

1.1	Thorium oxide powder derived from oxalate precipitated at 70°C with magnetic stirring and digested for 1 hour. Precipitation run 2.	4
1.2	Thorium oxide powder derived from oxalate precipitated at 10°C with magnetic stirring and digested for 1 hour. Precipitation run 6.	4
1.3	Thorium oxide powder derived from oxalate precipitated at 70°C with ultrasonic stirring and digested for 1 hour. Precipitation run 3.	5
1.4	Thorium oxide powder derived from oxalate precipitated at 10°C with ultrasonic stirring and digested for 1 hour. Precipitation run 1.	5
1.5	Thorium oxide powder derived from oxalate precipitated at 10°C with ultrasonic stirring and digested for 24 hours. Precipitation run 4.	6
1.6	Thorium oxide powder derived from oxalate precipitated at 10°C with magnetic stirring and digested for 24 hours. Precipitation run 5.	6
1.7	As-received Lot TB-2 thorium oxide powder supplied by Tennessee Nuclear Specialties.	8
2.1	Photomicrographs of the cross sections of sintered ThO ₂ pellet, processed from as-received Lot TB-2 powder and powder milled 16 hr and mechanically mixed ThO ₂ -20% UO ₂ powder	13
2.2	Tap density of pure ThO ₂ powder as function of ball milling time .	15
2.3	Effect of ball milling time on the sintered density of ThO ₂ pellets.	16
2.4	Green density as function of UO ₂ concentration in (Th,U)O ₂ pellets. The data points show the mean and range of at least four pellet densities.	17
2.5	Sintered density as a function of UO ₂ concentration for ThO ₂ -UO ₂ pellets. The data points show the mean and range of at least four pellets densities	18
3.1	Flowsheet for hybrid pellet fabrication.	21

LIST OF FIGURES (Cont'd)

3.2	Microstructure of sintered hybrid fuel pellet made from 200 μm spheres.	23
3.3	Etched microstructure from selected high density region from a sintered hybrid fuel pellet made from 200 μm spheres	23
3.4	Microstructure of a sintered hybrid pellet made from less than 53 μm spheres.	24
5.1	Equipment layout for TOFDL. Numbers denote work stations.	29

1.0 ThO₂ POWDER EVALUATION

G. D. White

This element has a two-fold objective: 1) the development and refinement of thoria and thoria-urania powder production processes amenable to remote operation that yield powders which will be more easily fabricated than those presently available and 2) the characterization of the resulting powders as well as powders derived by dry reprocessing methods and those commercially available. Work during fiscal 1978 included initiation of a study of thorium oxalate precipitation parameter effects on the fabricability of the derived oxide powder. Refinement of this process is needed to establish precipitation and decomposition parameters for producing thoria or thoria-urania powders which can be fabricated into dense pellets in a remote facility with minimum processing steps required.

1.1 Precipitation Parameter Evaluation

Thorium oxide powder is produced commercially by decomposing thorium oxalate which is precipitated in the reaction of thorium nitrate and oxalic acid. The commercially produced oxide powders must be milled extensively to produce fuel pellets with required density and microstructure.^(1.1) Since oxide powder particles produced by thermal decomposition retain the approximate size, shape, and texture of the oxalate particles,^(1.2) precipitation of the oxalate determines the important oxide particle and powder characteristics, which are relevant to pellet fabrication. Therefore, the optimization of oxalate precipitation parameters is key to obtaining highly sinterable powders.

Previous investigators^(1.2,1.3,1.4,1.5) have related oxalate precipitation parameters to certain oxide properties such as particle size, surface area, and particle morphology. Little work has been reported^(1.5) on the effects of these parameters on ceramic powder properties, i.e., compaction ratios, sinterability, and microstructure. Furthermore, none of the investigations have included the degree of agitation as a precipitation parameter in these studies even though it can have a large effect upon the precipitate particle morphology.^(1.7)

During FY-1978, a preliminary thorium oxalate precipitation study was conducted, and the physical properties and morphology of the powders produced have been evaluated. In addition to the degree of agitation, temperature and time of digestion were chosen as independent variables. Only forty grams of thorium oxide was produced from each precipitation. Table 1.1 lists the independent variables for each precipitation.

Table 1.1 Precipitation Parameter Evaluated

<u>Precipitation Run Number</u>	<u>Precipitation Temperature, °C</u>	<u>Digestion Time, Hr</u>	<u>Agitation Method</u>
1	10	1	Ultrasonic
2	70	1	Magnetic Stirrer
3	70	1	Ultrasonic
4	10	24	Ultrasonic
5	10	24	Magnetic Stirrer
6	10	1	Magnetic Stirrer

The precipitates were prepared by adding 1M oxalic acid to 1M $\text{Th}(\text{NO}_3)_4$ at approximately 5 ml/min and were filtered using a Buchner filter and No. 42 ashless paper. After drying at 110°C for 24 hours, the oxalate was decomposed by calcining at 900°C in air for 24 hours. For each precipitation, agitation was continued at temperature for the digestion time indicated. The surface area, particle size distribution, crystallite size by x-ray line broadening, and morphology by scanning electron microscopy were determined on samples of each powder. The remainder of the powders is being used for sintering tests.

Table 1.2 lists the properties of the six powders, and Figure 1.1 through 1.6 are scanning electron micrographs showing the ThO_2 powder morphologies. By comparing Figures 1.1 with 1.2, and 1.3 with 1.4, it is readily seen that temperature is a precipitation parameter having a very large effect upon powder and individual particle characteristics. The powder particles from the 70°C precipitations (Figures 1.1 and 1.3) were large and had a square plate-like or euhedral morphology. Portions of the magnetic stirred, 70°C precipitated material (Figure 1.1) had a rod-like morphology. All of the 10°C

TABLE 1.2 Powder Characteristics of Oxalate-Derived Thoria

Precipitation Number	X-Ray Crystallite Size, Å	B.E.T. Surface Area, m ² /g	Calculated* Surface Area, m ² /g	Calculated** Surface Area, m ² /g	Particle Size Distribution				
					0.2μm	0.5μm	%< 1.0μm	2.0μm	5.0μm
1	600 ± 9	1.80	6.0	10.0	12	20	61	88	97
2	816 ± 55	2.60	4.4	7.4	12	12	20	66	100
3	699 ± 63	2.62	5.0	8.6	4	4	19	70	100
4	560 ± 11	6.57	6.4	10.7	8	35	75	88	92
5	612 ± 14	3.90	5.9	9.8	5	13	44	97	100
6	635 ± 51	3.77	5.7	9.4	7	21	64	94	100

*Equation 1. $S = 3.6 \times 10^3/D$; $S = m^2/q$; D = x-ray crystallite diameter in Å; an empirical relationship for oxalate derived ThO₂ powder. (1.2)

**Equation 2. $S = 6/\rho D$ (the relation of a sphere's surface to its diameter); ρ = ThO₂ density in g/m³; D = x-ray crystallite diameter in m, and $S = m^2/q$.

FIGURE 1.1. Thorium oxide powder derived from oxalate precipitated at 70°C with magnetic stirring and digested for 1 hour. Precipitation run 2.

Figure 1.2. Thorium oxide powder derived from oxalate precipitated at 10°C with magnetic stirring and digested for 1 hour. Precipitation run 6.

3 μm

1 μm

FIGURE 1.3. Thorium oxide powder derived from oxalate precipitated at 70°C with ultrasonic stirring and digested for 1 hour. Precipitation run 3.

3 μm

1 μm

FIGURE 1.4. Thorium oxide powder derived from oxalate precipitated at 10°C with ultrasonic stirring and digested for 1 hour. Precipitation run 1.

3 μm

1 μm

FIGURE 1.5. Thorium oxide powder derived from oxalate precipitated at 10°C with ultrasonic stirring and digested for 24 hours. Precipitation run 4.

3 μm

1 μm

FIGURE 1.6. Thorium oxide powder derived from oxalate precipitated at 10°C with magnetic stirring and digested for 24 hours. Precipitation run 5.

precipitations produced particles (Figures 1.2, 1.4, 1.5, and 1.6) with primarily nodular or near-cubic morphologies. Thoria particles from magnetically stirred precipitations (Figures 1.1, 1.2, and 1.6) had well developed crystalline shapes, especially the 70°C precipitation (Figure 1.1), compared to the ultrasonically stirred material (Figures 1.3, 1.4, and 1.5). In each instance the magnetically stirred precipitate filtered more easily than its ultrasonically stirred counterpart. The 24 hr digestion time also appears to favor formation of particles with more developed crystalline shape (Figures 1.5 and 1.6) and also with improved filtering characteristics. The powder particles (Figures 1.4 and 1.5) from the ultrasonically agitated, 10°C precipitation appear to be fused together. This fused appearance could have resulted from directly introducing the dried oxalate hydrate into a 900°C furnace causing localized melting of very small particles of the hydrate. If the hydrate had decomposed before reaching its melting point, a structure of this type might not have occurred. Whether the fused appearance results from too rapid heating of the hydrate or not will be evaluated in future work. These two powders contain particle sizes greater than 5 μm in size, whereas the other four powders were 100% less than 5 μm . The photomicrographs indicate that these greater than 5 μm particles were agglomerates. The platelet morphology of the powder precipitated at 70°C is similar in character to that of the commercially available, oxalate derived ThO_2 powder (Figure 1.7). The platelets of the commercially available powder, however, are better defined than the materials (Figure 1.1 and 1.3) produced at 70°C. As discussed in Section 2 of this report, the commercially produced powder required extensive milling to achieve pellet densities of 97% TD.

A comparison of surface area measured by the B.E.T. method and surface area calculated from crystallite size can be used to judge the amount of open porosity contained within individual particles. In general, a high surface area is associated with a fine crystallite size and a highly porous particle. Allred and co-workers obtained surface areas between 5 and 10 m^2/g for oxalate derived ThO_2 powders precipitated at 10°C, 40°C, and 70°C and calcined at 900°C for 24 hr. In contrast, the powder precipitated at 10 and 70°C and calcined at 900°C for 24 hr in the present study had surface areas of 1.8

FIGURE 1.7. As-received Lot TB-2 thorium oxide powder supplied by Tennessee Nuclear Specialties.

to $6.6 \text{ m}^2/\text{g}$. When the morphology of the $1.8 \text{ m}^2/\text{g}$ material (Figure 1.1) is compared with that of the $6.6 \text{ m}^2/\text{g}$ material (Figure 1.4), the surface area of run 1 appears to be too low relative to the run 4 material. The surface area of the run 1 material will be remeasured.

The low measured surface area of the present study, relative to the values calculated from crystallite size, and relative to the values measured by Allred et al may be due to localized melting of the thorium oxalate hydrate during decomposition as discussed previously. The localized melting would reduce surface area without affecting crystallite size. In comparison to the approach used in the present work, Allred et al used very slow heating rates to decompose the oxalate, i.e., the oxalate was first dried, then decomposed at 375°C for 4 hr and at 400°C for 16 hr prior to calcination at 900°C . With this slow heating cycle, the oxalate hydrate could decompose before reaching its melting point resulting in a powder with a small crystallite size and high surface area.

1.2 Facility Development

Equipment and laboratory supplies to be used in the TOFDL for powder evaluation work have been purchased. Temporary laboratory facilities for use during construction were established in Building 325 and equipped with the necessary apparatus to do sinterability tests.

1.3 Future Activities

The powders prepared in the precipitation studies will be sintered, and based upon analysis of the data, further experiments will be designed. A new agitation device that incorporates both mechanical and ultrasonic agitations will be used. Much larger amounts of oxalate can be precipitated using this device. When the optimum parameters are established for the preparation of ThO_2 , uranium and thorium oxalates will be coprecipitated and calcined to the mixed oxide using these parameters. Freeze drying will also be investigated as a method of converting thorium nitrate to the oxide. The freeze-drying system is assembled and will be operated using nonradioactive materials until the TOFDL is operational. Compounds such as aluminum or ferric nitrate will be used to simulate the preparation of ThO_2 by the freeze-dry method.

REFERENCES

- 1.1 W. A. Weinreich, W. H. Britton, C. R. Hutchison, R. G. R. Johnson, and T. J. Burke, "Fabrication of High Density, High-Integrity Thoria-Base Fuel Pellets," Bettis Atomic Power Laboratory. Presented at symposium on Materials Technology of Thorium Fuels, American Nuclear Society Meeting, San Francisco, 1976.
- 1.2 V. D. Allred, S. R. Buxton, and J. P. McBride, "Characteristic Properties of Thorium Oxide Particles," J. Phys. Chem. 61 117-20 (1957).
- 1.3 M. Breyse, B. Claudel, and Y. Trambouse, "Effects of Conditions for Precipitating a Salt on the Texture of Its Thermal Decomposition Product. The Case of Thorium Oxalate," Bull. Soc. Chim. France, 1 201-4, WAPD-Tr-64 (1965).
- 1.4 C. R. Tipton, Jr. (ed), Volume I, Reactor Handbook, "Aqueous Fuel Systems," pp 389-93, Second Edition, Interscience Publishers, Inc., New York (1960).
- 1.5 A. S. Ayers, "Precipitation of Thorium Oxalate from Nitric Acid Solutions," CC-2962 (1945).
- 1.6 S. K. Kanton, R. V. Raghavan, and G. S. Tendolkar, "Sintering of Thorium and Thoria," P/1705, 6, Proceedings of the Second United Nations International Conference on the Peaceful Uses of Atomic Energy, Geneva (1958).

2.0 ThO₂ PELLET DEVELOPMENT

R. B. Matthews and N. C. Davis

The ThO₂ pellet development work is directed toward the definition and optimization of the unit operations required for the fabrication of ThO₂-based pellet fuels. The major objective is to define and optimize a reference flowsheet based on mixing and blending of ThO₂ and UO₂ powders. An additional objective is to outfit the TOFDL (Thorium Oxide Fuel Development Laboratory) with sufficient process and analytical equipment to carry out pellet development work. The flowsheet will be used as a standard to judge other processes against and will be the technique used to fabricate fuels containing up to 30 wt% UO₂ for the initial irradiation testings. Since previous work suggests that sintered pellet density decreases with increasing UO₂ concentration, the key to flowsheet development will be blending and milling of the oxide powders into a mix that will readily press and sinter to high density with a homogeneous distribution of the fissile component. To meet this objective, a method for fabricating high density ThO₂ pellets will first be established then the effect of UO₂ additions on fuel pellet properties and fabrication behavior will be evaluated.

2.1 Equipment Procurement

During the past year, process operations to be carried out in the TOFDL and equipment needs for fabrication, analytical, and support activities were defined. When completed, this advanced ceramics fabrication laboratory will be capable of detailed investigation of all the process steps in the ThO₂ and (Th,U)O₂ flowsheets. The following process steps will be studied:

- powder preparation, i.e., calcining, ball milling, attrition, mixing and blending,
- powder evaluation, i.e., surface area, density, thermal analysis, morphology, crystallite size,

- press feed preparation, i.e., pre-slugging, granulation and sizing,
- pellet pressing, i.e., double acting hydraulic press, single acting mechanical press,
- sintering, i.e., cold wall refractory metal furnace, hot-wall, ceramic insulated furnace,
- pellet evaluation, i.e., differential thermal analysis, ceramography, x-ray analysis, fractography,
- rod loading and inspection, i.e., atmosphere controlled loading box, He leak check and end cap welding systems.

In addition, the conversion of nitrate to sinterable oxide by precipitation and freeze drying will be evaluated in this laboratory.

2.2 Literature Review

To serve as a technical basis for future process development activities, a critical review of literature relevant to ThO₂-based fuel technology was completed. Areas included in the review are: Th resource availability, ThO₂ powder preparation, pellet fuel fabrication and fuel properties. This review is scheduled for publication by the end of the first quarter of FY-1979. A library has been established including copies of references pertinent to ThO₂-based fuels.

2.3 Fabrication Development

As-Received Powder. Preliminary tests were run on the as-received ThO₂ powder* (lot TB-2) to: 1) analyze the physical characteristics of the powder and 2) determine if the powder lot could be pressed and sintered into high density pellets without powder pretreatment. The surface area of the powder was 1.8 m²/g which is below that normally needed to obtain fuel pellets with high sintered density. The tap density was 2.7 Mg/m³. Even after attempts

* Supplied by Tennessee Nuclear Specialities, Jonesboro, Tennessee.

to preslug and granulate, the powder flowed poorly and the yield of intact pellets was low. Pellets with good physical integrity and green densities greater than 5 Mg/m^3 could be pressed when the powder was blended with 0.2 wt% Sterotex after slugging and granulation. Sound pellets were sintered in a cold wall, batch type furnace at 1650°C for 8 hr in Ar-50% H_2 flowing at $0.6 \text{ m}^3/\text{hr}$.

a. As-received, slugged and granulated, ThO_2 powder. b. ThO_2 powder milled 16 hr c. ThO_2 - UO_2 powder mechanically mixed.

FIGURE 2.1. Photomicrographs of the cross sections of sintered ThO_2 pellet, processed from as-received lot TB-2 powder and powder milled 16 hr and mechanically mixed ThO_2 -20wt% UO_2 powder.

Sintered densities increased with increasing green densities, i.e., pellets pressed to 6.0 Mg/m^3 green density sintered to $\sim 85\%$ TD; pellets pressed to 6.5 Mg/m^3 sintered to $\sim 90\%$ TD. The micrograph in Figure 2.1a shows that a typical pellet from this series has a coarse structure with random cracks and large pores. These results indicated that powder treatment was necessary to improve pressing and sintering characteristics of the as-received powder.

Effect of Ball Milling. The purpose of these tests was to determine the effect ball milling has on the subsequent pressing and sintering of ThO_2 powder from lot TB-2. Small rubber-lined laboratory mills, approximately 1 liter capacity, were loaded with 1 kg of ThO_2 powder. Approximately 50% of the mill volume was filled with powder and 6 mm tungsten carbide balls. The mills were run at approximately 100 RPM and the powder was sampled at 2 hr milling intervals up to 16 hr. An additional test was run 24 hr. The as-milled powders were then manually loaded into a 12 mm die which had been lightly lubricated with butyl stearate. Pellets were semiautomatically pressed at the same conditions as the unmilled powder. Pellets were sintered by heating at 300°C/hr to 1700°C , soaked for 8 hr and cooled at 400°C/hr in Ar-50% H_2 flowing at $0.6 \text{ m}^3/\text{hr}$. The following observations and comments summarize the results:

- Flowability of the powder improved significantly after about 6 hr of milling.
- As shown in Figure 2.2, a large increase in tap density is observed with 2 hr milling. Tap density increased to 3.6 Mg/m^3 after 8 hr milling, with little further increase after doubling the time to 16 hr.
- The surface area of the 12 hr ball milled material increased to $5.5 \text{ m}^2/\text{g}$ and reduced to $4.6 \text{ m}^2/\text{g}$ after 24 hr of milling.
- The green density increased from 6.0 Mg/m^3 for the as-received powder to 6.4 Mg/m^3 after 12 hr ball milling. Additional milling did not significantly change the green density.
- The sintered density improved rapidly with milling times greater than 6 hr and appears to reach a maximum geometric density of 97% TD after 12 hr of milling as shown in Figure 2.3.

FIGURE 2.2. Tap density of pure ThO_2 powder as function of ball milling time.

- Sintered densities of pellets pressed from powders milled for less than 6 hr were lower than pellet densities from the preslugged and granulated powders discussed in the previous section. The reason for this density difference is not understood.
- The yield of sound green pellets with a length to diameter ratio of 1 continued to increase with milling time up to 16 hr.
- Continued milling to 24 hr reduced tap density and appeared to make pellet processing more difficult, but did not change the density of sintered pellets.
- When powder processing and maximum sintered density are considered, 16 hr of ball milling is the best milling time for this powder lot.

Figure 2.1b shows a cross section from a 97% TD ThO_2 pellet processed from powder milled for 16 hr. The dramatic improvement in microstructure resulting from milling can be seen by comparing Figure 2.1a and 2.1b.

FIGURE 2.3. Effect of ball milling time on the sintered density of ThO₂ pellets. The data points show the mean and range of at least four pellet densities.

Binary Pellet Development. Thoria powder, ball milled 16 hr was used as the matrix material in preliminary ThO_2 - UO_2 pellet development study. Previous tests indicated the ThO_2 would sinter to densities greater than 97% TD and the UO_2 had been routinely sintered to 95% TD. The UO_2 was screened to minus 100 mesh and mechanically blended with the 16 hr milled ThO_2 to form compositions of 5, 10, 15, 20, and 30% UO_2 in ThO_2 . These powders were pressed and sintered under the same conditions as the pure ThO_2 powders. The density of the green pellets decreased nearly linearly with increasing UO_2 concentrations as shown in Figure 2.4

FIGURE 2.4. Green density as function of UO_2 concentration in $(\text{Th},\text{U})\text{O}_2$ pellets. The data points show the mean and range of at least four pellet densities.

The sintered density also decreased, but less rapidly than green density as shown in Figure 2.5. The rapid decrease in green density suggests that the blending step as well as the nature of the UO_2 powders could influence sintered density.

FIGURE 2.5. Sintered density as a function of UO_2 concentration for ThO_2 - UO_2 pellets sintered at 1700°C for 8 hr in Ar-50% H_2 . The data points show the mean and range of at least four pellets densities.

Figure 2.1c shows a cross section from a ThO_2 -20% UO_2 pellet. The microstructure consists of coarse (up to $3500\ \mu\text{m}$) ThO_2 particles surrounded by a matrix of $(\text{Th},\text{U})\text{O}_2$ and islands ($\sim 60\ \mu\text{m}$) of pure UO_2 . This segregated structure indicates that clustering of the ThO_2 component occurred during the mechanical mixing step. Microprobe analysis shows that the ThO_2 is highly dense and that the porosity is associated with the UO_2 phase.

2.4 Future Activities

Two areas which require more work have been uncovered: (1) simple mechanical blending of the powders is not acceptable (2) sintered density decreases with increasing UO_2 concentration. These areas will be the focus of attention during the next quarter. Blending and milling are the key operations for making high density, homogeneous ThO_2-UO_2 pellets with commercially available powders. Work has been initiated to improve the homogeneity of the mixed powders by optimizing these operations. Once the effects of mixing techniques have been isolated, the relationships between UO_2 concentration and sintered density can be assessed.

The next step will be flowsheet definition and optimization of the process using factorial experiments to determine the influence of the variables from each operation on sintered density. A full scale, kilogram quantity, production campaign of mechanically mixed ThO_2-UO_2 pellets is anticipated by the end of FY-1979.

3.0 HYBRID FUEL DEVELOPMENT

R. B. Matthews

The hybrid pellet fuel concept combines the head-end of the sol-gel sphere fabrication technique with the back-end of the standard pellet pressing and sintering technique.

The objectives of this element are to demonstrate that sol-gel microspheres can be pressed and sintered into acceptable fuel pellets, to optimize the process flowsheet, and to evaluate the feasibility of using the hybrid process in a remote fabrication facility.

A possible flowsheet for the fabrication of hybrid $\text{ThO}_2\text{-UO}_2$ pellets is shown in Figure 3.1. Thoria-urania microspheres will be fabricated by one of the sol-gel methods, dried and partially calcined. These microspheres become the press feed material for conventional pelleting of oxide fuels. The incentive for development of the hybrid process is to combine the advantages and reduce the disadvantages of both sphere-pac and pellet fuels in order to fabricate $\text{ThO}_2\text{-UO}_2$ fuels in a heavily shielded, remote fabrication facility. Potential advantages of the hybrid process over the more conventional production of pellets in a remote facility from precipitated powders are:

- fewer dusty operations, i.e., the elimination of milling, slugging and granulation steps from the pellet fabrication process,
- enhanced powder transport and flow properties due to the spherical shape of the powder particles,
- reduced sintering temperature due to the high activity of sol-gel spheres.

The experimental approach will be to procure various types of microspheres, systematically vary process variables using factorial experiments and evaluate changes in sintered density. The hybrid pellet process is only in the conceptual stage and many variables need to be evaluated before the process can be demonstrated. To date, relationships between sphere size, binder additions, and pressing pressure on pellets made from UO_{2+x} microspheres have been initially evaluated.

FIGURE 3.1. Flowsheet for hybrid pellet fabrication

3.1 Hybrid Pellet Fuel Fabrication

Three sizes of uranium oxide microspheres were pressed and sintered into pellets; their characteristics are listed in Table 3.1.

Table 3.1. Characteristics of Uranium Oxide Spheres

<u>Mean Diameter, μm</u>	<u>Tap Density, Mg/m^3</u>	<u>O/U</u>	<u>Best Single Pellet Density, Mg/m^3</u>
750	0.9	2.38	9.46*
200	1.5	2.53	9.50*
<53	1.6	2.28	10.26

*Cracked pellets

The spheres were fabricated at ORNL by the internal gelation process and calcined at 600°C in $\text{Ar-4\%H}_2$ for 4 hr. The spheres were pressed in a 13 mm die with opposed punches then sintered at 1450°C in $\text{Ar-50\%H}_2$ for 4 hr. The low density spheres were fragile and readily moved by electrostatic charges. The low tap density of the spheres caused abnormally high compaction ratios and problems with trapped air. Nevertheless, the spheres readily pressed into solid pellets. The pressing characteristics were sensitive to die lubricant additions, i.e., too little lubricant resulted in a low end-capping threshold and surface microcracks, while too much lubricant seemed to trap air in the die and the pellets fractured when ejected from the die. The pressing results showed that pressure had a significant effect on green density, but the sintered density was nearly independent of pressure and only sphere size influenced sintered density.

Pellets frequently cracked during sintering, and the amount of cracking increased with increasing sphere size. Pellets made from the coarse 750 μm spheres fell apart during sintering. Pellets made from the 200 μm spheres were intact after sintering, but extensive cracking surrounded individual spheres and cracks extended throughout the pellets (see Figure 3.2). Microstructures showed selected areas of very high density with no cracking or porosity at the sphere interfaces as shown in Figure 3.3

FIGURE 3.2. Microstructure of sintered hybrid fuel pellet made from 200 μm spheres.

FIGURE 3.3. Etched microstructure from selected high density region from a sintered hybrid fuel pellet made from 200 μm spheres.

Pellets made from fine spheres, less than 53 μm , were crack free and sintered to 93% TD with some porosity surrounding sphere clusters as shown in Figure 3.4.

FIGURE 3.4. Microstructure of a sintered hybrid pellet made from less than 53 μm spheres.

The high O/U ratios of these spheres (see Table 3.1) confuse the conclusions about the relationship between sphere size and sintered density. Release of excessive oxygen might inhibit sintering, and x-ray analysis showed that all the spheres except those less than 53 μm had some U_3O_8 present. However, the coarse spheres which made the poorest pellets had an intermediate O/U, so it is not clear whether size or stoichiometry is the most important parameter.

Microcracks appeared on the surface of as-pressed pellets made from the larger spheres so apparently sphere size influences cracking during pressing, and excessive off-gassing causes cracking during sintering. Clearly more detailed calcining studies are needed.

3.2 Future Activities

The feasibility of the hybrid process has been demonstrated, but we are a long way from having a viable pellet fabrication technique. The general approach during FY 1979 will be to establish relationships between the characteristics of as-received microspheres and calcining, pressing, and sintering behavior. Some of the important sphere characteristics are size, stoichiometry, composition, green density, surface morphology, surface area, and crystallite size. These characteristics are influenced in part by the sol-gel process and in part by calcining, so the first objective of this element is to understand the relationships between calcining conditions, i.e., temperature, heating rates and atmosphere, and sphere properties. The relationships between sphere properties and pressing and sintering behavior will fall out in sequence as part of the evaluation of sphere properties. Thoria spheres have been procured from General Atomic Company and evaluations will be initiated. In addition, calcining studies on as-dried UO_3 spheres are being started to isolate the effects of excess oxygen and sphere size on pellet fabrication. By the end of FY 1979, we should be in a position to assess the potential of the hybrid process, to specify the useable range of sphere properties and to define favorable calcining, pressing, and sintering operations for fabricating acceptable hybrid pellets.

4.0 IRRADIATION TEST PLAN

J. O. Barner

The objective of this task is to identify the irradiation testing and demonstration needs for the commercial utilization of pelletized $\text{ThO}_2\text{-UO}_2$ fuels.

A draft of an irradiation testing and demonstration plan for pelletized $\text{ThO}_2\text{-UO}_2$ fuels was prepared. The plan was based upon performing only those critical steady-state and safety-related experiments which are necessary to tie the experimental results to the existing UO_2 data base. The resultant "normalized" data base and the results from demonstration irradiations can then be used to license the pelletized $\text{ThO}_2\text{-UO}_2$ fuels for commercial utilization. The testing and demonstration irradiations include 1) critical behavioral steady-state testing to determine fuel stored energy, temperature, and fission gas release characteristics, as well as general behavior, 2) ramp testing to determine the propensity for cladding failure, 3) lead-rod demonstrations, 4) lead-assembly demonstrations, and 5) safety-related testing.

A conceptual design for fuel rods for a joint PNL/SRL (Savannah River Laboratory) program to study the fission gas release characteristics and dissolution of $\text{ThO}_2\text{-UO}_2$ fuels was prepared. The fuel rod design was based upon a commercial reactor design. A peak operating power of 59 kw/m (18w/ft) for the rods was selected based upon the expected operating fuel temperatures in a commercial plant and in the Savannah River reactors. Test objectives, a fuel test matrix and test rod and component sketches were supplied to Savannah River for review.

5.0 THORIUM OXIDE FUEL DEVELOPMENT LABORATORY

J. P. Pilger

The objective of this element is to modify and expand PNL's existing UO_2 fuel fabrication facilities to provide a laboratory where ThO_2 and $\text{ThO}_2\text{-UO}_2$ fuel pellets and fueled rods can be fabricated. This laboratory, the Thorium Oxide Fuel Development Laboratory (TOFDL), will also provide a capability for ThO_2 powder development and evaluation, and provide facilities for ceramography and analytical work. The TOFDL will provide the required space and facilities such that the program objectives can be accomplished safely and in accordance with current federal regulations governing radioactive material handling and containment. This element is subdivided into four areas of effort: laboratory preparation, facility design, major procurements, and construction.

5.1 Laboratory Preparation

Prior to construction of the TOFDL in the North Bay of 306W Building, large pieces of existing primary metal working equipment, i.e., rolling mills, furnaces, tensile frames, etc. were removed and reinstalled in another building. Old services--electrical conduits, piping, ductwork--and miscellaneous gear remaining from a variety of projects were removed from this space. Seven existing steam heating/evaporative cooling units were removed from the roof to clear the area for new HVAC ductwork. All site preparation work was completed by September 30, 1978.

5.2 Facility Design

In order to accelerate the design effort and to provide working drawings at the earliest possible date, the design effort went from conceptual design directly to the Title II Design phase. The laboratory layout is shown in Figure 5.1. Operations associated with ThO_2 or UO_2 powders are confined to the west end of the facility. A UO_2 pellet fabrication capability is being retained in the southwest corner of this area. $\text{ThO}_2\text{-UO}_2$ fuel pellets will be fabricated in work stations 1 through 11. ThO_2 powder development and

analysis will be done in the northwest corner in stations 12 through 20, while ceramography will be done in stations 21 through 24. A total of 23 of these stations will be fume hoods. The fume hoods are of the auxiliary air configuration wherein up to 70% of the hood air can be supplied from an auxiliary source. The auxiliary air does not require air conditioning and only minimal heating thereby reducing laboratory energy requirements. Fuel pellets will be sintered and fuel rods loaded, welded, pressurized, and inspected in the assembly area in east end of the laboratory. The HVAC system for the laboratory will supply conditioned air via chilled water and a steam heat exchanger. Additional energy conservation is provided through utilization of a closed loop heat recovery system. All air exhaust from the laboratory will be double HEPA filtered and monitored. Other effluents will be sampled and monitored for radioactive contamination. The conceptual design was completed March 27, 1978 and Title II design was completed October 17, 1978.

5.3 Equipment Procurement

In order to expedite procurement of the major project equipment items, specifications were written as soon as equipment needs were identified. Procurement action was initiated for 23 fume hoods, 2 HVAC exhaust fans, 3 HVAC air handling units, a chiller/compressor unit, and the HEPA filter units. The hoods, exhaust fans, and chiller/compressor are on site. The air handlers and filters are scheduled for delivery during the first quarter of FY 1979.

5.4 Project Construction

Laboratory construction was initiated August 18, 1978. Construction starts were phased to coincide with completion of Title II design packages. The first phase began with placement of exterior concrete and structural steel which is for support of the HVAC equipment. The second phase, installation of piping, began September 8, 1978. Installation of HVAC ductwork started October 3. Beneficial occupancy of the laboratory is projected for May.

THORIUM OXIDE FUEL DEVELOPMENT LABORATORY

FIGURE 5.1. Equipment layout for TOFDL. Numbers denote work stations.

ACKNOWLEDGMENTS

This work was performed in support of the Fuels Refabrication and Development (FRAD) program under contract EY-76-C-06-1830. Contributions by the following people are gratefully acknowledged: L. A. Bray for precipitation of oxalate powders, J. E. Coleman and J. L. Daniel for scanning electron microscopy, J. E. Lester, E. H. Shade, and J. E. Spasoff for performing fabrication related work, D. H. Parks for ceramography, J. W. Wald for x-ray diffraction studies, M. C. Burt (HEDL)* for performing powder characterization and W. I. Clark (HEDL) for microprobe analysis.

*Hanford Engineering Development Laboratory, Richland, Washington.

FRAD REPORT
DISTRIBUTION LIST

No. of
Copies

No. of
Copies

OFFSITE

OFFSITE

A. A. Churm
DOE Patent Division
9800 S. Cass Avenue
Argonne, IL 60439

Argonne National Laboratory
9700 South Cass Avenue
Argonne, IL 60439

Attn: Martin J. Steindler

Babcock & Wilcox
PO Box 1260
Lynchburg, VA 24505

Attn: C. Youell

Bettis Atomic Power Laboratory
Westinghouse Electric Corporation
PO Box 79
West Mifflin, PA 15122

Attn: W. A. Weinreich

Electric Power Research Institute
3412 Hillview Avenue
PO Box 10412
Palo Alto, CA 94304

Attn: E. Zebroski

Fluor Engineers & Constructors, Inc.
3333 Michelson Drive
Irvine, CA 92730

Attn: E. W. Neben

Gas Cooled Reactor Associates
3344 N. Torrey Pines Ct.
Suite 300
La Jolla, CA 92037

Attn: K. L. Highfill

General Atomic Company
PO Box 81608
San Diego, CA 92138

Attn: W. V. Goeddel

General Electric Company
175 Curtner Avenue
San Jose, CA 95125

Attn: P. Miller

Knolls Atomic Power Laboratory
PO Box 1072
Schenectady, NY 12301

Attn: D. J. Groetch

Los Alamos Scientific Laboratory
PO Box 1663
Los Alamos, NM 37545

Attn: G. R. Keepin

Oak Ridge National Laboratory
PO Box X
Oak Ridge, TN 37830

Attn: A. L. Lotts

Sandia Laboratory
Albuquerque, NM 87185

Attn: A. Camp

Savannah River Laboratory
E. I. duPont deNemours & Company
Aiken, SC 29801

Attn: J. D. Spencer

No. of
Copies

OFFSITE

2 U. S. Department of Energy
HQ/FCD
Washington, DC 20545

Attn: W. W. Ballard

U.S. Department of Energy
HQ/OSS
Washington, DC 20545

Attn: S. McDowell

2 U.S. Department of Energy
HQ/DNR
Washington, DC 20545

Attn: P. R. Clark
R. H. Steele

U.S. Department of Energy
HQ/RRT
Washington, DC 20545

Attn: D. E. Bailey

U.S. Department of Energy
Savannah River Operations Office
PO Box A
Aiken, SC 29801

Attn: T. Hindman

U.S. Department of Energy
Oak Ridge Operations Office
PO Box E
Oak Ridge, TN 37830

Attn: S. W. Ahrends

U.S. Department of Energy
Chicago Operations Office
9800 S. Cass Avenue
Chicago, IL 60439

Attn: A. Mravca

No. of
Copies

OFFSITE

27 DOE Technical Information Center

Westinghouse NFD
Westinghouse Electric Company
PO Box 355
Pittsburgh, PA 15230

Attn: C. Palmer

ONSITE

2 U.S. Department of Energy
Richland Operations Office
PO Box 550
Richland, WA 99352

Attn: P. A. Craig
H. E. Ransom

U.S. Department of Energy
FFTFPO
PO Box 550
Richland, WA 99352

Attn: J. J. Keating

Exxon Nuclear Company, Inc.
2101 Horn Rapids Road
Richland, WA 99352

Attn: O. Kruger

Hanford Engineering Development
Laboratory
PO Box 1970
Richland, WA 99352

Attn: T. T. Claudson

Hanford Engineering Development
Laboratory
Technology Management Center
PO Box 1970
Richland, WA 99352

Attn: E. A. Evans

No. of
Copies

Battelle, Pacific Northwest Laboratories
PO Box 999
Richland, WA 99352

Attn: S. Goldsmith

20 Pacific Northwest Laboratory

D. W. Brite
J. R. Carrell
T. D. Chikalla
R. M. Fleischman
S. Goldsmith
P. E. Hart
R. S. Kemper
L. R. Lambert
R. C. Liikala
T. I. McSweeney
J. F. Nesbitt
D. F. Newman
R. E. Schreiber
R. E. Sharp
R. P. Marshall
C. R. Hann
J. O. Barner
R. B. Matthews
G. D. White
N. C. Davis

5 Technical Information

2 Publishing Coordination