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IRRADIATION TESTING OF CERAMIC FUELS

Summary Report

By
G. Zuromsky
W. P. Chernock

September 1962

Nuclear Division
Combustion Engineering, Inc.
Windsor, Connecticut

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S U M M A R Y R E P O R T

IRRADIATION TESTING OF CERAMIC FUELS

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U. S. ATOMIC ENERGY COMMISSION

NUCLEAR DIVISION
COMBUSTION ENGINEERING, INC.
Windsor, Connecticut

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I. PREFACE

This report serves the dual purpose of:

1. Summarizing work on Contract AT(30-1)-2379, "The Development and Testing of Homogeneous Ceramic Fuels."
2. Summarizing work during the present contract period on Contract AT(30-1)-2936, "Irradiation Testing of Ceramic Fuels."

Both of these Contracts are with the United States Atomic Energy Commission as part of the Fuel Cycle Development Program.

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II. OBJECTIVES

The objectives of this program are:

- A. To establish the composition limits for thermally stable, single phase, face-centered cubic crystal structures in the zirconia rich region of the UO₂-CaO-ZrO₂ system and in the ceria rich end of the UO₂-CeO₂ system.
- B. To establish methods for fabricating high density pellets of the single phase, face-centered cubic solid solutions in both the zirconia and ceria base systems. These pellets would be used for phase diagram investigations. Enriched pellets would be used for the irradiation program.
- C. To determine the physical, thermal and chemical properties of selected compositions within the single phase, face-centered cubic phase fields in both the ceria and zirconia base systems.
- D. To establish the irradiation stability of selected compositions within the face-centered cubic phase fields in both the zirconia and ceria base systems after burnups of 40, 55, and 70 percent of the U-235 atoms and at maximum fuel temperatures approaching those of the melting points for each composition being irradiated.

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III. SUMMARY

A. Phase Diagram Studies

1. UO₂-ZrO₂-CaO System

An extensive single phase, face-centered cubic region was found in the ZrO₂ rich portion of the UO₂-ZrO₂-CaO system for powder compacts sintered at 1700°C or higher in vacuum, argon or in hydrogen. Long-time isothermal heat treatments at temperatures from 1000 to 2000°C restricted the thermally stable single phase cubic structures to compositions containing up to 12 m/o UO₂ and from 15 to 25 m/o CaO. Two-phase fields, face-centered cubic plus CaZrO₃ and face-centered cubic plus monoclinic bound the upper and lower limits of the single phase cubic region. The high CaO, high UO₂ compositions developed complex structures by reaction of CaZrO₃ with the face-centered cubic matrix during the isothermal heat treatments.

2. UO₂-CeO₂ System

Single phase, face-centered cubic solid solutions were obtained by air firing UO₂-CeO₂ compositions containing up to 21 m/o UO₂. These single phase structures were stable after extended heat treatments in argon at temperatures of 1500°C. Two distinct face-centered cubic phases were found after air firing samples containing 50 m/o UO₂ or greater. Extrapolation of lattice parameter data indicated that the two-phase structure originated at compositions between 21 and 30 m/o UO₂. The lattice parameter of one of these phases changed with variation in UO₂ content whereas the lattice constant of 5.427 Å⁰ for the second phase was invariant with UO₂ content. A section of a ternary phase diagram was postulated, which fits the experimental data.

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Two face-centered cubic solid solutions were found after sintering in argon or in hydrogen. These were identified as a ceria base solid solution and a substoichiometric ceria base solid solution.

B. Property Evaluations

1. Thermal Conductivity

Measurements of thermal conductivity by the steady state comparative method in the temperature range of 200°C to 950°C were made for samples containing 7 and 21 m/o UO_2 in CeO_2 and 4 and 15 m/o UO_2 in ZrO_2 (stabilized with 20 m/o CaO). Conductivities of 0.0209 to 0.0064 and 0.0070 to 0.0045 cal cm $\text{sec}^{-1} \text{cm}^{-2} \text{ } ^\circ\text{C}^{-1}$ were measured for 7 and 21 m/o UO_2 in CeO_2 , respectively, with the lower value in each range at the highest temperature. Results for the 4 and 15 m/o UO_2 in ZrO_2 samples were in the range of 0.0040 and 0.0050 cal cm $\text{sec}^{-1} \text{cm}^{-2} \text{ } ^\circ\text{C}^{-1}$ over the same temperature range.

2. Thermal Performance Testing

A resistance heated tungsten rod, located at the center of an eight-inch long stack of pellets contained in a stainless steel tube was used as the heat source for establishing thermal gradient conditions in these fuels. A water cooled jacket, surrounding the assembly was the heat sink and provided calorimetry data. Tests on 4 m/o UO_2 in CaO stabilized ZrO_2 with tungsten temperatures up to 2550°C developed microstructures resembling those obtained for UO_2 in a similar test under another Commission contract at CEND. These microstructures were also similar to those found for irradiated UO_2 .

3. Melting Points

The melting point apparatus, constructed for these evaluations, was based upon the use of a tantalum resistance furnace within which the sample was heated by radiation so that heater-fuel reactions were eliminated. Solidus and liquidus temperatures of 2635°C and 2685°C were measured for the 4 m/o UO_2 -stabilized ZrO_2 samples, whereas values of 2630°C and 2670°C were found for the 12 m/o UO_2 composition. Liquidus temperatures of 2420°C and 2335°C were measured for the 7 m/o and 21 m/c UO_2 - CeO_2 compositions, respectively. As a result of difficulties encountered in obtaining reliable solidus temperatures for the ceria base compositions, the solidus, used as a basis for the irradiation program, was established as 100°C below the liquidus for each composition.

4. Corrosion Tests

The low UO_2 single phase FCC solid solutions of both the ZrO_2 -rich and CeO_2 rich compositions exhibited excellent resistance to corrosion in 360°C degassed static water and in 625°C flowing steam. The maximum penetration for all pellets was less than one mil per year, based on 119 days' exposure to 360°C water or 210 days in 625°C steam. None of the pellets were fragmented nor developed corrosion products. The corrosion tests are being continued for an additional twelve-month period.

5. Chemical Analyses

The UO_2 contents of sintered pellets of ZrO_2 -base and CeO_2 -base compositions were determined by wet chemical methods of dissolution in sulfuric acid and titration with ceric sulfate. Analyses by means of X-ray fluorescence were

not suitable due to poor precision of the method. Gamma ray spectroscopy also showed low precision.

C. Irradiation Program

A program was initiated to determine the irradiation stability of single phase, face-centered cubic solid solutions of 4 m/o and 10.2 m/o UO_2 in stabilized ZrO_2 and 7 m/o and 21 m/o UO_2 in CeO_2 after fission burnups of 40, 55 and 70 percent of the U-235 atoms and with maximum center fuel temperatures just below melting. A series of capsule moves in ETR has been scheduled to provide higher fluxes as burnup proceeds and thus to maintain fairly constant maximum center temperatures.

The irradiation program includes six capsules, each of which contains five fuel samples, three of the zirconia base and two of the ceria base with almost equivalent UO_2 concentrations for each sample in a given capsule. The first series of three capsules is scheduled for insertion in MTR and ETR in November, 1962.

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IV. PHASE DIAGRAM STUDIES

A. Sample Preparation and Sinterability Tests

The composition, purity and source of the oxide starting materials, used in this investigation, are included in Table I . The samples were prepared by conventional powder metallurgy methods of cold pressing and sintering. Series of compositions were formed by dry milling appropriate weights of UO_2 (or U_3O_8) with CaO stabilized ZrO_2 or with CeO_2 in rubber lined steel jars using Burundum grinding cylinders. A typical milling time of eight hours was adequate for the preparation of well blended powder mixtures. The need for organic binders such as carbowax 4000 was eliminated by improved compaction methods which provided samples that were free of cracks and were of adequate green strength for handling. All compacts were pressed in double-acting steel dies in the form of cylindrical pellets, $3/8$ or $1/2$ inch in diameter and about $1/2$ inch in height. The die walls were dusted with zinc stearate powder to minimize wear of the die components and to facilitate compaction and ejection of the compacts. The as-pressed compacts were examined visually for cracks and weighed and dimensioned prior to sintering.

Sinterability tests conducted early in the program showed that the density of the sintered samples was essentially insensitive to the density of the as-pressed samples for compaction pressures in the range of 5 to 10 tsi¹ . The diametrical shrinkage of the sintered samples was decreased approximately 20 percent as the compaction pressure was increased from 5 to 50 tsi. This factor is considered to be significant in the preparation of fuel element inserts of rod or platelet configurations where close dimensional tolerances

would be required of the as-sintered product. However, for these studies all samples were pressed at 5 or 10 tsi to avoid shear or lamination cracks that developed at the higher compaction pressures.

An extensive sinterability study was conducted on two compositions in each of the two fuel systems. High density homogeneous samples were prepared by this method and were utilized in the determination of physical and thermal properties as well as for the irradiation program. The double sinter method was used in the preparation of the ZrO_2 -base compositions. Powder mixtures consisting of 20 m/o CaO stabilized ZrO_2 and 4 m/o or 12 m/o (10 w/o or 25 w/o) UO_2 were milled for eight hours and pressed at 2 tsi into large compacts. Single phase, face-centered cubic solid solutions were formed by sintering at 1800°C for one hour in vacuum (5×10^{-6} mm Hg). The sintered compacts were crushed to minus 200 mesh powder using the mortar and pestle and then milled for 8 or 16 hours in rubber lined steel jars using Burundum grinding cylinders. As noted previously, no binder or lubricant additions were made to the powder on the basis that suitable crack-free samples could be readily prepared. The samples were pressed at 5 tsi and sintered at 1800°C in purified argon for times ranging from 2 hours to 144 hours. The effects of milling time of 8 hours and 16 hours, respectively, and of sintering time at 1800°C upon bulk densities of samples of the two compositions are shown graphically in Figure 1. An increase in the milling time from 8 hours to 16 hours resulted in significantly improved densities for samples of the two compositions. In the case of the 4 m/o UO_2 samples, the density increased from 4.95 gm/cm^3 (88.4 percent of theoretical) to 5.30 gm/cm^3 (92.2 percent of theoretical) for the same sintering time of 66 hours at 1800°C .

Samples of the 12 m/o UO_2 composition prepared from the 16-hour milled powder showed a pronounced increase in the rate of sintering, attaining a maximum density of 6.00 gm/cm^3 (90.5 percent of theoretical) after about twenty hours at 1800°C . There was no significant increase in density by extending the sintering time at 1800°C to 144 hours. A more limited sinterability study was conducted on the two CeO_2 -base compositions containing 7 m/o or 21 m/o (10 w/o or 25 w/o) UO_2 . The powder mixtures, prepared with equivalent weights of U_3O_8 for UO_2 , were milled for 8 hours without binder or lubricant additions. The initial series of samples of the two compositions was air sintered at 1500°C for times of 4 or 16 hours to bulk densities of 96 to 98 percent of theoretical. A second series of samples attained bulk densities of 88 to 90 percent of theoretical by air sintering at 1450°C for one hour. The desired density of 94-95 percent of theoretical for the irradiation investigations was obtained by air sintering at 1475°C for 1/2 hour. The CeO_2 -base samples are highly sensitive to thermal stress and precautions of slow heating and cooling rates of at least 100°C per hour were necessary to prevent cracking or fragmentation of the samples.

Micro-examination of polished sections of the sintered samples from both oxide base compositions showed no evidence of contamination from the grinding media. Pickup of small amounts of the Burundum cylinders could result in low melting point glassy constituents which would have detrimental effects on the physical and mechanical properties of these fuel compositions. X-ray diffraction analyses of typical samples of the four compositions disclosed single phase, face-centered cubic structures. The diffraction patterns showed sharp maxima indicating that equilibrium structures were developed by the above sintering techniques. The majority of samples for the phase diagram

TABLE I

PROPERTIES OF THE OXIDE STARTING MATERIALS

UO ₂ -Depleted Ceramic Grade Mallinckrodt Nuclear Corp.		CeO ₂ -High Purity, Calcined Heavy Minerals Company		ZrO ₂ **--Hafnium Free Zirconium Corporation of America					
				0 M/o CaO	10 M/o CaO	20 M/o CaO	28 M/o CaO	35 M/o CaO	
Total U	87.6%	Other Rare Earths	0.1%	SiO ₂	0.015%*	0.017%*	0.021%*	-----	----
U ⁺⁴ in Total U	93.9%	Fe ₂ O ₃	0.1%	Fe ₂ O ₃	0.02	0.019	0.018	0.017%	0.016%
Fe	100 ppm*	CaO	0.05%*	Al ₂ O ₃	0.02	0.02	0.02	0.02	0.02
Ni	70 ppm*	SiO ₂	0.1%*	BaO	----	0.001	0.001	0.002	0.003
Si	40 ppm*	Average Particle Size	2 μ	MgO	0.01	0.054	0.09	0.13	0.18
Cr	30 ppm*		----	CaO	0.05	5.1	10.2	15.2	20.2
Cu	1 ppm*		----	H ₂ O ₂	0.006	0.006	0.006	0.005	0.005
Sn	1 ppm*								
Pb	1 ppm*								
B	0.2 ppm*								
O/U Ratio	2.04								
Eulk Density	1.00 gm/cc								
Sinterability Test at 1500°C for 4 Hours	10.36 gm/cc								

* Maximum

** Measured impurity levels in ZrO₂-CaO mixtures

EFFECT OF SINTERING TIME AT 1800°C IN ARGON ON BULK DENSITIES OF ZrO₂-BASE COMPOSITIONS WITH 4 M/O OR 12 M/O UO₂
 (Powder mixtures were milled for 8 hrs and 16 hrs, respectively)

Figure 1

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studies were prepared by these techniques. The samples for property determinations were prepared by modified methods due to the unusual size or shape of these samples. Their preparation will be discussed individually in the appropriate sections of this report.

B. Effects of Furnace Environments

The initial objective of the program was concerned with phase diagram studies to establish the composition limits of single phase, face-centered cubic structures in the ZrO_2 -rich and CeO_2 -rich portions of the UO_2 - ZrO_2 -CaO and UO_2 - CeO_2 systems. At that time, the effects of several furnace environments on sinterability, phase formation and homogeneity of structure of selected compositions in the two ceramic systems were investigated. In addition, this investigation was used as a basis for the development of special techniques which were required in the preparation of a variety of shapes for the determination of physical and thermal properties of these oxide compositions. The tests were conducted in oxidizing (air), reducing (hydrogen) and inert (vacuum or argon) atmospheres at temperatures to 2100°C . Evaluations for phases and microstructures were conducted by X-ray diffraction and microscopy methods.

1. Inert Atmosphere

The initial samples for phase diagram studies on the UO_2 - ZrO_2 -CaO system were prepared by sintering in vacuum at temperatures from 1500 to 1900°C . Samples of the ternary compositions were placed on a stabilized ZrO_2 plate contained in a tantalum boat constructed of 0.005 inch thick tantalum sheet. Sintering was conducted in the Brew Standard 420-B High Vacuum furnace. The vacuum sintering cycle involved heating to the sintering temperature during a three

to four hour period, holding at temperature for times from 2 to 16 hours and cooling to room temperature within a three to four hour period. The furnace pressure was maintained at 5×10^{-3} micron or better during sintering. Temperature measurements were made with a calibrated optical pyrometer.

Due to the high sample losses by volatilization at the elevated temperatures in vacuum, the furnace was modified to allow sintering in inert gases. Argon gas was purified by means of a zirconium chip "gettering" furnace in order to prevent oxidation of the tantalum heater element of the sintering furnace. The samples were initially heated in vacuum to about 1000°C to remove volatile constituents in the samples and container. Following completion of the outgassing process, argon was flowed into the furnace chamber and maintained at a slightly positive pressure during the sintering cycle. It was demonstrated by a series of sintering tests that identical structures were formed for the same compositions by sintering in vacuum or in argon. On the basis that lower losses resulted during sintering in argon than in vacuum, subsequent phase diagram samples of the ZrO_2 -base compositions were sintered in argon.

The UO_2 - CeO_2 samples were placed on a beryllia plate or rhodium metal foil, also contained in a molybdenum or tantalum boat, for sintering in vacuum or in argon at temperatures to 1700°C . All of the CeO_2 -base samples were highly reactive with the container materials constructed from beryllia, zirconia, thorium, tungsten, molybdenum, tantalum and rhodium at temperatures above 1500°C . As a result of high sample losses by volatilization above 1500°C in vacuum or in argon, sample preparation of the CeO_2 -base compositions was limited to several sintering tests at temperatures from 1350° to 1500°C in these furnace environments.

2. Oxidizing Atmosphere

A limited series of ZrO_2 -base samples were air sintered at temperatures to 1550°C in the silicon carbide element resistance furnace. Equivalent weight of U_3O_8 were substituted for UO_2 in the preparation of powder mixtures to avoid crumbling of the pellets during heating by oxidation of UO_2 to U_3O_8 . The samples were heated slowly to the sintering temperature during an 8 hour period, held at temperature from 2 to 16 hours and furnace cooled overnight (16 hours). A series of U_3O_8 - ZrO_2 - CaO samples was heated to 1500°C and air quenched by rapidly removing the samples from the hot zone of the furnace and cooling in still air. All samples except those of the 4, 12 or 15 m/o UO_2 compositions fragmented during cooling in air indicating the high thermal stress resistance of the single phase, low UO_2 compositions.

The majority of the phase diagram samples of the UO_2 - CeO_2 compositions were prepared by air sintering at temperatures of 1400 to 1500°C . The urania starting material was U_3O_8 . As mentioned previously, the CeO_2 -base samples were extremely thermal stress sensitive and precautions of slow heating and cooling rates were taken to prevent cracking and fragmentation of the samples.

3. Reducing Atmosphere

Hydrogen sintering was evaluated on the basis that potential cost advantages may be realized when compared with vacuum or argon sintering. Hydrogen does not react with UO_2 up to the melting point of the oxide and is known to remove excess oxygen with the formation of a stoichiometric oxide upon cooling. An oxygen-deficient structure is reported to be produced for zirconia² by heating in hydrogen. The effects of this structure on the sinterability of

UO₂-CaO stabilized ZrO₂ ternary compositions were evaluated. A limited hydrogen sinterability study was conducted on two CeO₂-base compositions containing 7 m/o and 21 m/o UO₂, respectively.

CaO stabilized ZrO₂-UO₂ (or U₃O₈) samples were contained in a covered molybdenum boat and sintering was conducted in a molybdenum wound alumina tube furnace with a continuous flow of 35 - 45 cubic feet per hour of hydrogen. The majority of the sintering runs utilized as-bottled hydrogen gas. Several runs were made for which the hydrogen was pre-purified to a dew point of minus 60°F using a De-Oxo Molecular Sieve drier and liquid nitrogen cold trap system. The sample boat was moved slowly into the hot zone of the furnace which was maintained at 1100-1200°C to minimize thermal stress cracking of the samples. The furnace temperature was increased at the rate of about 100°C per hour to the sintering temperature, held for 12 to 16 hours at temperature and cooled at the rate of 100-300°C per hour to room temperature. Temperature measurements were made with an optical pyrometer by sighting onto the pellets through a hole in the molybdenum furnace. Four experiments were conducted at 1425, 1525, 1675 and 1750°C, respectively. Sintering time at each of the four temperatures was twelve hours. All samples were furnace cooled to room temperature in hydrogen.

The effects of sintering temperatures on bulk densities are shown in Figures 2, 3, 4, and 5, inclusive. The sintering data on the 1425°C samples indicated that densification increased both with increasing UO₂ contents and with decreasing CaO contents. All compositions containing up to about 20 m/o UO₂ densified only slightly above the green densities. Compositions containing more than about 20 m/o UO₂ showed the improved sinterability with increasing UO₂ contents probably as a result of increasing concentrations of the

highly sinterable UO_2 . Shrinkage showed similar trends with UO_2 content.

The 1525°C samples, with the exception of the 10 m/o CaO series, showed marked improvement in densification. This effect was most pronounced for the low UO_2 compositions which had shown little to no densification at 1425°C . Sinterability behavior at 1675°C was examined as a function of bulk densities containing fixed UO_2 and variable CaO contents. The 4 m/o and 12 m/o UO_2 samples showed either no change or a slight decrease in density with increasing CaO content. This is expected on the basis of substitution of the lower specific gravity CaO for ZrO_2 in these samples. The higher UO_2 samples (containing constant 20, 27 or 38 m/o UO_2) showed improved densification with increasing CaO content. The presence of CaZrO_3 in the 28 and 35 m/o CaO series is believed to act as a sintering aid for the two-phase structures, face-centered cubic solid solution plus CaZrO_3 .

The 1750°C series showed sinterability trends similar to those observed for the 1675°C samples. The low UO_2 compositions of the 10 m/o and 20 m/o CaO series densified at lower rates at 1750°C than at 1675°C . The densities of the high UO_2 compositions with greater than 27 m/o UO_2 decreased after sintering at 1750°C . Samples prepared with UO_2 or U_3O_8 showed similar behavior.

The limited hydrogen sintering study was conducted on samples of two CeO_2 -base compositions containing 7 m/o or 21 m/o UO_2 , respectively. The first series was contained on a BeO plate in the molybdenum boat and was sintered at 1675°C for 16 hours in hydrogen. All pellets were fragmented due to thermal stress although the heating and cooling rates had been maintained at about 100°C per hour. The sample fragments could not be identified with

respect to which composition they originated from and no further evaluations were performed. The second series of duplicate samples with UO_2 and U_3O_8 , respectively, was sintered at 1700°C for 16 hours in hydrogen. The heating and cooling rates were reduced to $50\text{--}75^\circ\text{C}$ per hour. All samples were cracked but not fragmented.

The 7 m/o UO_2 (or U_3O_8) samples showed a higher degree of sensitivity to thermal stress cracking than the 21 m/o UO_2 (or U_3O_8) samples. Control samples of CeO_2 had cracked into several fragments whereas those of UO_2 had sintered to high density with no evidence of cracking. The molybdenum boat was discolored deep blue probably due to Ce_2O_3 vapor deposition.

VARIATION IN SINTERED DENSITY WITH SINTERING TEMPERATURE IN HYDROGEN FOR 10 M/O CaO STABILIZED ZrO_2 SERIES OF UO_2-ZrO_2-CaO COMPOSITIONS

Fig. 2

VARIATION IN SINTERED DENSITY WITH SINTERING TEMPERATURE IN HYDROGEN FOR 20 M/O CaO STABILIZED ZrO_2 SERIES OF UO_2 - ZrO_2 - CaO COMPOSITIONS

Fig. 3

VARIATION IN SINTERED DENSITY WITH SINTERING TEMPERATURE IN HYDROGEN FOR 28 M/O CaO STABILIZED SERIES OF UO_2 - ZrO_2 - CaO COMPOSITIONS

Fig. 4

X 52 M/O UO_2
 □ 35
 △ 27
 ○ 11
 ● 4

VARIATION IN SINTERED DENSITY WITH SINTERING TEMPERATURE IN HYDROGEN FOR 35M/O CaO STABILIZED ZrO_2 SERIES OF UO_2 - ZrO_2 -CaO COMPOSITIONS

Fig. 5

IV. PHASE DIAGRAM STUDIES

C. Isothermal Heat Treatments

A limited phase relationship study was conducted at the start of the program to identify the structures and to roughly outline the phase fields in the ZrO_2 -rich portion of the UO_2 - ZrO_2 - CaO system. The prime objective was the delineation of the single phase, face-centered cubic region in which compositions of nuclear interest occur. On the basis of available information on the binary phase diagrams of UO_2 , ZrO_2 and CaO , an initial group of fourteen compositions, representative of the ZrO_2 -rich ternary region and included in Table II, was investigated. Samples were vacuum or argon sintered at 1500, 1600, 1700, 1800 and 1900°C, respectively, for four hour periods and slowly furnace cooled. Both vacuum and argon sintered samples were used in the subsequent phase diagram studies on the basis that the same compositions developed identical structures by sintering in vacuum or in argon at 1800°C for four hours. Analyses of Debye-Scherrer patterns showed that a continuous series of face-centered cubic solid solutions were produced at temperatures of 1700°C and higher for compositions containing less than about 12 m/o (25 w/o) CaO . Two phase structures, face-centered cubic solid solutions plus CaZrO_3 were observed for compositions prepared with the 28 or 35 m/o (15 or 20 w/o) CaO stabilized ZrO_2 and containing up to about 30 m/o UO_2 . The CaZrO_3 was present also in the two stabilized ZrO_2 starting materials, in agreement with the established ZrO_2 - CaO phase diagram. The quantity of CaZrO_3 remained fixed for a given composition for the range of sintering temperatures employed but was found to decrease with increasing UO_2 content. This diminution in concentration of CaZrO_3 was established to be due to solid state reaction rather than to the dilution effects with UO_2 . A comparison was made of the intensities of the x-ray diffraction maxima

from the CaZrO_3 phase in mechanical mixtures of the same compositions that had been sintered at 1800°C . It was concluded that the observed significantly lower CaZrO_3 intensities for the sintered materials were due to solid state reaction. The CaZrO_3 phase was not observed for all compositions prepared with 28 or 35 m/o CaO stabilized ZrO_2 and containing greater than 30 m/o UO_2 .

A broadening of the diffraction maxima in the composition range of about 12 to 50 m/o UO_2 for samples heated below 1700°C was initially interpreted to mean a possible miscibility gap containing two face-centered cubic solid solutions of similar lattice spacing or to incomplete solid state reactions for the sintering conditions employed. A series of samples was sintered at 1600°C for 21 hours in argon to investigate the effect of longer sintering time on solid state reaction. A comparison of the X-ray films for the same compositions at 1600°C for the normal four-hour period and for twenty-one hours showed significantly sharper Debye lines for the twenty-one hour sintered samples. These evaluations indicated that line broadening was due to incomplete solid state reaction, essentially in agreement with Russian data³ in which minimum times for equilibrium for binary $\text{UO}_2\text{-ZrO}_2$ compositions were two hours at 1900°C and 200 hours at 1500°C . Based upon the above results, subsequent phase diagram studies were conducted on samples which were sintered at 1800°C for four hours in vacuum or in argon since single phase face centered cubic structures were produced by this heat treatment and because this heat treatment would be typical of that used for pellet fabrication. In addition, a selected number of heat treatments were conducted on 1750°C hydrogen sintered samples of the above compositions, at temperatures of 1000, 1300 and 1800°C in argon to investigate the effect of hydrogen versus argon sintering on phase stability.

The thermal stability of the single phase, face-centered cubic structures of the $\text{UO}_2\text{-ZrO}_2\text{-CaO}$ and $\text{UO}_2\text{-CeO}_2$ systems was investigated by a series of long-term annealing heat treatments in argon. The ZrO_2 -base samples were sintered at 1800°C in argon or in vacuum and then annealed for 28 day periods in argon at temperatures of 1000, 1300, 1400 and 1500°C , respectively. Additional sintered samples of the same compositions were argon annealed at 1700°C for seven days; at 1800°C for thirty hours and at 2000°C for twenty-four hours, respectively. The samples were contained on a stabilized ZrO_2 plate contained in high density zircon furnace tubes for temperatures up to 1500°C . The higher temperature heat treatments were conducted in argon in the Brew furnace. The samples were maintained at $\pm 10^\circ\text{C}$ of the desired temperature. Argon of reported purity of 99.995 percent provided an inert atmosphere during the heat treatments. The CeO_2 -base samples were contained on BeO disks during heat treatments at 1300 or 1500°C for 28 days in argon. Due to the high reactivity of these compositions with known refractories, the heat treatments were not extended beyond 1500°C to avoid sample contamination.

The effect of cooling rate on structure of three ZrO_2 -base compositions containing 4, 12 and 15 m/o UO_2 , respectively, was investigated. The first group of samples was rapidly cooled in the Brew furnace from 1800°C in argon. Optical pyrometer measurements showed an average cooling rate of 250°C per minute from 1800°C to about 750°C . No temperature measurements were taken below this value. The second and third groups of samples were slowly cooled overnight (16 hours) from 1500°C and from 1800°C , respectively, in argon. A comparison of X-ray diffraction and microscopy data on these

TABLE II

COMPOSITIONS IN THE UO_2 - ZrO_2 -CaO SYSTEM UNDER INVESTIGATION

Nominal Composition - Mole Percent			CaO Content in Stabilized ZrO_2
UO_2	ZrO_2	CaO	Mole Percent
12	79	9	10
21	71	8	10
4	77	19	20
9	73	18	20
12	71	17	20
15	68	17	20
21	63	16	20
29	57	14	20
38	50	12	20
4	69	27	28
12	62	26	28
21	57	22	28
26	55	19	28
38	44	18	28
4	62	34	35
12	56	32	35
27	47	26	35
35	42	23	35
52	31	17	35

samples indicated that these variations in cooling rates did not effect any significant changes in these single phase cubic structures. On this basis, it was considered reasonable to assume that there was no phase transformations between 1800°C and 1500°C. The region below 1500°C was investigated further by high temperature X-ray diffractometry and is reported elsewhere in this report. Accordingly, all heat treatments were conducted with the consideration that slow cooling in the furnaces did not alter the high temperature structures upon cooling.

D. Evaluation Methods

1. X-Ray Diffraction

The structures of the sintered samples were determined chiefly from X-ray diffraction patterns. The X-ray specimens were selected from the centers of the sintered samples and prepared by grinding in a mortar. The powder was mounted on a fine glass fiber for X-ray analysis. Care was taken to exclude the outer portions of the sintered samples where significant compositional changes may have occurred due to the sintering process. Diffraction patterns were obtained with a North American Philips X-ray diffraction unit using 114 mm Debye-Scherrer camera. Copper K α radiation filtered-through nickel foil was used. The "d" values and intensities of the diffraction peaks were compared with those in the ASTM X-ray powder data cards. Cell dimensions for several compositions in the two ceramic systems were determined by simple calculation from high angle "d" spacing measurements as well as by the Bradly-Jay extrapolation method from both photograms and diffractometer tracings.

2. Microscopy

Microscopic examinations of polished and etched sections of the sintered samples provided useful supplementary information on the identity of structures and on the degree of sinterability. The samples were mounted in room temperature setting epoxy resin and prepared by conventional metallographic techniques of grinding, polishing and chemical etching. Suitable etchants included 45 HNO₃- 5 Hf - 50 H₂O solution for the UO₂-ZrO₂-CaO samples and 50 HNO₃-50 H₂O solution for the UO₂-CeO₂ compositions. Immersion time in the etchant varied from two to thirty minutes, depending upon the composition and microstructure of the samples.

E. Zirconia-Base Isothermal Studies

In order to establish the composition limits for the single phase, face-centered cubic crystal structures near the zirconia rich corner of the UO₂-CaO-ZrO₂ phase system, a series of isothermal heat treatments, described in Section IV-C, was completed. Data obtained by X-ray diffraction and microscopy were used to establish phase boundaries resulting from each isothermal heat treatment.

Data for each heat treatment are presented in individual sections, below. Conclusions based on an analysis of these isothermal heat treatments are presented in Section E-8, below.

1. 1000°C Heat Treatment

Two series of samples were utilized for the phase diagram studies involving 1000°C heat treatments for compositions located in the ZrO_2 rich ternary region. Duplicate samples of the first series were prepared by sintering in vacuum or in argon at 1800°C for four hours prior to the isothermal heat treatment. The phases developed by argon or vacuum sintering are included in Figure 6. One group of these samples was heat treated at 1000°C for twenty-eight days in argon. The second group of the same series was heated in air at 1000°C for twenty-eight days in order to compare structural changes developed in an inert atmosphere with those changes following heating in air. The second series of samples of the same compositions as those of the first series were sintered in hydrogen at 1750°C for sixteen hours, furnace cooled to room temperature, and then reheated in argon at 1000°C for twenty-eight days. The phases formed by hydrogen sintering are shown in Figure 7. The relationships based on vacuum, argon or hydrogen sintered samples and then reheated in argon will be discussed jointly since very similar structures were formed by these heat treatments. The 1000°C heat treatment in air developed complex structures and the isotherm based upon this group of samples will be discussed separately in this section.

a. Heat Treatments in Argon

The general appearance of the phase fields for the ZrO_2 corner for vacuum or argon sintered and 1000°C argon reheated samples is shown in Figure 8.

A similar phase diagram based upon hydrogen sintered and 1000°C argon reheated samples is shown in Figure 9. X-ray diffraction and microscopy evaluation indicated a narrow single phase face centered cubic region for compositions containing from about 15 to 25 m/o CaO and up to a maximum of 12 m/o UO₂. All compositions containing more than 12 m/o UO₂ and less than about 15 m/o CaO formed a two phase region of face centered cubic plus monoclinic solid solutions. A second two phase region, face centered cubic plus CaZrO₃, bounded the upper limits of the single phase cubic and cubic plus monoclinic regions up to about 30 m/o UO₂. The high CaO, high UO₂ region formed complex structures consisting of CaUO₄ and face centered cubic solid solutions.

A typical microstructure of the single phase cubic compositions is shown in Figure 10a. These structures are highly resistant to chemical attack and required up to 30 minutes immersion in the HNO₃-HF-H₂O solution to delineate the grain boundaries. There was no evidence of impurity or decomposition phases for UO₂ contents up to 12 m/o UO₂ as a result of the 1000°C heat treatment in argon. A feather-like grain boundary phase was observed in the 15 m/o UO₂ sample prepared with 20 m/o CaO stabilized ZrO₂ (Figure 10b). At high magnification, the feather-like phase consisted of a very fine precipitate. This phase was identified by x-ray diffraction to be monoclinic ZrO₂ solid solution. The quantity of this phase increased by inward growth toward the center of the grains in the high UO₂ samples (Figure 10c). At the highest composition (38 m/o UO₂) investigated for this series, the monoclinic phase was the major structure containing islands of the cubic phase (Figure 10d). The change in structure from a feather-like

grain boundary phase to a more massive type appears to be determined by the UO_2 content whereas the quantity of this phase is dependent upon the CaO content. The monoclinic phase was rapidly attacked by the etchant resulting in a heavy buildup of reaction products.

The CaZrO_3 phase remained unchanged in appearance and in quantity as a result of the 1000°C argon heat treatment. The twinned structure, shown in Figure 11a, was rapidly etched by the acid solution. Continued immersion to outline the matrix structure resulted in complete removal of the CaZrO_3 phase, as shown in Figure 11b. The quantity and size of the CaZrO_3 decreased with increasing UO_2 content. There was no evidence of decomposition of this phase by solid state reaction with UO_2 during the 1000°C heat treatment.

The structures of the high UO_2 , high CaO compositions were not completely identified and are labeled as complex in Figures 8 and 9. A small amount of a fine precipitate for the 38 m/o UO_2 -22 m/o CaO at the grain boundaries may be CaUO_4 , although this could not be confirmed by x-ray diffraction. The precipitate for the 29 m/o UO_2 -14 CaO composition resembles that of the monoclinic phase observed in the 10 m/o CaO samples, and again this could not be confirmed by x-ray diffraction.

b. Heat Treatment in Air

The phase fields based on 1800°C argon sintered and then 1000°C air reheated samples is shown in Figure 12. The same group of 12 samples was removed from the furnace after accumulative heat treatments of 4, 7, 17 and 28 days, respectively, for visual examinations and weight and dimensional measurements. All samples remained intact for the 28 day heat treatment.

The low UO_2 (4 to 12 m/o) samples developed a tan to brown discoloration after the first 4 days heat treatment in air with no further changes in surface appearance for the remainder of the test period. The surfaces of the high UO_2 (21 to 38 m/o) samples remained a uniform grey color during the entire 28 day period. Density, shrinkage and weight change data are presented below. Similar measurements for argon heat treatments revealed insignificant changes.

(1) Density

The low UO_2 (4 to 12 m/o) compositions showed very slight increases of 2 to 4 percent after the first 4 days followed by no significant changes for the remainder of the 28 day period. The high UO_2 (21 to 38 m/o) samples showed slight increases and decreases of 1 to 3 percent after the first 4 days with no further changes for the remainder of the test period.

(2) Shrinkage

The low UO_2 samples showed minor variations of 0.1 to 0.2 percent in diametrical shrinkage whereas the high UO_2 samples expanded diametrically from 1.5 to 4.6 percent during the first 4 day heat treatment. There were no additional changes in the dimensions of all samples after the 28 day heat treatment.

(3) Weight Loss

The low UO_2 samples remained unchanged in weight during the 28 day heat treatment. The high UO_2 samples gained from 1 to 3 percent in weight during the first 4 days followed by minor weight variations for the remainder of

the test period.

Figure 12 shows further that the low UO_2 compositions have a high degree of structural stability in a high temperature oxidizing environment. The compositional range of the single phase face centered cubic region remained unchanged from that for the as-sintered sample with stable single phase structures for UO_2 contents to 12 m/o. This was confirmed by complete absence of minor phases by microscopy examinations. The two phase regions located on either side of the single phase cubic region exhibited similar stability of structures for compositions containing up to about 20 m/o UO_2 . Both second phases, CaZrO_3 and monoclinic, respectively, remained unchanged in appearance and formed sharp x-ray diffraction maxima. The five compositions located in the high UO_2 region developed complex structures that were not completely defined. Two of these compositions located near the two phase, face centered cubic plus CaZrO_3 field showed similar x-ray patterns which were indexed as follows:

- a. CaUO_4 (major phase)
- b. CaZrO_3 (minor phase)
- c. Face center cubic (minor phase)

The three compositions of lower CaO content are located near the face centered cubic plus monoclinic phase field. The x-ray patterns for these compositions are similar to each other but different from those of the two previous compositions. Phases identified include:

- a. Monoclinic solid solution (major phase)
- b. Hexagonal U_3O_8 (minor phase)
- c. Unknown minor phase indexed as BCC with an approximate lattice constant of 10.7Å

The multiphase structures were not delineated by the normal etching methods since heavy reaction products formed very rapidly for a large group of etchants investigated.

2. 1300°C Heat Treatment

The phase diagrams based on samples sintered in argon or in hydrogen and then reheated at 1300°C in argon, are shown in Figures 13 and 14. In general, the phase fields resemble those observed for the 1000°C heat treated argon atmosphere samples. The single phase cubic region includes compositions containing from 15 to 25 m/o CaO and up to 12 m/o UO₂. Structures for this composition range exhibited a high degree of thermal stability as evidenced by the complete absence of minor phases. The two phase field of face centered cubic plus CaZrO₃ has become more restrictive with a maximum UO₂ content of 10 m/o as compared to 12 m/o UO₂ for the 1000°C isotherms. The first evidence of thermal instability for the high CaO compositions is noted in the 12 m/o UO₂ samples which were hydrogen sintered and contained 25 and 31 m/o CaO, respectively. Figure 15 shows the partial decomposition of the CaZrO₃ phase by reaction with the face centered cubic matrix. The fine precipitate surrounding the CaZrO₃ phase was identified as CaUO₄ by x-ray diffraction. The 12 m/o UO₂ samples with the higher CaO content had developed the greater amount of the CaUO₄ phase. On this basis, a three phase field of face centered cubic plus CaZrO₃ plus CaUO₄ was located within a narrow region between about 8 and 11 m/o UO₂. The higher CaO compositions containing from about 13 to 35 m/o UO₂ are grouped in a single region for which unidentified multiphase structures were observed microscopically. The structure of the 15 m/o UO₂ composition in this region was two phase,

face centered cubic plus CaUO_4 , with no evidence of CaZrO_3 . The 21 m/o UO_2 samples contained islands of a duplex structure resulting from the decomposition of CaZrO_3 (Figure 16). The structure of the 29 m/o UO_2 sample consisted of a fine precipitate within the grains of the single phase matrix (Figure 17). Identity of these minor phases was not established by x-ray diffraction which revealed only single phase face-centered cubic structures. An x-ray pattern for a portion of the microscopy sample also showed an identical single phase cubic structure. The inability of the x-ray technique to detect these minor phases is attributed to their small volumes (less than 5 v/o) in the samples. The general appearance and etching characteristics of the fine precipitate in the 29 m/o UO_2 sample strongly suggest a monoclinic phase although this could not be confirmed. However, the presence of the monoclinic phase in the form of a massive precipitate (Figure 18) for the adjacent 38 and 52 m/o UO_2 compositions tends to support this view. These compositions are the upper limit of a broad face-centered cubic plus monoclinic phase field which included all low CaO compositions except those included in the single phase cubic region.

3. 1500°C Heat Treatment

The phase diagram based on 1800°C argon sintered and then 1500°C argon reheated samples, included in Figure 19, shows an interesting departure from the 1000 and 1300°C diagrams argon atmosphere. The single phase face centered cubic phase field has become more extensive occupying a continuous band of compositions ranging from 15 to 25 m/o CaO and including the 52 m/o UO_2 composition. The two phase field of face centered cubic plus CaZrO_3 has increased to include the 12 m/o UO_2 composition as was observed for the

1000°C isotherms. There was no evidence of decomposition of CaZrO_3 for any of the samples and the complete absence of CaUO_4 and other decomposition phases. The high UO_2 , high CaO compositions were established as single phase cubic by both x-ray diffraction and microscopy analyses. Similarly, the two phase face centered cubic plus monoclinic region occurred only for those compositions containing less than 15 m/o CaO . The monoclinic structure resembled that observed for the same compositions following the 1000°C argon heat treatment. None of the samples receiving the 1500°C argon heat treatment showed evidence of CaUO_4 or other decomposition products both by x-ray and microscopy evaluations.

It is postulated that the extensive phase field noted for the single FCC structure will extend over to the UO_2 corner and is thus indicative of complete solid solubility over the entire range of UO_2 compositions bounded by a narrow range of CaO compositions.

4. 1700°C Heat Treatment

This group of samples were sintered at 1800°C in argon and then reheated at 1700°C in argon for 7 days. The phase field is shown in Figure 20. The 1700°C heat treatment extended the single phase cubic region to include all compositions containing less than about 15 m/o CaO . The only two phase field of face centered cubic plus CaZrO_3 is of the same magnitude as was observed for the 1500°C isotherm. No other second phases were detected in any other samples with the exception of the CaZrO_3 . A comparison of the 1500° and 1700°C isotherms indicates a maximum temperature stability for the monoclinic phase at approximately 1600°C. Heating above this temperature

resulted in single phase cubic structures regardless of the CaO contents in the range of compositions investigated. All of the single phase cubic samples exhibited a high degree of resistance to chemical attack by the acid etchants similar to that noted for the low UO_2 single phase samples.

5. 1800°C Heat Treatment

Phase relationships presented in Figures 21 and 22, are based upon argon or hydrogen sintered samples which were reheated at 1800°C for 30 hours in argon. Both diagrams contain identical phase fields of face centered cubic and face centered cubic plus CaZrO_3 . These diagrams resemble very closely the diagrams determined from the as sintered samples and shown in Figures 6 and 7. The essential difference between the 1700° and 1800°C phase diagrams is found in the more extensive face centered cubic plus CaZrO_3 region in the 1800°C isotherms. This may be attributed to the stabilization of the CaZrO_3 phase at higher UO_2 contents at 1800°C. Again, no minor phases were observed for these groups of heat treated samples.

6. 2000°C Heat Treatment

A final group of 1800°C argon sintered samples were reheated at 2000°C for 24 hours in argon. Phase relationships based on these samples are shown in Figure 23. X-ray diffraction and microscopy evaluations showed good agreement of phase identification of the face centered cubic and CaZrO_3 structure. As in the case of the 1700° and 1800°C argon reheated samples, there was no indication of minor phases other than that of CaZrO_3 . These data confirm further the complete thermal stability of the low CaO, single phase cubic structures at temperatures above about 1600°C in argon.

It is concluded from these investigations that thermally stable, single phase, face centered cubic solid solutions are formed for ternary compositions containing less than 12 m/o UO_2 and 15 to 25 m/o CaO .

LEGEND

- - FCC
- - FCC + CaZrO_3

PHASES PRESENT AT ROOM TEMPERATURE IN THE UO_2 - ZrO_2 - CaO SYSTEMS FOR COMPOSITIONS SINTERED AT 1800°C IN ARGON OR IN VACUUM

Figure 6

LEGEND

- - FCC
- - FCC + CaZrO_3

PHASES PRESENT AT ROOM TEMPERATURE IN THE UO_2 - ZrO_2 - CaO SYSTEM FOR COMPOSITIONS SINTERED AT 1750°C IN HYDROGEN

Figure 7

LEGEND

- - FCC
- - FCC + CaZrO_3
- △ - FCC + MONOCLINIC
- ▲ - FCC + CaUO_4

PHASES PRESENT AT ROOM TEMPERATURE IN THE $\text{UO}_2\text{-ZrO}_2\text{-CaO}$ SYSTEM FOR COMPOSITIONS SINTERED AT 1800°C IN ARGON AND THEN REHEATED AT 1000°C IN ARGON FOR 28 DAYS

Figure 8

LEGEND

- - FCC
- - FCC + CaZrO_3
- Δ - FCC + MONOCLINIC
- ▲ - FCC + CaUO_4

PHASES PRESENT AT ROOM TEMPERATURE IN THE $\text{UO}_2\text{-ZrO}_2\text{-CaO}$ SYSTEM FOR COMPOSITIONS SINTERED AT 1750°C IN HYDROGEN AND THEN REHEATED AT 1000°C IN ARGON FOR 28 DAYS

Figure 9

10a
4 TO 12 M/O UO_2
SINGLE-PHASE FACE-CENTERED
CUBIC STRUCTURE

10b
21 M/O UO_2
FEATHER-LIKE GRAIN BOUNDARY PHASE IN
FACE CENTERED CUBIC MATRIX

10c
29 M/O UO_2
MASSIVE GRAIN BOUNDARY PHASE IN
FACE-CENTERED CUBIC MATRIX

10d
38 M/O UO_2
MASSIVE AGGREGATION OF FINE
PRECIPITATE IN FACE-CENTERED
CUBIC MATRIX

NOTE

ALL MAGNIFICATIONS ARE 500 X

**MICROSTRUCTURES OF UO_2 - ZrO_2 - CaO COMPOSITIONS FOLLOWING
ANNEALING HEAT TREATMENT AT $1000^\circ C$ FOR 28 DAYS IN ARGON**

Figure 10

MAG. 500 X

**Figure 11a - VIEW OF TWINNED STRUCTURE OF THE CaZrO_3 PHASE
FOR THE TWO PHASE $\text{UO}_2\text{-ZrO}_2\text{-CaO}$ COMPOSITIONS**

MAG. 500 X

**Figure 11b - VIEW OF STRUCTURE SHOWN IN Figure 11a FOLLOWING
SEVERE ETCHING TO OUTLINE THE MATRIX GRAIN
BOUNDARIES**

Figure 11

LEGEND

- - FCC
- - FCC + CaZrO_3
- △ - FCC + MONOCLINIC
- - MONOCLINIC + U_3O_8 + BCC
- - FCC + CaUO_4 + CaZrO_3

PHASES PRESENT AT ROOM TEMPERATURE IN THE $\text{UO}_2\text{-ZrO}_2\text{-CaO}$ SYSTEM FOR COMPOSITIONS SINTERED AT 1800°C IN ARGON AND THEN REHEATED AT 1000°C FOR 28 DAYS IN AIR

Figure 12

LEGEND

- FCC
- FCC + CaZrO_3
- △ FCC + MONOCLINIC
- ▲ FCC + CaUO_4
- FCC + CaZrO_3 + CaUO_4
- ▼ FCC + CaZrO_3 DECOMPOSITION PRODUCTS

PHASES PRESENT AT ROOM TEMPERATURE IN THE UO_2 - ZrO_2 - CaO SYSTEM FOR COMPOSITIONS SINTERED AT 1800°C IN ARGON AND THEN REHEATED AT 1300°C IN ARGON FOR 28 DAYS

Figure 13

LEGEND

- — FCC
- — FCC + CaZrO_3
- △ — FCC + MONOCLINIC
- ▲ — FCC + CaUO_4
- — FCC + CaZrO_3 + CaUO_4
- ▼ — FCC + DECOMPOSITION PRODUCTS

PHASES PRESENT AT ROOM TEMPERATURE IN THE UO_2 - ZrO_2 - CaO SYSTEM FOR COMPOSITIONS SINTERED AT 1750°C IN HYDROGEN AND THEN REHEATED AT 1300°C IN ARGON FOR 28 DAYS

MAG. 500X

ETCHED

STRUCTURE OF THE 12 M/O UO_2 , HIGH CaO
COMPOSITIONS SHOWING THE DECOMPOSITION
PRODUCT, $CaUO_4$

Figure 15

MAG. 500X

ETCHED

MULTIPHASE STRUCTURE FOR THE
HIGH CaO COMPOSITIONS CONTAINING
21 M/O UO_2

Figure 16

MAG. 500X

ETCHED

*MULTIPHASE STRUCTURE FOR THE HIGH CaO
COMPOSITIONS CONTAINING 29 M/O UO₂*

Figure 17

MAG. 500X

ETCHED

*TWO PHASE STRUCTURE, FACE-CENTERED CUBIC PLUS
MONOCLINIC, FOR THE HIGH CaO COMPOSITIONS
CONTAINING 38 M/O TO 52 M/O UO₂*

Figure 18

LEGEND

- — FCC
- △ — FCC + CaZrO_3
- — FCC + MONOCLINIC

PHASES PRESENT AT ROOM TEMPERATURE IN THE UO_2 - ZrO_2 - CaO SYSTEM FOR COMPOSITIONS SINTERED AT 1800°C IN ARGON AND THEN REHEATED AT 1500°C IN ARGON FOR 28 DAYS

Figure 19

PHASES PRESENT AT ROOM TEMPERATURE IN THE UO_2 - ZrO_2 - CaO SYSTEM FOR COMPOSITIONS SINTERED AT 1800°C IN ARGON AND THEN REHEATED AT 1700°C IN ARGON FOR 7 DAYS

LEGEND

- O - FCC
- - FCC + CaZrO_3

PHASES PRESENT AT ROOM TEMPERATURE IN THE UO_2 - ZrO_2 - CaO SYSTEM FOR COMPOSITIONS SINTERED AT 1750°C IN HYDROGEN AND THEN REHEATED AT 1800°C IN ARGON FOR 30 HOURS

Figure 21

LEGEND

- — FCC
- — FCC + CaZrO_3

PHASES PRESENT AT ROOM TEMPERATURE IN THE UO_2 - ZrO_2 - CaO SYSTEM FOR COMPOSITIONS SINTERED AT 1800°C IN ARGON AND THEN REHEATED AT 1800°C IN ARGON FOR 30 HOURS

Figure 22

LEGEND

- - FCC
- - FCC + CaZrO_3

PHASES PRESENT AT ROOM TEMPERATURE IN THE UO_2 - ZrO_2 - CaO SYSTEM FOR COMPOSITIONS SINTERED AT 1800°C IN ARGON AND THEN REHEATED AT 2000°C IN ARGON FOR 24 HOURS

Figure 23

F. Ceria-Base Phase Studies

A limited investigation was undertaken to determine the effect of various sintering and heat treating parameters on the phases found in the $\text{UO}_2\text{-CeO}_2$ system. The purpose of this investigation was to verify the existence of single phase, face-centered cubic solid solutions over the range of compositions of interest to this program and to determine the limiting UO_2 content for retention of a single phase structure.

Although much of the later work on the program was concentrated in the area of air fired samples, earlier investigations were concerned with hydrogen, vacuum and argon sintering atmospheres. Each of these areas is discussed below.

1. Initial Investigations

The initial effort on the program was concentrated on investigations of 14 and 30 m/o $\text{UO}_2\text{-CeO}_2$ compositions (containing both UO_2 and U_3O_8 as initial starting materials) which were sintered in air, vacuum, and argon at temperatures of 1350°C to 1550°C . Results of X-ray diffraction analyses indicated single phase, face-centered cubic crystal structures for both compositions after air firing at 1375°C and 1550°C for three and four hours, respectively, and after vacuum sintering at 1350°C for three hours. These results were confirmed by microscopic examination as shown in Figure 24. Samples of both compositions which were vacuum sintered at 1500°C for three hours, or argon sintered at 1400°C for three hours, exhibited two face-centered cubic crystal structures. The lattice parameters for these two face-centered cubic phases were comparable to those anticipated for a ceria

base solid solution and an oxygen deficient ceria base solid solution (higher lattice constant with less oxygen). The prospect of an incomplete reaction is difficult to assume on the basis that these structures were found also after sintering in vacuum at 1500°C for the same period of time that a single phase face-centered cubic structure was formed in the same environment at 1350°C .

At this early stage in the program, the results for air sintering with U_3O_8 as a starting material are of significant interest since these conditions probably represent the most economical approach to producing fuel pellets. Although additional investigations of other sintering atmospheres were undertaken, the importance of the air sintering method was emphasized later in the program and almost all of the effort in the latter stages of this investigation was concentrated on air-fired samples.

2. Hydrogen Sintering

A limited investigation of the influence of hydrogen sintering on solid solution formation was undertaken. Samples containing 7 and 21 m/o UO_2 (or equivalent U_3O_8) were sintered in hydrogen at 1700°C for sixteen hours with heating and cooling rates of 50° to 75°C per hour. Even with this low a heating and cooling rate, all samples exhibited a great tendency toward fracturing, probably as a result of the volume changes induced from the formation of lower oxides of cerium as a result of hydrogen sintering. Samples containing U_3O_8 exhibited higher bulk densities than those containing UO_2 , probably as a result of a greater inhibition to the formation of an oxygen deficient structure.

Typical microstructures of the ceria base samples, containing 0, 7, and 21 m/o UO_2 (or equivalent U_3O_8) are shown in Figures 25, 26, and 27. The microstructure (Figure 25) of the CeO_2 sample indicates a Widmanstätten structure as well as a discontinuous grain boundary phase. These minor phases are lower oxides of ceria, typical of those found in an investigation⁴ of the CeO_2 - Ce_2O_3 system. Additions of 7 m/o UO_2 (or U_3O_8) eliminated the Widmanstätten structure and diminished the massiveness of the grain boundary constituent. Addition of 21 m/o UO_2 (or U_3O_8) completely eliminated both constituents from the microstructure and formed an apparent single-phase solid solution. However, X-ray diffraction results indicate small remnants of substoichiometry resulting in wide diffraction lines. At this time, it is significant to note that a decrease in fracture and cracking tendency was observed with increasing UO_2 (or U_3O_8) content. This observation is consistent with the above results indicating less volume transformation to lower oxides with increasing UO_2 content.

The following conclusions were based upon the above investigation:

- a. UO_2 (or U_3O_8), in sufficient concentrations, can suppress the formation of lower oxides of ceria during sintering in a strongly reducing atmosphere such as hydrogen.
- b. Single phase, face-centered cubic structures were not produced by hydrogen sintering compositions of interest to this program.
- c. All samples exhibited a great tendency toward fragmentation and cracking. This tendency decreased with increased UO_2 (or U_3O_8) concentration as a result of inhibition to the formation of lower oxides.

3. Argon Sintering

Ceria base pellets, containing 7 and 21 m/o UO_2 were cold pressed from milled powder mixtures and presintered in vacuum at 1000°C . Pellets of both compositions were sintered at 1400, 1600, 1700 and 1800°C , respectively, for four hours in a flowing prepurified argon atmosphere. X-ray diffraction photograms for samples which were sintered in the temperature range of 1400° to 1700°C revealed a series of doublet lines typical of those described in Section F-1 as resulting from a ceria rich solid solution and an oxygen deficient ceria-base solid solution. The lattice parameter of one of the phases was very close to the value of $5.496 \text{ \AA}$ reported⁵ for an o/Ce ratio of 1.9. At 1800°C there was a marked tendency toward the formation of a single cubic phase, although, the diffraction lines were relatively broad.

Results of air sintering investigations followed by long time heat treatments in an argon atmosphere (see section 4, below) demonstrate good stability for the single phase, face-centered cubic crystal structure, once formed, in an argon atmosphere. Thus, the influence of an argon atmosphere during sintering is probably related to the removal of oxygen from CeO_2 prior to the formation of the stable solid solution. The formation of a near single phase structure after argon sintering at 1800°C is probably related to enhanced solid solution of the oxygen deficient ceria phase in the ceria rich solid solution.

On the bases of these data as well as the results obtained in hydrogen and in vacuum, the emphasis on the rest of the program was placed on air sintering investigations.

4. Air Sintering

Pellets of the compositions shown in Table III were prepared by air firing compacts, containing equivalent weights of U_3O_8 for UO_2 , at 1500° to $1550^\circ C$. A series of isothermal heat treatments was conducted on the air fired compacts at 1300 and $1500^\circ C$, respectively, for 28 day-periods in argon and at $1700^\circ C$ for four days in argon. Results of X-ray diffraction analyses, shown on Table III are plotted in Figure 28, together with data obtained from the literature.

Examination of data for the air fired samples prior to isothermal heat treatment revealed a variation in lattice constant with increased UO_2 content as plotted in Figure 28. Hund, Wagner and Peetz⁶ found a two phase region for UO_2 compositions in excess of 63 m/o. They reported a face-centered cubic phase with a lattice parameter of $5.441 \text{ \AA}$ as well as U_3O_8 . The results of the present investigation indicate the retention of the single-phase, face-centered cubic crystal structure for solid solutions containing up to 30 m/o UO_2 . At 50 m/o UO_2 , a two phase region is found and consists of two distinct face-centered cubic phases. The lattice parameter for one of these phases is relatively insensitive to UO_2 content whereas the lattice parameter of the other cubic phase is sensitive to UO_2 content. Further evaluation of the data indicate a high probability that the two-phase structure originates between 21 and 30 m/o UO_2 . The data for the 30 m/o sample is probably an average of two lattice constants, one at $5.425 \text{ \AA}$ and another at a value slightly higher than the $5.432 \text{ \AA}$ noted on Figure 28 for this composition. It is significant that extreme broadening of the back reflection lines was found for this

particular sample, indicative of the possible presence of two face-centered cubic structures of almost identical lattice constants. The probable origin of these two face-centered cubic phases will be discussed later in this Section of the report.

Samples which were isothermally annealed for periods up to 28 days in argon at temperatures up to 1500°C exhibited no change in crystal structure with only minor changes in lattice constants. Samples which were annealed at 1700°C in argon had reacted with the BeO container and it is believed that this reaction caused the broad diffraction peaks noted for these samples.

In an attempt to assess the influence of oxygen-rich and oxygen deficient (argon) atmospheres on phase equilibria in the $\text{UO}_2\text{-CeO}_2$ system, a series of heat treatments were conducted. These investigations were aimed at following the progression of oxygen pickup as a function of UO_2 content (added as equivalent U_3O_8). Pellets containing 14, 21, 30, 50 or 73 m/o UO_2 in CeO_2 were air fired at 1500°C for 8, 36 and 130 hours, respectively. A second series of pellets of the same compositions was air fired at 1500°C for eight hours and then reheated in argon for 130 hours at 1500°C.

A third series of pellets of selected compositions was triple air fired at 1500°C with the introduction of a crushing and mixing operation as well as X-ray diffraction analyses after each of the first two firings. The total sintering time was twelve hours and the third sinter was followed by an argon anneal at 1500°C with X-ray diffraction analyses before and after annealing.

The first series of pellets, containing 21 m/o UO_2 or less, exhibited sharp X-ray diffraction maxima after air firing at 1500°C for 8, 36 or 130 hours. Compositions with 30 m/o or higher UO_2 showed a trend toward a two phase structure, as evidenced by diffused diffraction peaks. A two phase structure, similar to that reported above for the 30, 50 and 73 m/o UO_2 concentrations of 30 m/o or greater and after 130 hours of exposure in air. Again, the lattice constant of $5.427 \text{ \AA}$ found for this second face-centered cubic phase was invariant with UO_2 content.

Data pertinent to this series of samples are included in Table IV and lattice constants as a function of UO_2 content are plotted in Figure 29. Although all curves tend to overlap, it is significant that the data for argon heat treatments are closest to those for the shortest air firing times, indicating that oxygen pickup and not time is the important parameter responsible for the differences between 8, 36 and 130 hour sintering times in air. Further substantiation of this behavior for these compositions was obtained during triple sintering and crushing investigations in which X-ray diffraction patterns were becoming more diffuse with each successive sinter. Subsequent heat treatment at the same temperature of 1500°C in argon removed all traces of line broadening. On this basis, it is believed that a hyperstoichiometric solid solution phase was formed after extensive heat treatment in air at 1500°C .

The stability of the single phase cubic structures with 21 m/o or less UO_2 may be associated with the stabilization of the U^{+4} ion by ceria which is present as the major constituent. For UO_2 compositions of 30 m/o or greater, the ability of ceria to stabilize the solid solution against oxidation

may become diminished. Thus, the formation of the second face-centered cubic phase, with extended heat treatment in air, may be explained on the basis of oxygen pickup to form a ternary system, $\text{UO}_2\text{-CeO}_2\text{-O}$, containing solid solution phases $(\text{U,Ce})\text{O}_2$ and $(\text{U,Ce})\text{O}_{2-x}$. The postulated ternary system would be required to contain a two phase field such that variation in oxygen content will permit a given composition to cross a number of tie lines. These tie lines must be oriented in such a fashion that the location of one of the tie lines is greatly dependent upon UO_2 content, whereas the location of the other end of the tie line is almost invariant with respect to UO_2 composition. Such a scheme would be consistent with the data obtained to date for the air fired samples in which two phases, when formed, exhibit different lattice constants, one of which appears to be invariant with UO_2 content and the other dependent upon UO_2 content. This hypothetical diagram would explain the single and two-phase, face-centered cubic structures developed as a function of air firing (oxidation) and the subsequent removal of oxygen by heating in argon with the subsequent return to single phase, face-centered cubic structures. Air firing the low UO_2 compositions for 8 or 36 hours resulted in too low an oxygen pickup to permit the ternary composition to enter the two phase field. However, even after 8 hours in air, the higher UO_2 compositions showed evidence of entering the two phase field. Heating in air for 130 hours allows sufficient oxygen pickup to move all compositions with the exception of that containing 14 m/o UO_2 , into the two phase region.

Although further investigation of the ternary system would represent an interesting venture, it is outside of the scope of this program. The above results have shown single phase, face-centered cubic crystal structure is

obtained by air firing $\text{UO}_2\text{-CeO}_2$ compositions containing at least 21 m/o UO_2 (added as U_3O_8) and representing the limit of interest for this program.

Furthermore, the long term thermal stability of this single phase face-centered cubic structure was demonstrated for temperatures up to 1500°C and for time up to 28 days in argon, used as a substitute for helium normally loaded into fuel elements of this type.

TABLE III

X-RAY DIFFRACTION DATA FOR $\text{UO}_2\text{-CeO}_2$ COMPOSITIONS

UO ₂ Content m/o	Heat Treatment	Number of Phases	Appearance of X-Ray Pattern	Lattice o Constant-A
14	1500°C - 8 hours - air	1 FCC	Sharp	5.416
21	1500°C - 8 hours - air	1 FCC	Slightly diffused	5.420
30	1500°C - 8 hours - air	1 FCC	Slightly diffused	5.430
50	1500°C - 8 hours - air	1 FCC	Slightly diffused	5.443
73	1500°C - 8 hours - air	1 FCC	Highly diffused	5.455
14	1500°C - 36 hours - air	1 FCC	Sharp	5.417
21	1500°C - 36 hours - air	1 FCC	Slightly diffused	5.423
30	1500°C - 36 hours - air	1 FCC	Slightly diffused	5.430
50	1500°C - 36 hours - air	1 FCC	Slightly diffused	5.438
73	1500°C - 36 hours - air	1 FCC	Highly diffused	---- *
14	1500°C - 130 hours - air	1 FCC	Sharp	5.415
21	1500°C - 130 hours - air	1 FCC	Slightly diffused	5.420
30	1500°C - 130 hours - air	2 FCC	Slightly diffused	(5.427 5.430
50	1500°C - 130 hours - air	2 FCC	Slightly diffused	(5.427 5.440
73	1500°C - 130 hours - air	2 FCC	Highly diffused	---- *
14	All samples air fired at 1500°C for 8 hours and then reheated at 1500°C for 130 hours in argon.	1	Sharp	5.417
21		1	Sharp	5.424
30		1	Sharp	5.430
50		1	Sharp	5.442
73		1	Sharp	5.452

* Patterns too diffused for determination of lattice constants.

TABLE IV

X-RAY DIFFRACTION DATA FOR AIR FIRED UO_2 - CeO_2 COMPOSITIONS

Composition m/o UO_2^* m/o CeO_2		History	Phases	Lattice Parameter
0	100	Starting Material, As-Received	FCC	5.411
0	100	Starting Material, Air Fired 1300°C for 3 Hours	FCC	5.411
7	93	Air Fired 1500°C - 60 Hours	FCC	5.415
7	93	Air Fired 1500°C - 24 Hours + 28 Days in Argon at 1300°C	FCC	5.413
7	93	Air Fired 1500°C - 24 Hours + 4 Days in Argon at 1700°C	FCC**	5.427
14	86	Air Fired 1375°C - 3 Hours	FCC	5.419
14	86	Air Fired 1550°C - 4 Hours	FCC	5.419
14	86	Air Fired 1500°C - 68 Hours	FCC	5.419
14	86	Air Fired 1500°C - 4 Hours + 28 Days in Argon at 1000°C	FCC	5.418
14	86	Air Fired 1550°C - 4 Hours + 28 Days in Argon at 1300°C	FCC	5.419
14	86	Air Fired 1500°C - 4 Hours + 28 Days in Argon at 1500°C	FCC	5.418
14	86	Air Fired 1500°C - 4 Hours + 4 Days in Argon at 1700°C	FCC**	5.426
21	79	Air Fired 1500°C - 60 Hours	FCC	5.426
21	79	Air Fired 1500°C - 24 Hours + 28 Days in Argon at 1300°C	FCC	5.421
21	79	Air Fired 1500°C - 24 Hours + 4 Days in Argon at 1700°C	FCC**	5.427

* Added as equivalent U_3O_8

** Back reflection lines broad

TABLE IV

(Continued)

Composition m/o UO_2 m/o CeO_2		History	Phases	Lattice Parameter
30	70	Air Fired 1375°C - 3 Hours	FCC***	5.432
30	70	Air Fired 1550°C - 4 Hours	FCC**	5.432
30	70	Air Fired 1500°C - 4 Hours + 28 Days in Argon at 1000°C	FCC	5.424
30	70	Air Fired 1550°C - 4 Hours + 28 Days in Argon at 1300°C	FCC	5.428
30	70	Air Fired 1500°C - 4 Hours + 28 Days in Argon at 1500°C	FCC	5.427
30	70	Air Fired 1500°C - 4 Hours + 4 Days in Argon at 1700°C	FCC**	5.432
50	50	Air Fired 1500°C - 16 Hours	2 FCC	(5.425) (5.438)
73	27	Air Fired 1500°C - 16 Hours	2 FCC	(5.426) (5.453)

* Added as equivalent U_3O_8

** Back reflection lines broad

*** Back reflection lines sharper than for 1550°C fired

ETCHED

MAG. 500X

Fig.24 - SINGLE PHASE STRUCTURE TYPICAL FOR THE
 $\text{UO}_2 - \text{CeO}_2$ COMPOSITIONS UNDER INVESTIGATION

MAG 500 X

ETCHED

STRUCTURE OF CERIUM OXIDE CONTROL SPECIMEN SINTERED
AT 1700°C IN HYDROGEN

Fig. 25

MAG 500 X

ETCHED

STRUCTURE OF 7M/O UO_2 (AS U_3O_8) - 93M/O CeO_2

COMPOSITION DEVELOPED BY SINTERING AT 1700°C IN
HYDROGEN

Fig. 26

MAG 500 X

UNETCHED

STRUCTURE OF 21 M/O UO_2 (AS U_3O_8) - 79 M/O CeO_2
COMPOSITION SINTERED AT 1700°C IN HYDROGEN

Fig. 27

LATTICE CONSTANT - COMPOSITION
RELATIONSHIPS ON THE $UO_2 - CeO_2$
SYSTEM

Figure 28

LATTICE CONSTANT-COMPOSITION
RELATIONSHIPS ON THE UO_2 - CeO_2 SYSTEM

Figure 29

G. High Temperature X-Ray Diffraction Investigations

Early in the program, it was demonstrated that identical single-phase structures may be developed by either very rapid cooling ($20,000^{\circ}\text{C}/\text{hour}$) or by slow cooling (100°C per hour) in the furnace from the sintering temperature of 1800°C . A series of isothermal sections from 1000 to 2000°C was constructed upon the assumption that the cubic structures do not undergo a polymorphic transformation at temperatures below their melting points. In order to confirm the thermal stability of these cubic structures at elevated temperatures and to determine the thermal expansion coefficients of selected oxide compositions, a high temperature X-ray diffraction furnace and specimen holder were designed and constructed for this program.

A view of the furnace and the housing is shown in Figure 30. The system is attached to a standard diffractometer head which contains the drive motor and gearing for proper scanning rotation of the sample and the Geiger counter. The housing, machined from a single piece of brass, contains a series of water channels for internal cooling during elevated temperature operation. A hollow spindle extends through the rotating center shaft of the diffractometer and serves the dual purposes of supporting the housing and furnishing an air evacuation line to the housing. Two circumferential beryllium windows, 0.010 inch in thickness, each covers about 90 degrees of arc. The furnace is constructed as a single removable unit and consists of an inner resistance element of tantalum sheet, and two heat shields also of tantalum sheet. The sample holder is in the form of a cantilever paddle, machined from high density stabilized ZrO_2 , and is located within the furnace. The flat plate sample, $3/8 \times 3/4 \times 1/8$ inch in dimensions, is contained in a pocket at the free end of the paddle.

The root of the paddle is attached to a shaft extending through the rear of the housing. A lever attached to the shaft allows mechanical alignment of the sample. An axial tube located in the front cover of the housing contains a sight port with a magnetically operated rotating shutter. Temperature measurements with an optical pyrometer and direct observations of the sample are made by sighting through a telescope mounted to the base table which supports the diffractometer.

To obtain satisfactory diffraction data, it is essential that the sample be accurately positioned with regard to the diffractometer geometry. The two prime requirements are that the sample plane lies on the axis of rotation and that the sample plane has the correct angular alignment about this axis. The first element of alignment is accomplished by rotation of the sample plane through a small arc into coincidence with the axis of rotation of the diffractometer. The second element of sample alignment, adjustment of angular orientation of the sample plane, is accomplished by rotating the entire housing with respect to the central shaft of the diffractometer. The telescope is adjusted so that the image of its cross hair intersection falls upon the axis of rotation and so that one of the hairs lies on the line for $\theta = 0$ degree.

Alignment techniques for the high temperature X-ray diffraction specimen holder have been developed, which permit accurate alignment while the sample is at temperature. Small misalignments, either as parallel displacements from diffractometer geometry from the axis of rotation of the sample, rotation about the axis of rotation or combinations of these misalignments, were found to be of small influence on the lattice constants when least square extrapolation methods were employed. It was found that gross misalignments could be observed

through the sighting telescope and that alignments could be performed by means of external controls.

The specimen holder (without a sample) was operated at temperatures up to about 1500°C without incident as a check on performance capabilities of the unit.

Important information on the reliability of room temperature alignments for elevated temperature application was obtained through an evaluation of a stabilized ZrO_2 sample. Analysis of diffractometer traces at room temperature and at 800°C yielded lattice constants of 3.923 and 3.954 Å, respectively. An average thermal expansion coefficient of 9.0×10^{-6} per°C was calculated, which compared favorably with a value of 8.9×10^{-6} per°C quoted in the literature.⁷ Accurate temperature measurement by optical means, through the sighting telescope was difficult on the basis of absorption and emissivity corrections which must be applied. These corrections were dependent upon explicit knowledge of emissivity values for the solid solutions being studied and the assumption that volatilization did not occur in such a fashion to influence absorption factors. Since both of these factors could not be accurately obtained, another method for temperature measurement was investigated.

The utilization of an internal standard to provide accurate temperature data appeared to be attractive. The requirements imposed on the internal standard included the following:

1. Existence of accurate thermal expansion data.
2. Non-reactivity with solid solution samples within the temperature range of interest.
3. Non-overlap of diffraction peaks with solid solution samples, especially in the back reflection region, with X-ray wavelengths which

optimize the data for the solid solution samples.

The basic method which was to be employed consisted of obtaining diffractometer data from mixtures of the internal standards and the solid solution fuels as a function of temperature.

Analysis of these data would provide lattice parameters for the internal standard at various approximate temperatures. A comparison of the lattice parameter of the internal standard at same approximate elevated temperature with the room temperature value would then permit the calculation of thermal expansion.

From a standard plot of thermal expansion as a function of temperature, an accurate value for the elevated temperature can be obtained. Analysis of the lattice constants for the solid solution samples would then yield accurate data for thermal expansion between two well-established temperatures.

A number of different methods of incorporating an internal standard with the solid solution compacts was evaluated and included:

1. Parallel pairs in which one sample was the internal standard and the other was the solid solution. Both samples were in the X-ray beam.
2. A solid solution plate containing inserts of the internal standard material.
3. A solid solution plate with a thin surface layer of internal standard material powder.

4. A compact containing an intimate mixture of solid solution fuel and internal standard.

The materials which were evaluated for possible use as an internal standard were:

1. Tungsten
2. Tantalum
3. BeO
4. Al_2O_3
5. Platinum

Evaluation of the geometric configurations and candidate materials indicated that the best approach was the use of a compact containing a mixture of solid solution fuel and platinum powder.

ZrO_2 base samples containing 4, 10.2 and 12 m/o UO_2 were pressed, sintered and crushed. These solid solution powders were mixed with approximately 20 m/o platinum powder. The powder mixture was pressed at 10 tsi and the resultant compacts were heated in an argon atmosphere at 1350°C to provide sufficient strength for handling. X-ray diffraction and metallographic examination of these compacts, as well as samples which have been run in the high temperature diffractometer unit up to 1400°C , reveal no evidence of interaction between platinum and the ZrO_2 - base solid solution fuels. No reaction with platinum is anticipated up to a temperature of at least 1700°C , which is within 73°C of the melting point of platinum.

A series of three ZrO_2 -base solid solutions containing 4, 10.2 and 12 m/o UO_2 and a platinum internal standard have been evaluated at temperatures up to 1400°C .

Figure 31a contains the calibration curve used for platinum to obtain accurate temperature data. Figure 31b contains lattice parameter data for the three ZrO_2 -base solid solutions for temperatures up to 1400°C .

An analysis of these data indicates the following thermal expansion coefficients:

<u>Composition (m/o UO_2)</u>	<u>TEC ($\times 10^{-6}/^\circ\text{C}$)(Range 20° to 1000°C)</u>
4	9.83
10.2	10.00
12	10.00

The expansion coefficients in the range of 20 to 1000°C could best be described by the following equation for the 4 and 12 m/o UO_2 compositions:

$$\text{TEC } 4 \text{ m/o } \text{UO}_2 = 5.1512 + 4.047 \times 10^{-5} t + 9.710 \times 10^{-9} t^2$$

$$\text{TEC } 12 \text{ m/o } \text{UO}_2 = 5.1783 + 4.688 \times 10^{-5} t + 1.476 \times 10^{-9} t^2$$

The diffractometer charts for the entire angular spectrum were evaluated to determine the stability of the face-centered cubic phases. For all temperatures and all compositions denoted by data points on Figure 31b, only single phase, face-centered cubic solid solution structures were observed.

VIEW OF HIGH TEMPERATURE X-RAY DIFFRACTION CAMERA

Figure 30

Figure 31a

THERMAL EXPANSION OF PLATINUM

Figure 31b

THERMAL EXPANSION OF THE ZrO_2 -BASE COMPOSITIONS WITH 4 M/O, 10.2 M/O OR 12 M/O UO_2 THERMAL EXPANSION COEFFICIENTS FOR ZrO_2 -BASE COMPOSITIONS

Figure 31

Figure 31

V. PROPERTY EVALUATIONS

Compositions in the single phase, face-centered cubic region of the $\text{UO}_2\text{-CaO-ZrO}_2$ and $\text{UO}_2\text{-CeO}_2$ systems were selected for evaluation of thermal, physical, corrosion, and chemical properties. Each set of evaluations is treated separately.

The first two evaluations, discussed below, are concerned with the thermal properties of the fuel and fuel element. Both types of evaluations were needed on the basis that the amount of heat that can be removed from a given fuel element is a direct function of the thermal conductivity of the fuel as well as the thermal conductance of the fuel element as a whole. Two separate programs were instituted to determine both of the above characteristics. The first investigation was performed on subcontract to Materiadyne Corporation and consisted of thermal conductivity measurements up to 925°C on two compositions in each of the ZrO_2 and CeO_2 base systems. The second investigation, performed at Combustion Engineering, Inc., Nuclear Division, consisted of out-of-pile thermal conductance measurements on simulated fuel elements containing these same fuel compositions. These thermal conductance measurements were performed under thermal conditions approaching those anticipated in a power reactor. Conductances for central fuel temperatures as high as 2300°C were measured. Both types of data are extremely important and are being utilized in the design of the irradiation experiments on these fuel compositions.

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A. Thermal Conductivity

1. Introduction

As a result of the inherent problems involved in setting up thermal conductivity test apparatus, it was determined that the most expeditious method for obtaining these data would be to subcontract this operation to a group which was well established in the field. On this basis, proposals were solicited from a number of organizations to obtain thermal conductivities in the range of 200°C to 1200°C for 4 and 15 m/o UO_2 in 20 m/o CaO stabilized ZrO_2 and for 7 and 21 m/o UO_2 in CeO_2 .

After careful evaluation of all proposals, Materiadyne Corporation was selected. Materiadyne Corporation utilized equipment and personnel at Alfred University as a result of a previous agreement between the two institutions.

2. Equipment and Test Conditions

Thermal conductivity measurements were made in a steady state, comparative type apparatus modeled after that described in Franci and Kingery⁸, with modifications⁹ to permit controlled atmosphere testing at elevated temperatures. Although the equipment was capable of measurements above

1000°C, the longitudinal thermal gradients limited the reliability of measurements for temperatures to less than this value. The optimum precision of the apparatus was $\pm 5\%$ between 250° and 700°C, based upon repetitive measurements on a standard cube of Al_2O_3 . Data were obtained for temperatures up to 925°C.

Zircon bodies of various porosities obtained from Titanium Alloy Manufacturing Company were used as comparative standards for this investigation. The temperature dependency of the measured thermal conductivities for these standard samples is given in Figure 32a. The standard associated with each sample is shown below:

<u>Specimen Number*</u>	<u>Composition (m/o)</u>	<u>Zircon Standard Used</u>
Z-10	4 UO_2 -19 CaO -77 ZrO_2	149-D
Z-30	15 UO_2 -17 CaO -68 ZrO_2	149-D
C-10	7 UO_2 -93 CeO_2	ZRG-4
C-30	21 UO_2 -79 CeO_2	ZRG-4 up to 523°C 149-D from 509°C to 849°C

*This designation will be used throughout this section for sample identification.

Thermal conductivities of the two ZrO_2 -base samples were measured in an atmosphere of purified argon. These samples lost their original greenish hue and appeared light grey in color after the tests. However, no differences in structure or in lattice constants were observed by X-ray diffraction and microscopy to account for the change in color. A slight decrease in stoichiometry may be a factor responsible for the color change. The presence of argon in the furnace during the tests on the CeO_2 -base samples resulted in inconsistent temperature fluctuations.

These two samples were, accordingly, tested in air on the basis that the samples were initially fired in air and additional heating, also in air, would not significantly affect property changes.

3. Sample Preparation

Samples, in the form of one inch cubes with opposite faces ground flat and parallel, were required for the above test apparatus. In addition, it was desirable to utilize cold pressing and sintering techniques typical of those utilized for the phase diagram investigations.

The initial compacts were pressed in the shape of large cubes to facilitate grinding to the required finish dimensions. All samples of this shape developed fine lamination cracks which were not eliminated by further improvements in the pressing techniques. On this basis, the decision was made to press large cylinders and to cut cubes of the required size from these cylinders. The die was modified so that cylindrical compacts, 1.9 inches in diameter and about 1.5 inches in height, could be prepared. The die walls were dusted with zinc stearate to facilitate compaction and ejection of the powder compact. A compaction pressure of 2 tsi provided green compacts free of lamination and shear cracks, and of sufficient strength for handling purposes. The powder mixtures were blended and comminuted by milling for eight hours in rubber-lined steel jars using Burundum grinding cylinders. Organic binders were not added to the powder mixtures since compacts of suitable green strength were readily produced without such additions and because entrapment of binder within the compacts caused cracking, on previous

tests, due to explosive release of residual vapor products at the elevated temperatures. Furthermore, very long heating times were required to fully volatilize all of the binder material from the large compacts.

A major problem was concerned with the cracking of compacts during sintering as a result of high thermal stresses developed by relatively high heating and cooling rates. This type of failure was eliminated by maintaining heating and cooling rates of 50-75°C/hour. Thermal stresses in the compacts were further reduced by use of ceramic containers or enclosures during sintering.

A series of compacts of two ZrO_2 -base compositions with 4 m/o or 15 m/o UO_2 were sintered at 1800°C for 4 to 16 hours in vacuum or in purified argon to bulk densities of 88-90% of theoretical. A high degree of structural homogeneity was obtained by the use of solid solution powders, i.e., crushing and milling previously sintered compacts and repressing and sintering at 1800°C. Results of these investigations are presented in Table V. These results indicated that the final density achieved by the 4 m/o UO_2 samples was not a function of time for 1 to 16 hours nor of atmosphere (vacuum or argon). However, the sinterability of the 15 m/o UO_2 composition improved with time.

Significant improvements in density and crack resistance were observed for samples of both compositions which were prepared from solid solution powders and sintered in vacuum for 16 hours. On this basis, the ZrO_2 -base samples for this investigation were sintered in vacuum at 1800°C.

for 16 hours to bulk densities of 88-89% of theoretical.

Considerable difficulty was experienced in preparing crack-free compacts of the 7 m/o or 21 m/o UO_2 (added as U_3O_8) - CeO_2 compositions due to their high susceptibility to thermal stress cracking. Compacts, free of cracks and with densities of 94-95% of theoretical, were prepared from comminuted samples which had been air fired previously. The compacts were enclosed in ceramic containers during sintering and heating and cooling rates of 30-50°C/hour were employed. A sintering time of 60 hours at 1500°C in air was required. Compacts prepared in this manner were free of surface and internal cracks.

Cylindrical compacts of the four compositions were shaped into oversize cubes by means of a diamond saw, and the cube faces ground flat and parallel to within a tolerance of ± 0.001 inch on the edge in a milling machine using diamond wheels and water as the coolant. Thermocouple slots, 0.100 inch wide by 0.040 inch deep, were cut into two opposite faces of the one inch cube samples. A view of the test sample is shown in Figure 33. Bulk densities based on dimensional and weight measurements of the finished ground samples are tabulated below in Table VI.

TABLE VI

BULK DENSITIES OF THERMAL CONDUCTIVITY SAMPLES		
Composition m/o	Bulk Density	
	gm/cm ³	Percent T.D.
4 UO_2 -77 ZrO_2 -19 CaO	5.14	89.5
15 UO_2 -68 ZrO_2 -17 CaO	5.67	89.8
7 UO_2 -93 CeO_2	7.01	94.0
21 UO_2 -79 CeO_2	7.53	96.0

The structures of all compositions were identified to be single phase, face-centered cubic by X-ray diffraction and microscopy. All samples were free of minor phases* and exhibited excellent structural homogeneity. The grain size of the ZrO_2 -base samples was 30 to 70 microns whereas that of the CeO_2 -base samples was 50 to 100 microns.

4. Results and Discussion

The conductivities for 100% dense material were calculated from the measured values by use of Loeb's equation¹⁰ for porosity:

$$K_{\text{solid}} = \frac{K_{\text{measured}}}{1 - \text{Pore Volume}}$$

Results of the thermal conductivity tests on the four compositions are presented in Tables VII through X and are plotted in Figures 32b and 32c together with curves for thermal conductivity of stabilized ZrO_2 ,¹¹ UO_2 ,¹² and two CeO_2 base compositions¹³.

It is interesting to note that in both series of compositions, lower conductivities were found for samples with higher UO_2 contents. This is expected according to the findings of Kingery¹⁴ and other investigators on the thermal conductivity of solid solutions. The small difference between the two stabilized ZrO_2 - UO_2 compositions is attributed to the fact that stabilized ZrO_2 is already a solid solution and, therefore, additions of UO_2 do not have as large an effect as they would if UO_2 was

*Later phase diagram investigations indicated a minute trace of a monoclinic phase in similar ZrO_2 base samples with 15 m/o UO_2 . Reevaluation of the samples used in this study failed to reveal the presence of this phase.

the only addition to ZrO_2 . Kingery reports a slightly positive slope for the thermal conductivity of stabilized ZrO_2 , as indicated in Figure 32b. However, the slope of the curves of the thermal conductivities for the two stabilized ZrO_2 - UO_2 compositions is slightly negative.

In the CeO_2 - UO_2 series, the difference in thermal conductivity between the two compositions is of the order that was expected. The conductivity of the 7 m/o UO_2 -93 m/o CeO_2 sample decreased rapidly from 0.0209 to 0.0064 $\text{cal cm}^{-1} \text{sec}^{-1} \text{cm}^{-2} \text{ } ^\circ\text{C}^{-1}$ while that for the higher UO_2 sample (21 m/o UO_2) decreased almost linearly from 0.0070 units to 0.0045 units for the same temperature range of 200 to 950 $^\circ\text{C}$. These data are in good agreement with the thermal conductivity measurements on the 15 m/o UO_2 -85 m/o CeO_2 and the 30 m/o UO_2 -70 m/o CeO_2 compositions, reported by Ploetz, et al¹³, and shown in Figure 32c. Typical conductivity data for UO_2 , reported by Hedge and Fieldhouse¹², ranges from 0.014 at 200 $^\circ\text{C}$ to 0.006 $\text{cal cm}^{-1} \text{sec}^{-1} \text{cm}^{-2} \text{ } ^\circ\text{C}^{-1}$ at about 1000 $^\circ\text{C}$. It is noted that at the elevated temperatures, the thermal conductivities of the homogeneous solid solutions are within 25% of that reported for UO_2 . An approach closer to the UO_2 value is expected at still higher temperatures and will be demonstrated in the next section of this report, covering thermal conductance measurements of these fuel compositions at temperatures to 2200 $^\circ\text{C}$.

In conclusion, thermal conductivity measurements by the steady state method show essentially constant values of 0.004-0.005 $\text{cal cm}^{-1} \text{sec}^{-1} \text{cm}^{-2} \text{ } ^\circ\text{C}^{-1}$ for stabilized ZrO_2 with 4 m/o or 15 m/o UO_2 in the temperature range of 200 to 950 $^\circ\text{C}$. These results are in agreement with the theory that additions of a solute to a single phase solid solution have little

effect upon thermal conductivity. The thermal conductivity of the $\text{UO}_2\text{-CeO}_2$ solid solutions was lowered as the UO_2 content increased from 7 m/o to 21 m/o UO_2 at temperatures from 200 to 950°C . These data are in good agreement with conductivity curves for the 15 m/o or 30 m/o $\text{UO}_2\text{-CeO}_2$ solid solutions, reported in the literature. In all cases, the thermal conductivities were determined at temperatures below 1000°C where radiant heat transfer effects are negligible.

TABLE V

SINTERABILITY DATA ON $\text{UO}_2\text{-ZrO}_2\text{-CaO}$ THERMAL CONDUCTIVITY SAMPLES

<u>Composition-m/o</u>			<u>Sintering Conditions</u>			<u>Sintered Properties</u>			<u>Condition of Sintered Specimen</u>	<u>Comments</u>
UO_2	ZrO_2	CaO	Temp. $^{\circ}\text{C}$	Time- Hours	Atmosphere	Density gm/cm^3	Weight Loss %	Shrinkage %		
4	77	19	1800	1	Vacuum	5.04	0.7	16.1	Not Cracked	Milled As - Received Oxides
4	77	19	1800	16	Vacuum	5.01	0.7	14.5	Not Cracked	Milled As - Received Oxides
4	77	19	1800	4	Argon	5.07	2.8*	12.3	Cracked	Milled As - Received Oxides
15	68	17	1800	1	Argon	5.45	2.0*	9.5	Cracked	Milled As - Received Oxides
15	68	17	1800	4	Argon	5.74	3.4*	14.6	Cracked	Milled As - Received Oxides
15	68	17	1800	16	Vacuum	5.53	1.2	12.2	Not Cracked	Milled As - Received Oxides
4	77	17	1800	1	Vacuum	5.04	0.5	14.3	Cracked	Solid Solution Powder
4	77	17	1800	16	Vacuum	5.23	1.8	12.5	Not Cracked	Solid Solution Powder
15	68	17	1800	16	Vacuum	6.04	1.3	13.8	Not Cracked	Solid Solution Powder

* Contained 2 w/o binder (20 percent solution of Carbowax 4000 in water)

TABLE VII

Thermal Conductivity Results for Z-10

Temp. °C	K_m cal cm sec ⁻¹ cm ⁻² °C ⁻¹	K_s cal cm sec ⁻¹ cm ⁻² °C ⁻¹
207	.0048	.0055
235	.0051	.0058
278	.0059	.0056
303	.0049	.0056
387	.0047	.0053
429	.0045	.0051
492	.0046	.0052
505	.0045	.0051
600	.0046	.0052
672	.0045	.0051
848	.0043	.0049

TABLE VIII

Thermal Conductivity Results for Z-30

Temp. °C	$\text{cal cm sec}^{-1} \text{cm}^{-2} \text{°C}^{-1}$	$\text{cal cm sec}^{-1} \text{cm}^{-2} \text{°C}^{-1}$
175	.0045	.0051
215	.0046	.0052
287	.0045	.0051
379	.0043	.0049
449	.0040	.0045
457	.0040	.0045
575	.0043	.0049
688	.0043	.0049
794	.0043	.0049
840	.0042	.0048

TABLE IX

THERMAL CONDUCTIVITY RESULTS FOR C-10

Temp. °C	K_m cal cm sec ⁻¹ cm ⁻² °C ⁻¹	K_s cal cm sec ⁻¹ cm ⁻² °C ⁻¹
212	0.0209	0.0222
215	0.0210	0.0223
334	0.0144	0.0153
365	0.0137	0.0146
474	0.0101	0.0107
526	0.0098	0.0104
612	0.0083	0.0088
657	0.0071	0.0076
734	0.0068	0.0072
857	0.0066	0.0070
925	0.0064	0.0068

TABLE X

THERMAL CONDUCTIVITY RESULTS FOR C-30

Temp. °C	K_m	K_s
	cal cm sec ⁻¹ cm ⁻² °C ⁻¹	cal cm sec ⁻¹ cm ⁻² °C ⁻¹
202	0.0070	0.0074
303	0.0065	0.0069
420	0.0059	0.0063
509	0.0053	0.0056
523	0.0049	0.0052
630	0.0050	0.0053
707	0.0050	0.0053
778	0.0053	0.0056
843	0.0048	0.0051
849	0.0045	0.0048

$K \text{ (cal cm}^{-1} \text{ sec}^{-1} \text{ cm}^{-2} \text{ }^{\circ}\text{C}^{-1} \text{)}$

* KAPL-1918

THERMAL CONDUCTIVITY versus TEMPERATURE

Figure 32

**THERMAL CONDUCTIVITY SAMPLE IN THE AS-SINTERED
CONDITION (ON LEFT) AND AS A FINISH GROUND
ONE-INCH CUBE (ON RIGHT)**

Figure 33

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B. Thermal Performance Testing

1. Introduction

The data reported in Section V-A, above, provides thermal conductivity values for four solid solution fuels at temperatures approaching 1000°C. However, additional thermal data was needed for temperatures close to the melting points. These data were developed by out-of-pile thermal conductivity tests. Apart from providing basic information on thermal performance of selected compositions of these homogeneous ceramic fuels, values obtained were utilized in the design of irradiation samples. Details of this latter application are discussed in Section VI-C, below.

2. Equipment and Test Conditions

The techniques and apparatus developed at CEND¹⁵ on another Fuel Cycle Contract AT(30-1)-2863 have been applied to establish the thermal characteristics of these homogeneous ceramic fuels. This method employed a heating source consisting of a tungsten electrode which extended axially through a stack of sintered test pellets. The I^2R loss of the electrode was the source of heat which flowed through the fuel, fuel cladding gap, and stainless steel cladding. A water cooled jacket enclosed the sample to develop the desired thermal gradients in the pellets. This method of heating produced a predictable temperature profile in the fuel pellets.

Test samples consisting of an 8-inch long stack of hollow cylindrical pellets were mounted on the tungsten electrode and sheathed in stainless steel tubing. All pellets were ground to provide a diametral clearance of

0.006 inch between the pellets and the 0.072 inch diameter tungsten rod, and a 0.004 inch clearance with the inside diameter of the cladding. The outside diameter of each pellet (0.468 inch) was ground with respect to its center hole to obtain good concentricity and dimensions.

A series of five sight holes of various depths (0.050, 0.100, 0.150 and 0.198 inch) was drilled through the clad and fuel in the central portion of the assembled test unit at 1/2 inch intervals along the axis. Sight hole diameters were 0.070 and 0.040 inches, respectively, in the cladding and fuel pellets, and these holes were positioned with respect to each other to permit continued and uninhibited optical pyrometer sighting under all anticipated relative movements as a result of differences in thermal expansion. During the test, samples were contained in a water cooled jacket to develop desired thermal gradients. Measurements of coolant flow rate as well as inlet and outlet coolant temperatures permitted the calculation of heat balance and served as a check on the power input by the tungsten electrode. Cladding temperatures were measured by means of a chromel-alumel thermocouple in contact with cladding near the center of the sample.

The test assembly is shown in Figure 34. This entire test assembly was contained in a pyrex bell jar which was evacuated and then backfilled with prepurified helium. The helium gas pressure was maintained at slightly above atmospheric, during the tests.

Temperatures within the pellets at predetermined radial distances from the tungsten heating element and the temperature of the surface of the tungsten rod were obtained by means of optical pyrometer readings through the sight

holes, previously described. Power input to the test sample was established by the current through the tungsten electrode and the voltage drop within the fuel pellet column. Voltage probes which were used consisted of a tungsten wire clad in alumina. These probes were spring loaded to contact the electrode at each end of the fuel pellet column.

The testing procedure consisted of the following operations after all components had been assembled, as shown in Figure 34.

- a. Electrode power was increased slowly until the temperature range (about 800°C) for temperature measurement with the optical pyrometer was reached. This constituted the first data point.
- b. Data were recorded at steady state conditions. The following information was recorded at each data point:
 - 1) Temperature within the fuel at predetermined radial positions.
 - 2) Cladding temperature.
 - 3) Coolant temperature rise and coolant flow rate.
 - 4) Voltage and amperage on tungsten electrode.
- c. Similar measurements were obtained for new data points at various intervals up to 2300°C .
- d. When thermal cycling was investigated, the first heat-up was to a lower temperature than the maximum temperature attained on subsequent cycles. Data were obtained under steady state conditions for both heating and cooling portions of the cycle.

3. Results and Discussion

The discussion of the results will be centered on the zirconia base compositions on the basis that it has not been possible to obtain data for the ceria base samples.

a. Ceria Base Compositions

Attempts were made to conduct thermal conductance tests on 7 m/o and 21 m/o $\text{UO}_2\text{-CeO}_2$ samples. In all instances, failures of the heating element were related to ceria-tungsten reactions near 1200°C . Prior to failure of the heating element, a white deposit was observed in the radial sight holes and a yellow-green reaction product formed on the tungsten rod. The deposits were identified by means of X-ray diffraction as containing cerium tungstate ($2 \text{ CeO}_2 \cdot 3 \text{ WO}_3$) and UO_2 as major constituents, with minor amounts of $\text{UO}_{2.25}$ and $\text{UO}_{2.32}$. There was no evidence of $\text{UO}_2\text{-CeO}_2$ solid solution in the reaction products. Thus, ceria based solid solutions react vigorously with tungsten when in contact at relatively low temperatures, 1200°C , to form a low melting point cerium tungstate and uranium oxides. Attempts to diminish the tungsten reaction problem by the introduction of barrier sleeves between the fuel and the heater also resulted in heater failures at fairly low fuel temperatures, due to interactions between the tungsten and the barrier at the relatively high heater temperatures required to overcome the ΔT in the barrier and the new interface to produce fuel temperatures within the measurable optical pyrometer range. On the positive side, the pellets withstood the severe thermal gradients in the test without fragmenting, although thermal stress cracking was observed. This is in contrast to the severe fragmentation which was sometimes found for ceria-base pellets at

cooling rates of 200°C to 300°C per hour during the sintering process.

b. Zirconia Base Compositions

In contrast to the ceria-base samples, important and useful data were obtained for the zirconia base specimens. Early tests were performed on the 4 m/o UO_2 -19 m/o CaO -77 m/o ZrO_2 and 12 m/o UO_2 -9 m/o CaO -79 m/o ZrO_2 compositions. Microstructure changes observed for both compositions were similar. A test sample was heated slowly to a tungsten rod temperature of 2310°C when dendritic deposits were observed in the radial sight hole on the heater. An increase in temperature to 2380°C resulted in additional deposition and subsequent sealing of the hole.

A series of transverse sections was made along the length of the sample and these sections were subjected to microscopic examination to determine changes in microstructure as a result of the high thermal gradients established in the pellets. An analysis of the observed microstructures is given below. Typical microstructures are shown in Figure 35.

1) End Regions (Up to one inch from each end)

As a result of the high axial heat losses on ends of the sample, no changes in microstructure occurred over one inch lengths at both sample ends. All pellets had radial cracks with no evidence of fragmentation.

2) Intermediate Regions. (One to three inches from each end)

The region of the pellets adjacent to the heater rod contained a light brown translucent structure of almost theoretical density. The inner region of

this zone contained a large concentration of voids as well as a continuous network of fine cracks. Some evidence of metal pickup was observed in this region but in no instance did the metal represent a continuous phase. The outer portion of this zone contained massive columnar grains which were essentially free of voids, cracks, or free metal. This heat affected zone was separated sharply from the remainder of the pellets. The outer zone exhibited a number of circumferential cracks adjacent to the boundary. These cracks were probably formed as a result of shrinkage during densification of the hotter central zone. Changes in microstructure or obvious alterations in pore volume were not observed in the outer zone. Typical microstructure is shown in Figure 35.

3) Middle Region

This group of pellets exhibited the greatest changes in microstructure. In general, the microstructure was similar to that described immediately above with the exception that the radius of the heat-affected inner zone had been increased significantly.

In the next and most significant test series, ZrO_2 base pellets stabilized with 20 m/o CaO and containing 4 m/o or 12 m/o UO_2 were thermally cycled to 2400°C . Representative data, presented in Figures 36 and 37, relate the effective thermal conductance (K_{eff}) of the fuel element with the tungsten electrode temperature. The general shape of the K_{eff} versus temperature curves is similar to that encountered for UO_2 and reported by Bates¹⁶ and other investigators. The results for these homogeneous ceramic fuel compositions, after thermal cycling, can be explained best on the

basis of microstructural changes which have taken place in the fuel, as evidenced in Figure 35. The temperature at which the formation of the columnar or large equiaxed grains begins has not been firmly established for these fuels, although a temperature in the vicinity of 1450°C is suggested on the basis of data contained in Figures 36 and 37. This temperature is in the neighborhood of the minimum temperature generally accepted for the onset of grain growth in UO_2 . The improvement in thermal conductivity on the heating cycle can be attributed to a combination of the following three factors:

- a) An increase in the thermal conductivity of the central portion of the fuel as a result of grain growth as well as the formation of columnar grains.
- b) An increase in clad-fuel contact pressure with increase in temperature resulting in improvements in gap conductivity.
- c) Radiative heat transfer associated with UO_2 translucency observed by Hanford at elevated temperatures.

As stated previously, it is probable that all three mechanisms are operating during the first heating portion of the thermal cycle and for this reason, K_{eff} increases sharply with temperature after a given minimum temperature is exceeded. Both the increase in clad-fuel contact pressure and the translucency of the fuel are recoverable phenomena as the temperature is decreased. The permanent change in microstructure after the first heating cycle is then the mechanism contributing to the permanent increase in K_{eff} , found after the first cooling cycle. Subsequent reheating and cooling

did not produce permanent changes in K_{eff} , a result which is expected based upon the above discussion. The general increase in K_{eff} with increasing temperature noted for subsequent thermal cycles is attributed to the activation of the second and third factors noted above. Consideration of yielding of the cladding as a result of high clad-fuel contact pressures at elevated temperatures leads one to the conclusion that, if a small amount of yielding did occur, this would be effective only in reducing K_{eff} at the low temperature end of the cycle. This factor would be masked during the first cycle by the large increase in K_{eff} as a result of the microstructural changes. However, subsequent cycles were conducted to still higher temperatures and the effect of yielding on K_{eff} would have been observed. In the absence of such evidence, the following were concluded:

- (1) The large improvement in K_{eff} after the first cycle is associated with the formation of large columnar and large equiaxed grains as well as densification in the central region of the fuel.
- (2) The gradual increase in K_{eff} with increasing temperature, noted for all cycles, is attributed to a combination of higher clad-fuel contact pressures and the radiative heat transfer. The relative magnitude of each constituent has not been established.

Utilization of these data is discussed in more detail in Section VI of this report.

THERMAL PERFORMANCE APPARATUS
Figure 34

unetched

MAG. 50 X

MICROSTRUCTURAL CHANGES DUE TO HIGH THERMAL GRADIENTS.
A portion of the tungsten heater is shown on left and the as-sintered fuel structure is shown on right

Figure 35

THERMAL CONDUCTANCE DATA ON THE 4 M/O UO_2 - 77 M/O ZrO_2 - 19 M/O CaO COMPOSITION

Figure 36

THERMAL CONDUCTANCE DATA ON THE
12 M/0 UO_2 -71 M/0 ZrO_2 -17 M/0 CaO COMPOSITION

Figure 37

C. Melting Point Determinations

1. Introduction

An accurate determination of the melting points for these solid solution fuels was essential in establishing the maximum temperatures which could be used by a designer in utilizing these fuels. These data became of particular importance in the design of specimens and capsules for the irradiation test program, discussed in Section VI below. Attainment of fuel temperatures above these melting points could lead to serious uncertainties in evaluating irradiation results.

Data on melting points have been used also in establishing the liquidus temperature for phase diagram regions which have been investigated.

2. Equipment and Test Conditions

Initial attempts to establish the melting points for these homogeneous ceramic fuels were based on the utilization of a tungsten ribbon-filament type apparatus, similar to that¹⁷ used for UO_2 . This technique required intimate contact between the sample and the tungsten. It will be shown later that reactions between tungsten and the ZrO_2 base samples resulted in erroneous data. On this basis, the apparatus was modified.

In the method which was employed first, a fragment of a sintered pellet was placed on a tungsten ribbon which was resistance heated. Pre-purified helium was passed through the furnace at a pressure slightly above one atmosphere to prevent oxidation of the components and to minimize volatilization at elevated temperatures. Earlier results indicated a need for a

flowing helium system on the basis of vapor deposition of intermediate oxides of tungsten on the surface of the bell jar containing the test unit. This deposit resulted in erroneous temperature measurements by means of an optical pyrometer. Elimination of this problem permitted accurate measurements to be made. Although some melting point data for materials such as platinum and Al_2O_3 were obtained, there was evidence of a tungsten- ZrO_2 reaction, resulting in substantially lower melting points for ZrO_2 than those reported in the literature. On this basis, the first modifications to the apparatus were introduced. The sample holder was redesigned to permit three-dimensional adjustment of the sample relative to the tungsten ribbon. The sample shape was altered to that of a slender rod which extended into the V-shaped trough in the tungsten ribbon without touching the ribbon. Electrode posts were water cooled to prevent overheating of the bell jar. A tantalum heat shield with viewing ports for temperature measurement was introduced to enclose the sample and the tungsten heater.

Some problems were encountered with sample and/or heater sagging, resulting in either contact or severe heat loss. Further modifications to the test apparatus were made. The unit which was finally evolved and which was found to be extremely successful for this program is shown in Figure 38. The heater is a horizontal cylinder, $1/8$ inch in diameter by 1 inch in length, with about $3/4$ inch of the central section enclosed by three concentric thermal shields. The heater and thermal shields were fabricated from 0.002 inch thick tantalum sheet. Water cooled stainless steel electrode posts support the heater and thermal shields and provide electrical contact with the heater. Power to the unit was by means of a

6 KVA stepdown transformer providing up to 500 amperes at 12 volts. The sample, in the form of a slender rod, was supported at one end in a stainless steel holder with the opposite end extending axially into the heater. The entire test assembly was enclosed within a sealed pyrex chamber. A flow of pre-purified argon gas was maintained in the test chamber at a pressure slightly above atmospheric.

An optical pyrometer was focused on the end face of the sample inside the furnace and provided a means for temperature measurements as well as visual observations. The temperature, at which slight rounding of the corners and edges of the sample tip was observed, was taken as the solidus; the liquidus was established at the temperature for the formation of a globule at the sample tip. A number of materials (Pt, Mo, Al_2O_3 , and BeO) with known melting points were melted to provide the proper corrections for emissivity, calibration of the optical pyrometer, and absorption through the window of the pyrex enclosure. Some indication of the sensitivity of the test technique as well as the skill of the operator is demonstrated in Table XI, below, where solidus and liquidus temperatures were measured with the optical pyrometer even when the spread in temperature was as little as 40°C in the temperature range of 2700°C .

3. Results and Discussion

The test apparatus developed on this program and described above was used in establishing the melting points of selected compositions in the ZrO_2 (stabilized with 20 m/o CaO) and CeO_2 base systems. Samples of CeO_2 and stabilized ZrO_2 , without UO_2 additions, were also included. A total of six to ten samples of each composition were melted. All samples were

heated rapidly to within 200° to 300°C of their anticipated melting points and then at a reduced rate to the solidus and then the liquidus. Melting point data for these materials are presented in Table XI.

Well defined solidus and liquidus points were found for all compositions investigated for the ZrO_2 base system. These data points were reproducible to within $\pm 10^\circ\text{C}$, based on a series of 6 to 10 measurements.

CeO_2 base samples exhibited extensive volatilization at temperatures above 2000°C and erroneous indications of sample tip rounding occurred due to this volatilization, as the melting point was approached. The heating procedure for the CeO_2 base samples was altered to provide for a slow heating rate to 1500°C, a rapid rate to 2300°C to reduce vaporization, and a slow heating rate up to the first sign of melting. It was not possible to separate the solidus and liquidus in this system, and the first sign of liquation at the sample tip was reported as the liquidus.

These data have been utilized in the design of the irradiation program. The maximum temperatures which will be permitted in these fuels during irradiation have been established as just below the solidus for the ZrO_2 -base compositions and 100°C below the liquidus for the CeO_2 -base compositions. The latter value is believed to be a most conservative estimate of the solidus based upon an analysis of other binary phase diagrams with CeO_2 .

VIEW OF MELTING POINT APPARATUS
Figure 38

MELTING POINTS OF THE SOLID SOLUTION FUELS

SYSTEM	UO ₂ -CONTENT M/O	TEMPERATURE - °C		
		SOLIDUS	LIQUIDUS	LITERATURE
ZrO ₂ - BASE	0	2660	2700	2710 (1)
	4	2635	2685	—
	12	2630	2680	—
CeO ₂ - BASE	0	—	2500	2600 (2)
	7	—	2425	—
	21	—	2325	—

(1) LAMBERTSON, W.A. and GUNZEL, F.H., REFRACTORY OXIDE MELTING POINTS, AECD-3465

(2) HANDBOOK OF CHEMISTRY AND PHYSICS, 42nd EDITION, CHEMICAL RUBBER PUBLISHING COMPANY

TABLE XI

D. Corrosion Tests

1. Introduction

The utilization of any fuel material in water reactor systems requires an intimate knowledge of the resistance of the fuel material itself in contact with the coolant. Even with a defect clad condition and with fuels which can exhibit catastrophic corrosion failures in water, the cladding usually can be relied upon to offer some degree of protection to prolong the period required for catastrophic failure so that the necessary detection systems can become operative. Although there was no reason to suspect the corrosion resistance of these homogeneous ceramic fuels in water or steam on the basis of known properties of the three starting constituents, it was deemed desirable to demonstrate reliability in these environments in the unclad condition. It is on this basis that this corrosion investigation in both 360°C water and 625°C steam was initiated.

2. Equipment and Test Conditions

Major emphasis has been placed on testing pellets in both the ZrO_2 and CeO_2 base systems with compositions shown in Table XII. These compositions represented the range of UO_2 contents of interest for the irradiation program. Testing was conducted in static 360°C degassed water at neutral pH in autoclaves at 2700 psi, and in flowing steam at 625°C and at atmospheric pressure. Very early in the program, a preliminary screening evaluation of the corrosion behavior of single and two phase compositions in the zirconia base system was conducted in static, degassed water at 360°C in an autoclave at 2700 psi. The compositions investigated are shown in Table XIII. The method of preparation

for these pellets differed from that used later in the program for compositions shown in Table XII. Pellets, with compositions shown in Table XIII, were prepared by cold pressing at 5 tsi and sintering at 1800°C for 4 hours in pre-purified argon. The total test period was 75 days.

Pellets of compositions shown in Table XII were prepared by a number of different methods. The zirconia base samples were cold pressed at 5 tsi and sintered at 1800°C for 16 hours in vacuum. These pellets were crushed, milled, recompact and resintered for 16 hours in prepurified argon to bulk densities of 92 to 94 percent of theoretical. CeO₂ base samples were prepared by pressing U₃O₈-CeO₂ compacts and air sintering at 1500°C, followed by crushing, milling, recompact, and resintering in air at 1500°C to bulk densities of 94 - 95 percent of theoretical. UO₂ control pellets were prepared by pressing ceramic grade UO₂, taken from the same batch of material used for the zirconia base samples, and sintering for 16 hours at 1750 C in hydrogen to densities of 94 - 96 percent of theoretical. The 20 m/o CaO stabilized ZrO₂ pellets were sintered for 16 hours at 1800°C in prepurified argon to densities of 92 to 94 percent of theoretical. CeO₂ control samples were prepared by air firing compacts at 1500°C for 16 hours to 90 - 92 percent of theoretical density.

Pellets selected for inclusion in the corrosion test program were carefully inspected for evidence of cracks, chips, or other surface defects. Only those pellets which were free of defects were selected for testing. Randomly selected pellets were subjected to metallographic and X-ray diffraction examination which demonstrated that samples of all compositions, shown in Table XII, exhibited single phase, face-centered cubic crystal

structures, with excellent homogeneity and absence of surface or internal cracks.

Weight gain data for corrosion test results are not desirable unless it can be established that a tight and adherent corrosion film had formed. Visual examinations at 15X and 100X were conducted on specimens prior to and following corrosion testing. In all instances, there was no evidence of any loose deposits. To insure against the possibility of including loose deposits in the evaluation data, all samples were carefully scrubbed in hot distilled water, vacuum oven dried, weighed, dimensioned and, again, examined visually. Weight change data were calculated from the dimensions and weights of the samples.

3. Results and Discussion

a. Tests in 360°C Water

The data obtained on this program are divided into three separate test series. The first test was a 75 day screening test of pellets with compositions shown in Table XIII. The second test was for a 42 day period for pellets with compositions shown in Table XII. This second test was terminated after an autoclave malfunction, after the 42 day shutdown had exposed all samples to air at about 360°C for a period of about 18 hours. All 42 day data reported were for measurements made prior to the air exposure. A new set of samples was prepared with compositions given in Table XIV. This set of samples was tested in the third test series to a total of 119 days. These tests are continuing.

1) First Test Series

Test specimens were in the form of pellets which were 1/2 inch diameter by 1/4 inch thick. Samples were removed after 7, 14, 28, 46, 60 and 70 days for measurements and visual examination. The same samples were reinserted for additional test periods. Corrosion data, plotted as $\text{mg/dm}^2/\text{day}$, are presented in Figure 39. These data indicate a general trend toward increasing weight gain with increasing UO_2 content. All specimens demonstrated sharp decreases in the rate of weight gains with increasing exposure times. Significant physical changes were not found in any of the specimens as a result of these tests and the dimensions of all samples were essentially unchanged. There was no indication of loose corrosion product buildup as demonstrated by negligible weight losses of 0.0001 to 0.0002 grams for all samples following scrubbing in hot distilled water and vacuum drying for 4 hours at 200°C .

The as-sintered samples were essentially free of surface pores or other defects and showed sharply defined grain boundaries. After 75 days of testing, scattered pitting was observed on some of the samples, with the incidence of pits increasing with UO_2 content above 15 m/o and with increasing amounts of the second phase. In the worst case, pit depths of no greater than 0.001 inch were encountered. Evaluation of weight gain data for samples containing greater than 15 m/o UO_2 is questionable on the basis of the pitting effects encountered. Some of the two phase structures developed a fine adherent corrosion product on the surface. The two phase structures with higher UO_2 contents also exhibited evidence of accelerated grain boundary attack, a result which was not unexpected

due to the concentration of the second phase, calcium zirconate, at the grain boundaries. Thus, the good weight gain performance of these compositions is a result of a combination of higher weight gains and local corrosion and pitting losses resulting in apparently good corrosion performance as indicated in Figure 39. This is a classic example of the dangers involved in utilizing weight gain data for corrosion investigations in which pitting or non-adherent corrosion products are found. It is significant that these phenomena were observed primarily for compositions which were not single phase and thus out of the range of interest for this program. Data for zirconia base samples containing less than 15 m/o UO_2 are believed to be reliable on the basis that the requirements for utilizing weight gain data have been fulfilled. On this basis, weight gain data (and weight loss data for some CeO_2 base samples) have been used for the remainder of the program for samples exhibiting a single phase, face-centered cubic crystal structure.

The general conclusion reached at this stage of the program was that the corrosion behavior of 20 m/o CaO stabilized ZrO_2 samples containing up to 15 m/o UO_2 was good on the basis of the absence of metallographic evidence of surface attack, a very low pitting incidence which may be associated with opening up of surface pores, and acceptable weight changes during test. The maximum penetration rate calculated for this class of samples was less than one mil penetration per year, based on 75 day data.

2) Second Test Series

Pellets of compositions shown on Table XII were exposed to 2700 psi, degassed water in an autoclave at 360°C for 42 days, consisting of a series of 14 day test periods. Twelve samples of each composition were

included in the test program. Three samples of each composition were removed at the end of each 14 day test period for detailed evaluation and the test was continued on the remaining samples. Some of the samples which had been subjected to non-destructive evaluation were reinserted in the test environment. Corrosion data for these samples are shown in Figure 40. Each data point represents an average value for three to five samples of each composition examined after each of the three 14 day exposure periods.

All ZrO_2 base samples with the exception of the ZrO_2 control specimens exhibited high average weight gains for the first 14 day period. Subsequent corrosion rates for each of the next two fourteen day test periods were much lower for all compositions with the exception of the 4 m/o UO_2 samples which already exhibited a lower corrosion rate after the first 14 day test period but then dropped close to the rate exhibited by the other compositions, after the third 14 day test period. The higher corrosion rate for the 4 m/o UO_2 samples may be a result of their location in steam at the upper region of the autoclave during the second test period. Placement of these samples in the lower portion of the autoclave during the third test period resulted in the significant decrease in the corrosion rate observed. This same argument cannot be applied for the high rates for all samples during the first 14 day exposure. Microexamination after the first exposure period revealed numerous, fine radial microcracks in the polished and etched samples which were not present in the as-sintered samples. These cracks were not visible in the surfaces of the samples under low power (15X) magnification. The initially higher corrosion rates may be a result of

the large increase in real surface area (as a result of these microcracks) above the geometric area used as a basis for the weight change calculations. These views are substantiated by the very low corrosion rates for the next two 14 day test periods during which time the sample showed no additional cracking.

There was no evidence of surface pitting or general corrosion penetration of the samples following all tests. Microexamination of all sections revealed no evidence of attack.

Similar trends in corrosion rate were observed with the CeO_2 base samples as indicated in Figure 40. However, these were weight losses. The surfaces of all samples were uniformly dulled in appearance with evidence of a fine corrosion discoloration on the 21 m/o UO_2 samples. Cross-sectional examinations after the first 14 day test period revealed fine microcracks, similar to those observed in the ZrO_2 base samples but to a lesser extent. Again, these microcracks were not present in the samples before corrosion testing and their extent or population did not increase after each of the next two test periods. The surfaces of the samples were free of general or preferential attack. Microexamination of these samples revealed no evidence of surface or subsurface attack or reaction. The maximum penetration for the zirconia and ceria base fuel samples are 1 mils per year and 2 mils per year, respectively, based on 42 day data.

The corrosion rates of the three starting materials: UO_2 , stabilized ZrO_2 , and CeO_2 are on the order expected for these refractory oxides. All samples retained their original as-sintered appearance. Micro-

examinations disclosed that the samples were completely free of cracks, pitting or surface attack.

During the startup of the autoclave for a fourth 14 day test period, the above mentioned malfunction caused all samples to be heated in air at 360°C for a period of about 18 hours. At this point, it was decided to avoid ambiguities in interpreting longer term test data. On this basis, this test series was terminated and a new set of samples was fabricated.

3) Third Test Series

A minimum of five samples of each of the pellet types shown in Table XIII were prepared in a similar manner to those described immediately above for the second test series. Test conditions were similar to those used in the second test series. Periodic examinations were made for at least five pellets of each composition, after 28, 56 and 119 days. Corrosion data are plotted as weight loss or weight gain in Figure 41. The general trends in the data are similar to those encountered in the second test series with the following exceptions:

- a) The 17.5 m/o $\text{UO}_2\text{-CeO}_2$ samples exhibit weight gains.
- b) The single sintered 7 m/o $\text{UO}_2\text{-CeO}_2$ sample exhibits much lower weight losses than the double sintered samples in the second test series or in this test series.
- c) The ceria control sample exhibits a small weight gain.

The general shape of curves for all compositions with the exception of the double sintered 7 m/o UO_2 ceria samples was in the direction of lower corrosion rates with increasing time. In addition, the adverse effect

of increasing UO_2 concentrations is apparent.

The reason for the apparently anomalous behavior of ceria base samples in this test series, when compared with previous data on CeO_2 , is not understood at this time. However, it is significant that, with the exception of the double sintered samples, the weight changes for the ceria base samples were below those for the zirconia base samples, and weight changes for both sets of samples were greatly reduced during latter stages of testing. (A single sinter method had been previously selected for fabrication of the ceria base samples for irradiation testing.) Metallographic examination of pellets after 119 day exposure is being initiated and it is hoped that this may shed some light on the apparently anomalous behavior of the ceria base samples.

The maximum penetration rates for the ceria and zirconia base samples was less than one mil per year, based on 119 day data and including the double sintered ceria base samples.

These tests will be continued for one year with interim examinations every three months.

b. Tests in 625 °C Steam

Seven to twelve pellets of each of the compositions shown in Table XII were corrosion tested in flowing steam, with the samples at 625°C. These pellets were placed in a stainless steel wire basket located in a stainless steel tube furnace. Distilled water which was used for steam generation was degassed by means of bubbling argon.

The first test shutdown occurred after seven days when fragments of some of the samples were observed in the condensate water. At this time, the furnace was shut down and the samples were removed, washed in distilled water, vacuum dried, weighed, measured and examined visually. No visual evidence of cracking or spalling was observed for all samples with the exception of the UO_2 pellets, which had disintegrated into a relatively fine powder. This was the origin of the debris noted in the condensate water. Weight change data obtained after this initial 7 day test period are plotted in Figures 42 and 43, together with data for times up to 210 days.

These solid solution samples were continued in test for an additional fourteen days, together with a new batch of UO_2 pellets. The solid solution samples showed no change in appearance whereas the UO_2 samples had fragmented. A second fourteen-day test period, with a new batch of UO_2 included, produced similar results. Debris from the UO_2 samples was identified as U_3O_8 by X-ray diffraction. Incomplete deaeration of the water used for generating the steam was the probable cause of the UO_2 oxidation.

Weight change data for all test periods are presented in Figures 42 and 43. These data indicate a definite leveling off of corrosion rates for all compositions following the first seven-day exposure. The slopes of the weight gain curves increase slightly with increasing UO_2 content for the ZrO_2 base samples, whereas an essentially constant weight loss is observed for the CeO_2 base samples. There has been no visible adverse effect on these solid solution pellets after 210 days' exposure to 625°C steam.

The previously observed adverse influence of increasing UO_2 concentrations is shown also by the curves in Figure 42. The maximum penetration for the zirconia and ceria base samples is less than one mil per year, based upon 210 days of testing.

Metallographic examination of one pellet from each composition after 210 days of testing has been initiated. These tests in steam will be continued for one year with periodic examinations every three months.

TABLE XII

COMPOSITION OF CORROSIONTEST SAMPLES

Pellet Type	Mole Percent		
	UO ₂	[*] ZrO ₂	CeO ₂
1	100	---	---
2	---	---	100
3	---	100	---
4	4	96	---
5	12	88	---
6	15	85	---
7	7	---	93
8	21	---	79

* Containing 20 m/o CaO

TABLE XIII

COMPOSITION OF SCREENING TEST SAMPLES

Pellet Type	Mole Percent			Number of Phases Present
	UO ₂	ZrO ₂	CaO ₂	
1	4	77	19	1
2	9	73	18	1
3	12	71	17	1
4	21	63	16	1
5	29	57	14	1
6	38	50	12	1
7	4	69	27	2
8	21	57	22	2
9	38	44	18	1
10	4	62	34	2
11	12	56	32	2
12	27	47	26	2
13	52	31	17	1
14	12	79	9	1
15	21	71	8	1

TABLE XIV

COMPOSITION OF SAMPLES USED IN THIRD TEST SERIES

Pellet Type	Mole Percent		
	UO ₂	ZrO ₂ *	CeO ₂
1	---	---	100
2	---	100	---
3	7	---	93 (single sinter)
4	17.5	---	82.5
5	7	---	93 (double sinter)
6	4	96	---
7	12	88	---

* Containing 20 m/o CaO

AUTOCCLAVE CORROSION TEST No. 1 - 360°C H_2O
Figure 39

AUTOCCLAVE CORROSION TEST No. 2
360° H₂O

Figure 40

AUTOCLAVE CORROSION TEST No.3
360°C H₂O

Figure 41

CORROSION DATA FOR ZrO₂ BASE AND CeO₂
 BASE COMPOSITIONS EXPOSED TO 625°C STEAM
 (Mg/Dm² vs EXPOSURE TIME)

Figure 42

CORROSION DATA FOR ZrO₂ BASE AND CeO₂ BASE
COMPOSITIONS EXPOSED TO 625°C STEAM
(Mg/Dm²/DAY vs EXPOSURE TIME)

Figure 43

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E. Chemical Analyses

1. Introduction

An accurate assay of the uranium content of the ceria and zirconia base samples was necessary as a back-up for the phase diagram studies as well as for the irradiation samples. Possible differences in volatilities of the various constituents in the atmospheres and at the temperatures employed for some of these investigations required the development of analytical chemical techniques capable of confirming compositions of the sintered products. A literature survey failed to uncover a readily applicable solution to this problem. The three approaches which were evaluated included wet chemical methods, gamma spectrometry and X-ray fluorescence. Evaluations of each of these methods are discussed below.

2. Equipment and Test Conditions

a. Wet Chemical Method

Ceria base samples were dissolved by heating in 1:1 sulfuric acid with the addition of a small amount of 30% H_2O_2 . Zirconia base samples were fused with potassium pyrosulfate and the fused product dissolved in 10% sulfuric acid and oxidized with a 2% K MnO_4 solution. For both the ceria and zirconia base samples, the sulfuric acid solutions were reduced in a Jones Reductor and aerated to convert the uranium to U (IV). Ten ml of 10% FeCl_3 and 15 ml of 35:15 $\text{H}_3\text{PO}_4\text{-H}_2\text{SO}_4$ solution were added. U (IV) reduces Fe (III) to Fe (II). The resultant ferrous ion was titrated with either ceric sulfate, using arthophenanthroline as an indicator or with potassium dichromate, using sodium diphenylamine as the end point indicator.

b. Gamma Spectrometry

A comparison was made of the gamma emission of the sample with a standard of approximately the same composition. The powdered sample was placed in a 4 ml vial and counted in a well type Na I (Tl) crystal using a single channel pulse height analyzer. The 185 kev gamma radiation, one gross gamma emission above 30 kev, as well as other regions of the spectrum were measured.

c. X-Ray Fluorescence

This method is based upon the evaluation of the intensity ratios of the peaks of the L_{α} , and K_{α_2} lines from uranium and zirconium, respectively. The source of X-rays was a tungsten tube operating at 45 KV with a LiF crystal analyzer. This analyzer acted as a diffraction grating for the fluorescent X-rays and ensures that only those rays diffracted at a given angle can enter the counter. Quantitative analysis of a particular element is based on the linear relationship of intensity of the characteristic wavelengths for that element with the quantity of that element in the sample.

3. Results and Discussion

X-ray fluorescence methods did not prove feasible because of poor precision between the uranium content of mechanical mixtures and sintered compacts. This was probably caused by matrix effects which resulted from a difference in the microscopic structure between the two materials. Results from gamma-ray spectroscopy also showed low precision. The measurement of the U-235 gamma-ray proved impractical because of the low abundance in the

depleted uranium employed for these investigations. Attempts to use other gammas also proved to be unfeasible because sintering appeared to change the gamma/uranium ratio. Although it is possible that the uranium content of enriched samples could be established by this method, no further work was performed in this area on the basis that excellent data were obtained by the wet chemical method.

Results obtained by the wet chemical method on mechanically mixed and sintered samples are shown in Table XV. The coefficient of variation over all the results is 0.25%. A comparison of the results for the mechanically mixed and sintered samples of the same batch indicates no loss of UO_2 during sintering.

Although the ceric sulfate and potassium dichromate titrations give equivalent results, it was decided to perform the analysis of the samples for irradiation testing using the ceric sulfate titration because the endpoint is more readily detectable. In addition, back-titration with ferrous sulfate permits a correction for any slight over-titration.

TABLE XV

RESULTS OF WET CHEMICAL METHOD

System	Nominal w/o UO_2	Test Method	w/o UO_2 Found
$\text{UO}_2\text{-CeO}_2$	14.42	Ceric Sulfate Titration	14.40 (a)
$\text{UO}_2\text{-CeO}_2$	12.53	Ceric Sulfate Titration	12.52 (a)
$\text{UO}_2\text{-CeO}_2$	10.00	Ceric Sulfate Titration	10.00 (b)
$\text{UO}_2\text{-CeO}_2$	10.00	Ceric Sulfate Titration	9.99 (b)
$\text{UO}_2\text{-CeO}_2$	30.00	Ceric Sulfate Titration	29.77 (b)
$\text{UO}_2\text{-CeO}_2$	30.00	Ceric Sulfate Titration	29.85 (b)
$\text{UO}_2\text{-CeO}_2$	30.00	Ceric Sulfate Titration	29.78 (b)
$\text{UO}_2\text{-CeO}_2$	10.00	Potassium Dichromate Titration	9.97 (a)
$\text{UO}_2\text{-CeO}_2$	10.00	Potassium Dichromate Titration	9.93 (a)
$\text{UO}_2\text{-CeO}_2$	10.00	Potassium Dichromate Titration	10.00 (b)
$\text{UO}_2\text{-CeO}_2$	10.00	Potassium Dichromate Titration	9.90 (b)
$\text{UO}_2\text{-CeO}_2$	25.00	Potassium Dichromate Titration	24.75 (a)
$\text{UO}_2\text{-CeO}_2$	25.00	Potassium Dichromate Titration	24.78 (a)
$\text{UO}_2\text{-CeO}_2$	25.00	Potassium Dichromate Titration	24.68 (b)
$\text{UO}_2\text{-CeO}_2$	25.00	Potassium Dichromate Titration	24.89 (b)
$\text{UO}_2\text{-(90 w/o ZrO}_2\text{-10 w/o CaO)}$	10.00	Potassium Dichromate Titration	9.96 (a)
$\text{UO}_2\text{-(90 w/o ZrO}_2\text{-10 w/o CaO)}$	10.00	Potassium Dichromate Titration	9.99 (a)
$\text{UO}_2\text{-(90 w/o ZrO}_2\text{-10 w/o CaO)}$	10.00	Potassium Dichromate Titration	9.96 (b)
$\text{UO}_2\text{-(90 w/o ZrO}_2\text{-10 w/o CaO)}$	10.00	Potassium Dichromate Titration	9.91 (b)
$\text{UO}_2\text{-(90 w/o ZrO}_2\text{-10 w/o CaO)}$	25.00	Potassium Dichromate Titration	25.03 (a)
$\text{UO}_2\text{-(90 w/o ZrO}_2\text{-10 w/o CaO)}$	25.00	Potassium Dichromate Titration	24.79 (a)
$\text{UO}_2\text{-(90 w/o ZrO}_2\text{-10 w/o CaO)}$	25.00	Potassium Dichromate Titration	24.93 (b)
$\text{UO}_2\text{-(90 w/o ZrO}_2\text{-10 w/o CaO)}$	25.00	Potassium Dichromate Titration	24.89 (b)

(a) Mechanical mixture

(b) Sintered pellet

VI. IRRADIATION PROGRAM

A. General

An irradiation program has been initiated with the object of determining the performance of these solid solution fuels at fission burnups of 40, 55 and 70% of the U-235 atoms and at temperatures just below melting. The irradiation program includes six capsules containing samples of four compositions as shown in Table XVI

Each capsule contains three fuel samples of the zirconia base and two samples of the ceria base compositions. All samples are instrumented. Bulk densities of 90% and 94% of theoretical for the ZrO_2 and CeO_2 base samples, respectively, have been established. The sample design and dimensions for each composition are given in Figure 44 and Table XVII respectively. Details of the calculations and assumptions leading to this design will be discussed in Section B, below.

All irradiations are to be controlled in a manner which will insure that center melting will not occur. The following melting temperatures have been established as a basis for this program:

1. ZrO_2 -Base Compositions

The melting points of the 4 and 10.2 m/o UO_2 samples are based on the solidus temperatures of 4775°F and 4765°F, respectively.

2. CeO_2 -Base Compositions

As a result of the difficulty in obtaining reliable solidus temperatures, the melting points of the CeO_2 base compositions with 7 and 17.5 m/o UO_2

were established, for this program, as 200°F below the liquidus temperatures or 4190°F and 4035°F, respectively.

On the basis of an uncertainty in experimental flux conditions as well as the firm requirements that melting is not to occur, application of a safety factor of about $\pm 800^\circ\text{F}$ has established 4000°F and 3200°F as the target centerline temperatures for the ZrO_2 and CeO_2 base samples.

An attempt will be made to operate all capsules at their maximum heat generation rates so that target maximum fuel temperatures can be maintained. This requirement necessitates a number of capsule movements to increasingly higher flux positions as burnup and thus fuel depletion increase.

Out-of-pile thermal conductance measurements made on the ZrO_2 base materials are being used as one of the bases for sample design. Details of this approach are presented in Section B, below. Difficulty has been experienced in obtaining useful thermal conductance data on the CeO_2 base samples due to ceria-tungsten heater reactions. Attempts which were made to eliminate this reaction by providing a BeO sleeve around the tungsten heater did not prove successful. On this basis, the ratio of measured thermal conductivities at 900°C of the CeO_2 base to ZrO_2 base compositions was used to approximate the values for the CeO_2 base compositions at temperatures greater than 900°C. Thermal conductivities for these materials at 900°C were reported in NYO-2996.

Post irradiation testing will include the following:

- a. Visual inspection of capsules
- b. Puncture of capsule and collection of gas, if any

TABLE XVI

COMPOSITIONS AND TARGET BURNUPS

Capsule Number	Target Fission Burnup (% U-235 Atoms)	Composition of Fuel
1	40	7 m/o UO_2 in CeO_2 4 m/o UO_2 -77 m/o ZrO_2 -19 m/o CaO
2	55	7 m/o UO_2 in CeO_2 4 m/o UO_2 -77 m/o ZrO_2 -19 m/o CaO
3	70	7 m/o UO_2 in CeO_2 4 m/o UO_2 -77 m/o ZrO_2 -19 m/o CaO
4	40	17.5 m/o UO_2 in CeO_2 10.2 m/o UO_2 -72.2 m/o ZrO_2 -17.6 m/o CaO
5	55	17.5 m/o UO_2 in CeO_2 10.2 m/o UO_2 -72.2 m/o ZrO_2 -17.6 m/o CaO
6	70	17.5 m/o UO_2 in CeO_2 10.2 m/o UO_2 -72.2 m/o ZrO_2 -17.6 m/o CaO

TABLE XVII

IRRADIATION SAMPLE DIMENSIONS

Sample Type	Composition	Percent Burnup	Nominal Pellet Diameter	"A" Overall Length	"B" Gas Length*
1	Z10	40	0.350	2.25	0.300
2	Z10	55	0.350	2.25	0.300
3	Z10	70	0.350	2.25	0.300
4	Z22	40	0.250	2.50	0.550
5	Z22	55	0.250	2.50	0.550
6	Z22	70	0.250	2.50	0.550
7	C10	40	0.300	2.25	0.300
8	C10	55	0.300	2.25	0.300
9	C10	70	0.300	2.25	0.300
10	C25	40	0.190	2.50	0.550
11	C25	55	0.190	2.50	0.550
12	C25	70	0.190	2.50	0.550

* 100% fission gas release was assumed.

DESIGN FOR IRRADIATION SAMPLES

Figure 44

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- c. Cutting capsule and removing heat transfer medium
 - d. Visual inspection and macrographs of fuel cladding
 - e. Puncture of cladding, collection and identification of fission gases
 - f. Density of fuel sections
 - g. Metallography
 - h. X-ray diffraction
 - i. Burnup analysis
 - j. Corrosion testing
- B. Bases for Irradiation Sample Design

In order to evolve a sample design which will provide a maximum ability to meet optimum irradiation test conditions, a number of parameters had to be established. These parameters included the following:

- 1. Fuel pellet conductivity
- 2. Dimensions and tolerances
- 3. Tentative specimen design
- 4. Thermal conductance of the fuel clad assembly
- 5. Perturbation factors determined from a nuclear mockup

The following data have been established for the above parameters. The thermal conductivity values calculated from the CEND and the Materiadyne experimental data for the ZrO_2 and CeO_2 fuel material alone are as follows:

$$Z10: * \quad K = 1.16 \quad \frac{BTU}{hr-ft-^{\circ}F} \quad C10: * \quad K = 1.66 \quad \frac{BTU}{hr-ft-^{\circ}F}$$

* Z10 - designates fuel composition 4 m/o UO_2 -77 m/o ZrO_2 -19 m/o CaO
 * C10 - designates fuel composition 7 m/o UO_2 -93 m/o CeO_2

$$\text{Z22:}^* \quad K = 0.93 \quad \frac{\text{BTU}}{\text{hr-ft-}^\circ\text{F}} \quad \text{C25:}^* \quad K = 1.18 \quad \frac{\text{BTU}}{\text{hr-ft-}^\circ\text{F}}$$

An evaluation was made to determine if the CEND thermal conductivity data were self-consistent. With the exception of the data points for the Z10 sample for the temperature range of 1440 to 1670^oF, agreement is reasonably good based on constant ^{**}"Q" values.

The clad to pellet gap clearance and tolerances on this clearance were established to provide the minimum gap consistent with fabrication and assembly requirements. These are:

- a. Minimum cold diametral clad to pellet clearance 0.0005 inch
- b. Maximum cold diametral clad to pellet clearance 0.0015 inch

This gap provides a gap to pellet radius ratio consistent with high contact conductance. At a value for this ratio of about 0.01, the gap conductance becomes a small factor in overall sample conductance, contributing less than 10% to the final value. Thus, variations in actual gap conductance with temperature will provide only a very small change in total sample conductance. The thermal conductance for the fuel cladding assembly was calculated on the basis of dimensions and tolerances established by fabrication requirements, the ZrO₂ thermal conductivity values, and the gap conductance values as determined by diametral gap to pellet diameter ratios.

The following values for the fuel and cladding assembly were established:

-
- * Z22 - designates fuel composition 10.2 m/o UO₂-72.2 m/o ZrO₂-17.6 m/o CaO
 - * C25 - designates fuel composition 17.5 m/o UO₂-92.5 m/o CeO₂
 - ** Heat generated per unit volume

Z10:	$K_{\text{eff}} = 1.00$	$\frac{\text{BTU}}{\text{hr-ft-}^{\circ}\text{F}}$
Z22:	$K_{\text{eff}} = 0.80$	$\frac{\text{BTU}}{\text{hr-ft-}^{\circ}\text{F}}$
C10:	$K_{\text{eff}} = 1.33$	$\frac{\text{BTU}}{\text{hr-ft-}^{\circ}\text{F}}$
C25:	$K_{\text{eff}} = 0.88$	$\frac{\text{BTU}}{\text{hr-ft-}^{\circ}\text{F}}$

Details of calculations and assumptions utilized as a basis for irradiation sample designs are presented in Section C.

C. Calculation of Fuel Pellet Conductivities

The calculation of fuel pellet thermal conductivities for the Z10 and Z22 samples was based on test data obtained from the Materiadyne Corporation, reported in NYO-2996, and CEND out-of-pile thermal conductance data as shown in Figures 45, 46 and 47. In addition, early values for the fuel radii were used. These were based upon a tentative design which was later modified slightly by nuclear mock-up data. The change in diameter was too small to alter the conclusions reached as a result of these calculations. To convert the out-of-pile test data to suitable in-pile information, the following extrapolations were made and are presented in Figures 48 and 49.

1. For a given temperature the out-of-pile radius was transformed to the corresponding in-pile radius at that temperature.
2. To extend the data to $T_{\text{max}} = 4800^{\circ}\text{F}$, the temperature scale was plotted in percent T_{max} .
3. Since the test data were obtained on a 0.450 inch diameter pellet and the Z10 pellet diameter is 0.350 inch while the Z22 pellet diameter is

0.250 inch, the radius scale was plotted as percent r_o where (r_o = radius of the pellet).

4. The in-pile temperature profile curve was obtained from report number NYO-9012, CEND-141, Figure F-1. It was assumed that the general profile for the in-pile and out-of-pile temperature versus radius relations would not change with changes in T_{max} and r_o .

5. Since the test data show that thermal conductivity is a function of temperature, the related K (thermal conductivity) values from Figures 45, 46, and 47 were tabulated for each temperature region.

6. Tables XVIII and XIX were constructed to relate the in-pile temperature versus radius relations to be used in calculating the average conductivity of the fuel (K_f).

7. The simple heat conduction formula: $\Delta T = \frac{Qa^2}{4K}$ for uniform heat generation in a cylindrical element was extended to take into account the variable thermal conductivity, thus:

$$\Delta T = \frac{Qa^2}{4} \left[\frac{a^2 - a_1^2}{K_1} + \frac{a_1^2 - a_2^2}{K_2} + \dots \right]$$

where, Q = Heat generated per unit volume

ΔT = Temperature drop between center of elements and outer surface of the elements

a = Radius of fuel

K_i = Average conductivity value in the region a_{i-1} to a_i

a_i = percent a = percentage of pellet radius at which a temperature measurement was made

The following thermal conductivities for the fuel were calculated:

$$\begin{array}{l} \text{Z10:} \\ \Delta T = \frac{Qa^2}{4} \left[\frac{1 - (.89)^2}{1.05} + \frac{(.89)^2 - (.78)^2}{.89} + \frac{(.78)^2 - (.64)^2}{1.34} + \frac{(.64)^2}{1.34} \right] \end{array}$$

$$K_{\text{fuel}} = 1.16 \text{ BTU/hr-ft-}^\circ\text{F}$$

$$\begin{array}{l} \text{Z22:} \\ \Delta T = \frac{Qa^2}{4} \left[\frac{1 - (.95)^2}{1.02} + \frac{(.95)^2 - (.90)^2}{.77} + \frac{(.90)^2 - (.76)^2}{.57} + \frac{(.76)^2}{1.30} \right] \end{array}$$

$$K_{\text{fuel}} = 0.93 \text{ BTU/hr-ft-}^\circ\text{F}$$

If the CEND experimental data are reliable, then the heat flow across the surfaces at which temperature measurements were made should balance.

Hence,

$$Q = \frac{2\pi \Delta T}{\ln a_i/a_j} \quad \text{and,}$$

$$Q_1 \approx Q_2 \approx Q_3 \text{ etc.}$$

In general, the data in Table XX are in good agreement with the exception of the 1440 to 1670°F range on the Z10 pellet. Except for possible error in the optical pyrometer reading, no good explanation for the discrepancy can be given.

The approach used for the CeO₂ base samples was similar to that utilized above, with the exception that the input data were derived from the Materiadyne values reported in NYO-2996 and values obtained from the literature¹³. A plot of these values is given in Figure 33c. The out-of-pile data, extrapolated to in-pile conditions, are included in Table XXI.

TABLE XVIII

EXPERIMENTAL RADIAL TEMPERATURE DISTRIBUTION FOR Z10 AND Z22

Measured Temperature (°F)	Percent $T_{\max}^*$	Radius at Measured Temperature (Inches)	Percent Pellet Radius
<u>Z10</u>			
3300	70	0.037	8
2500	52	0.088	20
1800	38	0.138	31
1500	31	0.187	41
900	18	0.225	100
<u>Z22</u>			
3350	70	0.037	8
2700	56	0.088	20
1850	38	0.138	31
1500	31	0.187	41
900	19	0.225	100
<u>In-Pile Temperature Profile</u>			
4800	100		0
4080	85		49
3070	64		71
2016	42		86
1000	21		100

* $T_{\max}$ = 4800°F

TABLE XIX

EXTRAPOLATION OF DATA TO IN-PILE CONDITION

Percent $T_{\max}^*$	Percent Radius	Radius Designation	K
<u>Z10</u>			
100	0	a_4	1.34
70	64	a_3	1.34
52	78	a_2	0.89
38	89	a_1	1.05
18	100	a	
<u>Z22</u>			
100	0	a_4	1.30
56	76	a_3	1.30
38	90	a_2	0.57
31	95	a_1	1.02
19	100	a	

$$*T_{\max} = 4800^{\circ}\text{F}$$

TABLE XX

TABULATION OF HEAT BALANCE DATA

ΔT	K	a_i/a_j	$Q/2 \pi$
<u>Z10</u>			
3380-2500	1.34	2.35	(1020)
2800-2150	1.34	2.35	(1380)
2360-1780	0.89	1.58	1060
2150-1610	0.89	1.58	1120
1730-1590	1.50	1.36	1130
1670-1440	1.50	1.36	694
<u>Z22</u>			
3330-2680	1.30	2.35	1065
3180-2520	1.30	2.35	990
2680-1860	0.57	1.58	1075
2520-1790	0.57	1.58	936
1860-1480	0.77	1.36	1000
1790-1400	0.77	1.36	964

TABLE XXI

IN-PILE TEMPERATURE PROFILE

$T_{\text{meas.}}^{\circ\text{F}}$	Percent T_{max}^*	Percent Radius	K (BTU/hr-ft- $^{\circ}\text{F}$)
<u>C10 Composition</u>			
1697	42	88	1.55
1353	34	93	1.65
1133	28	96	2.01
689	17	100	3.32
<u>C25 Composition</u>			
1560	39	90	1.16
1304	33	94	1.29
971	24	98	1.26
788	20	100	1.53

* $T_{\text{max}} = 4000^{\circ}\text{F}$

**THERMAL CONDUCTIVITY VS TEMPERATURE
FOR Z10 AND Z22 COMPOSITIONS**

Figure 45

**RADIAL TEMPERATURE DISTRIBUTION
FOR Z10 COMPOSITION**

Figure 46

**RADIAL TEMPERATURE DISTRIBUTION
FOR Z22 COMPOSITION**

Figure 47

Z10 TEMPERATURE PROFILE

Figure 48

Z22 TEMPERATURE PROFILE

Figure 49

The thermal conductivity of the fuel was calculated from the relation:

$$\Delta T = \frac{Qa^2}{4} \left[\frac{a^2 - a_1^2}{K_1} + \frac{a_1^2 - a_2^2}{K_2} + \dots \right]$$

$$\text{For ClO: } \frac{1}{K_f} = \left[\frac{1 - (.96)^2}{3.32} + \frac{(.96)^2 - (.93)^2}{2.01} + \frac{(.93)^2 - (.88)^2}{1.65} + \frac{(.88)^2}{1.55} \right]$$

$$K_f = 1.66 \text{ BTU/hr-ft-}^\circ\text{F}$$

$$\text{For C25: } \frac{1}{K_f} = \left[\frac{1 - (.98)^2}{1.53} + \frac{(.98)^2 - (.94)^2}{1.26} + \frac{(.94)^2 - (.90)^2}{1.29} + \frac{(.90)^2}{1.16} \right]$$

$$K_f = 1.18 \text{ BTU/hr-ft-}^\circ\text{F}$$

D. Dimensions and Tolerances

Fabrication dimensions and tolerances and their relations to stress, assembly diametral gap and clad-to-pellet conductance are presented in Appendix A. dimensions used were those for the tentative design. Conclusions reached apply, also, to the final design dimensions which are very close to the values used here. Final design dimensions are given in Table XIII. Parameters, used for calculations in Appendix A, are given below:

$$\Delta R_c = \text{Free expansion of clad}$$

$$\Delta R_f = \text{Free expansion of fuel}$$

$$\Delta R_e = \text{Expansion due to stress (to yield)}$$

$$\sigma_y (347 \text{ clad}) = 35,000 \text{ psi @ } 600^\circ\text{F}$$

$$E (347 \text{ clad}) = 20 \cdot 10^6 \text{ psi @ } 600^\circ\text{F}$$

$$\alpha (347 \text{ clad}) = 9.5 \cdot 10^{-6} \text{ in/in } ^\circ\text{F @ } 600^\circ\text{F}$$

$$\alpha (\text{ZrO}_2) = 5.3 \cdot 10^{-6} \text{ in/in } ^\circ\text{F @ } 900^\circ\text{F}$$

$$K (347 \text{ clad}) = 12 @ 600^\circ\text{F}$$

As shown in Appendix A, all values for the ratio of gap clearance to pellet radius are 0.012 or less, thus providing a gap conductance whose change exerts very little influence on the total sample conductance. Yielding of the clad, even if temperature as high as 4800°F are attained, will produce volume changes of less than one percent. This will permit accurate post irradiation evaluation of irradiation induced damage effects resulting in volume changes.

E. Irradiation Sample Design

Table XIII lists the pellet compositions, percent burnup, nominal diameters and lengths, consistent with data established above. Figure 44 shows the proposed pellet and sample design. It should be noted that:

1. The tube and end cap material is Type 347 stainless steel.
2. The spring is tungsten, 0.015 inch diameter wire, containing approximately two active coils.
3. The upper end cap has a thinned section for post-reactor gas release puncturing.

4. Dimensions "A" and "B", listed in Figure 44, appear in Table XVII.

5. Pellet diameters will be within 0.002 inch of the nominal given in Table XVII. The difference in diameter between pellet O.D. and clad O.D. will be no less than 0.0005 inch and no greater than 0.0015 inch.

F. Thermal Conductance of the Fuel Clad Assembly

The following data were used to establish the overall thermal conductance of the pellet and clad assembly:

<u>Diametral Clearance</u> <u>Pellet Diameter (Inch)</u>	<u>Conductance*</u> <u>(BTU/hr-ft²-°F)</u>
0.005	1600
0.010	1250

Since,

$$\Delta T = \frac{Qa^2}{4K_f} + \frac{Qa^2}{2} \left[\frac{1}{h_a a} + \frac{1}{K_c} (\ln b/a) \right] \quad (1)$$

where, K_c = Clad conductivity

h_a = Gap conductance

b = Clad O.D.

a = Clad I.D.

rewriting Equation 1,

$$\Delta T = \frac{Qa^2}{4} \left[\frac{1}{K_f} + \frac{2}{h_a a} + \frac{2}{K_c} (\ln b/a) \right] \quad (2)$$

we can now regard the term in brackets as an overall conductivity coefficient.

Sample calculations are given in Appendix B.

*Reference Uranium Dioxide: Properties and Nuclear Applications
Edited by J. Belle, U.S. Government Printing Office (pp 608-609)

G. Calculation of Fission Gas Release

The fission gas volumes and pressures were calculated using equations (1), (2) and (3) below, assuming 100% fission gas release:

$$\text{Weight of U}^{235} \text{ in pellet} = \quad (1)$$

$$\left(\frac{\text{Theoretical density}}{\text{of specimen}} \right) \left(\frac{\text{Actual density}}{\text{Theoretical density}} \right) \left(\frac{\text{Volume of}}{\text{pellet}} \right) \left(\frac{\% \text{UO}_2}{100} \right) \left(\frac{\text{wgt U}}{\text{wgt UO}_2} \right) \left(\frac{\% \text{U}^{235}}{100} \right)$$

$$\text{Volume of fission gas at S.T.P.} = \quad (2)$$

$$\left(\text{Weight U}^{235} \right) \left(\frac{\% \text{ Burnup}}{100} \right) \left(\frac{\# \text{ Fission gas atoms}}{\text{Total \# fissions}} \right) \left(\frac{\text{Liters}}{\text{gm}} \right) \left(\frac{\text{in}^3}{\text{cm}^3} \right)$$

$$P_2 = \left(\frac{V_1}{V_2} \right) \left(\frac{T_2}{T_1} \right) P_1 \quad (3)$$

where:

$$(a) \quad \frac{\text{weight U}}{\text{weight UO}_2} = \frac{235}{267} = 0.880$$

$$(b) \quad \frac{\% \text{ U}^{235}}{100} = 0.93$$

$$(c) \quad \frac{\text{liters}}{\text{gm}} = \frac{22.4}{235} = 0.0953$$

$$(d) \quad \frac{\# \text{ Fission gas atoms}}{\text{Total \# fissions}} = 0.262$$

$$(e) \quad \frac{\text{cm}^3}{\text{in}^3} = 16.38$$

$$\begin{array}{llll}
 \text{(f)} & T_1 & = & 530^{\circ}\text{F} \\
 & T_2 & = & 1060^{\circ}\text{F} \quad \text{Assuming gas space is at } 600^{\circ}\text{F} \\
 \text{(g)} & P_1 & = & 14.7 \text{ psi}
 \end{array}$$

The fission gas data along with the current pellet diameters and sample dimensions are included in Table XXII.

TABLE XXII

FISSION GAS RELEASE DATA

Composition	Percent BU	Pellet Diameter Inch	Total Sample Length Inch	Minimum* Gas Gap Length Considered Inch	Volume Fission Gas At STP-in ³	Pressure Fission Gas At 600°F-psi
Z10	40	0.350	$2\frac{1}{4}$	$\frac{1}{4}$	0.62	755
Z10	55	0.350	$2\frac{1}{4}$	$\frac{1}{4}$	0.85	1035
Z10	70	0.350	$2\frac{1}{4}$	$\frac{1}{4}$	1.08	1315
C10	40	0.300	$2\frac{1}{4}$	$\frac{1}{4}$	0.72	1050
C10	55	0.300	$2\frac{1}{4}$	$\frac{1}{4}$	0.98	1430
C10	70	0.300	$2\frac{1}{4}$	$\frac{1}{4}$	1.25	1825
Z22	40	0.250	$2\frac{1}{2}$	$\frac{1}{2}$	0.75	875
Z22	55	0.250	$2\frac{1}{2}$	$\frac{1}{2}$	1.03	1005
Z22	70	0.250	$2\frac{1}{2}$	$\frac{1}{2}$	1.31	1520
C25	40	0.190	$2\frac{1}{2}$	$\frac{1}{2}$	0.56	1360
C25	55	0.190	$2\frac{1}{2}$	$\frac{1}{2}$	0.77	1875
C25	70	0.190	$2\frac{1}{2}$	$\frac{1}{2}$	0.98	2385

*Final gap length is 0.050 inch greater than these values.

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H. Irradiation Parameters

Battelle Memorial Institute has been awarded the contract for irradiation capsule design, irradiation test monitoring and post irradiation evaluation. Emphasis at BMI has been placed upon the following:

1. Analysis of the interdependence of irradiation parameters.
2. An abbreviated nuclear mockup study.
3. Capsule design.

Work in these areas has led to the irradiation schedule shown in Figure 50 and in Table XXIII. Maintenance of target centerline fuel temperatures as fuel burnup progresses has been a major consideration in these irradiations and a significant portion of pre-irradiation planning was expended in this effort. All of the data reported above in Sections A through G, have been utilized to establish conditions which will not permit fuel melting. In addition, a constant ΔT of about 3400°F , based upon the ZrO_2 base samples, was desired. On this basis, a capsule relocation plan was evolved which involved movement of capsules to increasingly higher fluxes as irradiation progressed. Tentative relocation schemes are shown in Figures 51 and 52. The elapsed times indicated are based on reactor operating days. The temperatures shown are the initial temperatures for each flux level. A design criterion which was selected to avoid melting on the basis of flux tolerances of $\pm 15\%$ was the adoption of reference centerline temperatures of 4000°F and 3400°F for the ZrO_2 and CeO_2 base fuels, respectively. These temperatures are approximately 800°F below the respective melting points for these fuels.

A further precaution, with respect to melting, has been adopted for capsules 43-1, 43-4, and 43-6, which are scheduled to be inserted first. These capsules will be located for one full reactor cycle at fluxes 20% lower than the initial values indicated in Table XXIII. If the predicted performance of these capsules in this lower flux is achieved, these will be moved to positions indicated by the initial flux values in Table XXIII. These precautions were included in the program with the full realization that one cycle of irradiation may be sacrificed. The advantage to be gained by this sacrifice is a more intimate knowledge of capsule performance in the test reactor environment with no risk of overshooting any design parameters.

Although it is anticipated that these fuels will exhibit acceptable characteristics after 70% fission burnup, an insertion scheme was devised which permits evaluations at lower burnups, if this becomes necessary. This feature has been incorporated in the schedule shown in Figure 50. A provision has been made for examining the 40 a/o burnup specimens at a time when other specimens have reached 20 and 30 a/o burnup. Thus, if unexpected damage is found at the 40 a/o burnup level, specimens at lower burnups will be available for examination. The schedule which was finally devised, incorporated the above features while minimizing the total irradiation time.

Nuclear mockup experiments in the Shielding Facility of the Battelle Research Reactor have been completed and the results indicate that the perturbation factor, as a function of burnup, is in close agreement with that calculated by the method of W. B. Lewis¹⁸.

The capsule design is essentially complete. This design incorporates a double wall configuration with a one inch outside diameter. Heat transfer contact between the two containment vessels are made by fins which are machined as an integral part of the inner vessel. The axial length of fin per inch of capsule is adjusted on the basis of nuclear heat generation rates. Each capsule will contain five samples in the sequence shown on the table in Figure 50. All samples will be immersed in sodium. Each capsule will contain twelve thermocouples; two for each sample, and two disposed radially in the sodium.

The fabrication of irradiation samples, in accordance with Figure 44 and Table XVII has been initiated. Problems of different sinterabilities with different batches of ceramic powders have been overcome for all compositions. A satisfactory weld procedure has been developed for the Type 347 stainless steel cladding design based on Figure 44. It is anticipated that samples will be at BMI by October 12, 1962, in time for insertion in MTR and ETR on November 26, 1962.

TABLE XXIII

SUMMARY OF IRRADIATION REQUIREMENTS FOR BMI 43 SERIES IRRADIATION
CAPSULES AS ESTABLISHED BY PRE-IRRADIATION AND CAPSULE DESIGN ANALYSES

Capsule Number	Required Burnup of ZrO ₂ -Base Fuels, a/o (By Fission)	Unperturbed Thermal Neutron Flux, x 10 ¹⁴ nv		Total Estimated Irradiation Time, Days	ESTIMATED SCHEDULE			
					Assumed Capsule Insertion Date	Estimated Total		Estimated Capsule Discharge Date
						Number of Reactor Cycles		
		Initial	Final			ETR	MTR	
43-1	40	0.9	1.4	253	Nov. 1962	11	--	Feb. 1964
43-2	55	0.9	1.7	345	June 1962	15	--	March 1965
43-3	70	0.9	2.9	437	March 1963	19	--	June 1965
43-4	40	0.85	0.85	373	Nov. 1962	--	22	Feb. 1964
43-5	55	0.85	1.15	511	May 1963	22	--	Aug. 1965
43-6	70	0.85	2.0	647	Nov. 1962	28	--	Feb. 1966

BMI-43 SERIES CAPSULE SCHEDULE
Figure 50

NOTE:
TEMPERATURES IN PARENTHESES ARE FOR C-10 FUEL

TENTATIVE IRRADIATION SCHEDULE FOR Z-10 FUELED CAPSULES
Figure 51

NOTE:

TEMPERATURES IN PARENTHESES ARE FOR C-25 FUEL

TENTATIVE IRRADIATION SCHEDULE FOR Z-22 FUELED CAPSULES

Figure 52

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1. "The Development and Testing of Homogeneous Ceramic Fuels; Summary Report," NYO-2991, May 1960.
2. Rychkewitch, E., "Oxide Ceramics", p. 382, Academic Press, New York, 1960.
3. Voronov, M.M., Zoitekhova, E.A., and Danilin, A.S., "Phase Equilibrium Diagrams of the UO_2 - ZrO_2 and ThO_2 - ZrO_2 Systems," Paper No. 2490, 6, Second United Nations International Conference on the Peaceful Uses of Atomic Energy (1958).
4. D. J. M. Bevan, "Ordered Intermediate Phases in System CeO_2 - Ce_2O_3 ," J. Inorg. and Nuclear Chemistry, Vol. 1, 45-59, 1956.
5. Brauer, C., and Gradingner, H., Z. Anorg. Allg. Chem. 277, 89 (1954).
6. Hund, F., Wagner, R., and Peetz, U., Z. Elektrochem., 56, 61-65 (1952).
7. Geller, R. F., and Yavorsky, P. J., "Effects of Some Oxide Additions on the Thermal Length Changes of Zirconia," Research Paper RPL662, Journal of Research of the National Bureau of Standards, Vol. 35, July 1945.
8. Franci, J., and Kingery, W. D., "Thermal Conductivity: IV, Apparatus for Determining Thermal Conductivity by a Comparative Method; Data for Pb, Al_2O_3 , BeO and MgO," J. Am. Ceram. Soc., 37 (2, Part II) 80-84 (1954).
9. Truesdale, R. S., "Construction of a Steady State Comparative Apparatus for Measuring Thermal Conductivity and a Study of Volume Effect of Grain Boundaries on Thermal Conductivity," M. S. Thesis, Alfred University, 1960.
10. Loeb, A. L., "Thermal Conductivity: VIII, A Theory of Thermal Conductivity of Porous Materials," J. Am. Ceram. Soc., 37 (2, Part II) 96-99 (1954).
11. Kingery, W. D., Franci, J., Coble, R. L. and Vasilos, T., "Thermal Conductivity: X, Data for Several Pure Oxide Materials Corrected to Zero Porosity," J. Am. Ceram. Soc., 37 (2, Part II), 107-110 (1954).
12. Hedge, J. C. and Fieldhouse, I. B., "Measurement of Thermal Conductivity of Uranium Oxide," Armour Research Foundation Report, AECU-3381, September 20, 1956.

13. Ploetz, G. L., Muccigrosso, A. T. and Krystyniak, C. W., "Properties of Urania-Ceria Bodies for Fuel Applications," KAPL-1918, April 4, 1958.
14. Francl, J., and Kingery, W. D., "Thermal Conductivity: IX, Experimental Investigation of Effect of Porosity on Thermal Conductivity," J. Am. Ceram. Soc., 37 (2, Part II), 99-107 (1954).
15. Murtha, B. E., and Chernock, W. P., "The Development and Testing of the UO₂ Fuel Element System; Summary Report," CEND-141, June 1961.
16. Bates, J. L., "Thermal Conductivity of UO₂ Improves at High Temperatures," Nucleonics 19, June 1961.
17. Wisnyi, L. G. and Pijanowski, S. W., "The Thermal Stability of Uranium Dioxide," KAPL-1702, November 1, 1957.
18. Lewis, W. B., Nucleonics, October 1955.

Appendix A: Dimensions and Tolerances

Case I: $Z_{10} - r = 0.170$

$$\Delta R_c = (0.170) (9.5) 10^{-6} (600-70) = 0.856 \cdot 10^{-3}$$

$$\Delta R_f = (0.170) (5.3) (10^{-6}) (2700-70) = 2.369 \cdot 10^{-3}$$

$$\Delta R = (0.170) \left(\frac{35,000}{20 \cdot 10^6} \right) = 0.298 \cdot 10^{-3}$$

- a. If radial assembly clearance = 0.00025 minimum, then amount of permanent yielding at 4800°F of the tube will be $\Delta R = (2.369 - 0.856 - 0.298 - 0.25) 10^{-3} = 0.97 \cdot 10^{-3}$ and the new cold gap clearance will be $1.22 \cdot 10^{-3}$ radial.

- b. If radial assembly clearance is 0.00075, then the amount of permanent yielding

$$\Delta R = (2.369 - 0.856 - 0.298 - 0.75) = 0.47$$

and the new cold gap clearance will also be $1.22 \cdot 10^{-3}$ radial.

Thus,

$$\frac{\text{Cold gap clearance}}{\text{Pellet radius}} = 0.0071$$

Case II: $Z_{10} - r = 0.150$

$$\Delta R_c = 0.755 \cdot 10^{-3}$$

$$\Delta R_f = 2.09 \cdot 10^{-3}$$

$$\Delta R_e = 0.263 \cdot 10^{-3}$$

- a. If the radial assembly clearance is 0.00025 minimum, then amount of permanent yielding at 4800°F is

$$\Delta R = (2.09 - 0.755 - 0.263 - 0.25) = 0.82 \cdot 10^{-3},$$

and the new cold gap is $1.07 \cdot 10^{-3}$.

Thus,

$$\frac{\text{Cold gap clearance}}{\text{Pellet radius}} = 0.0071$$

Case III: Z22 - r = 0.125

$$\Delta R_c = (0.125) (9.5) 10^{-6} (600-70) = 0.629 \cdot 10^{-3}$$

$$\Delta R_f = (0.125) (5.6) 10^{-6} (2700-70) = 1.84 \cdot 10^{-3}$$

$$\Delta R_e = (0.125) \left(\frac{25,000}{20 \cdot 10^6} \right) = 0.14 \cdot 10^{-3}$$

- a. If minimum radial assembly clearance = 0.00025 minimum, then amount of permanent yielding at 4800°F of the clad will be

$$\Delta R = (1.84 - 0.629 - 0.14 - 0.25) = 1.019 \cdot 10^{-3}$$

and the new cold gap clearance will be $1.27 \cdot 10^{-3}$,

thus,

$$\frac{\text{Cold gap clearance}}{\text{Pellet radius}} = \frac{1.27 \cdot 10^{-3}}{0.125} = 0.01$$

Similar calculations made for the radial gap to pellet radius for the CeO₂-base samples have provided the following values:

$$\text{C10: } \frac{\text{Radial gap}}{\text{Pellet radius}} = \frac{1.80 \times 10^{-3}}{0.150} = 0.012$$

$$\text{C25: } \frac{\text{Radial gap}}{\text{Pellet radius}} = \frac{1.10 \times 10^{-2}}{0.095} = 0.012$$

Appendix B: Thermal Conductance Calculations

For Z10, r = 0.170,

$$\frac{1}{K_{\text{eff}}} = \frac{1}{1.16} + \frac{2}{1250 \left(\frac{0.170}{12} \right)} + \frac{2}{12} \left(\ln \frac{0.190}{0.170} \right)$$

$$\frac{1}{K_{\text{eff}}} = 0.862 + 0.113 + 0.018$$

$$K_{\text{eff}} = \frac{1.00}{\text{hr-ft-}^{\circ}\text{F}} \quad \text{BTU}$$

for Z10, r = 0.150,

$$\frac{1}{K_{\text{eff}}} = \frac{1}{1.16} + \frac{2}{1250 \left(\frac{0.150}{12} \right)} + \frac{2}{12} \left(\ln \left(\frac{0.170}{0.150} \right) \right)$$

$$= 0.862 + 0.128 + 0.0204$$

$$K_{\text{eff}} = \frac{1.01}{\text{hr-ft-}^{\circ}\text{F}} \quad \text{BTU}$$

for Z22, r = 0.125,

$$\frac{1}{K_{\text{eff}}} = \frac{1}{0.93} + \frac{2}{1250 \left(\frac{0.125}{12} \right)} + \frac{2}{12} \left(\ln \left(\frac{0.145}{0.125} \right) \right)$$

$$= 1.07 + 0.154 + 0.012 = 1.24$$

$$K_{\text{eff}} = \frac{0.80}{\text{hr-ft-}^{\circ}\text{F}} \quad \text{BTU}$$

for C10, r = 0.160

$$\frac{1}{K_{\text{eff}}} = \frac{1}{1.66} + \frac{2}{1000 \left(\frac{0.160}{12} \right)} + \frac{2}{12} \left(\ln \frac{0.180}{0.160} \right)$$

$$= 0.602 + 0.150 + 0.019$$

$$K_{\text{eff}} = 1.33 \text{ BTU/hr-ft-}^{\circ}\text{F}$$

for C25, r = 0.095

$$\frac{1}{K_{\text{eff}}} = \frac{1}{1.18} + \frac{2}{1000\left(\frac{0.095}{12}\right)} + \frac{2}{12} \left(\ln \frac{0.115}{0.095} \right)$$

$$K_{\text{eff}} = 0.88 \text{ BTU/hr-ft-}^{\circ}\text{F}$$