FINAL SUMMARY REPORT

MASTER

IRRADIATION TESTING OF CERAMIC FUELS

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Significant contributors to the program at Combustion Engineering, Inc., were C. E. Burdick, A. Emery, W. C. Taylor, D. E. Mahagin and G. W. Lindemann.

INTRODUCTION

The general objective of this program was the development of a ceramic fuel, capable of burnups to high U-235 depletions, for use in high enrichment concepts. Specific objectives of this program are summarized below:

1) To establish the composition limits for thermally stable, single phase, face-centered cubic crystal structures in the zirconia rich region of the $\text{UO}_2\text{-CaO-ZrO}_2$ system and in the ceria rich end of the $\text{UO}_2\text{-CeO}_2$ system.

2) To establish a method for fabricating high density pellets of the single phase, face-centered cubic solid solutions in both the zirconia and ceria base systems.

3) 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.

4) 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 of interest.

This report contains a summary of work performed under Contract AT(30-1)-2936. Further details of this research and development effort are reported in the following Summary Reports:

CEND-158 (NYO-2998), September, 1962

CEND-190, September, 1963

CEND-2936-222, November, 1964

The present Summary Report contains six sections, as follows:

I. PHASE RELATIONSHIPS

A summary is presented of phase relationships in both the zirconia and ceria base systems. Investigations of the influence of sintering atmospheres as well as pellet fabrication parameters are included. Although rigorous phase diagram determinations were not within the scope of this effort, evaluations of phase relationships were required to isolate limits of composition within which a single phase, face-centered cubic crystal structure is retained throughout the temperature range of interest.

II. EX-REACTOR PROPERTY EVALUATIONS

A summary is presented of important properties of fuels under consideration. Included are evaluations of thermal conductivity, melting points, thermal stability, thermal expansion and corrosion resistance in water and steam.

III. FABRICATION OF IRRADIATION TEST SAMPLES

The effort directly related to the fabrication and ex-reactor characterization of fuel and irradiation samples is summarized.

IV. IRRADIATION TESTING

A description of the capsule design as well as a summary of important considerations upon which the target irradiation test conditions were based are provided. A summary is made of in-reactor conditions attained for these fuels.

V. POST-IRRADIATION EXAMINATION

Results which are summarized include visual inspection, gamma scanning, dimensional density measurements, fission gas release, metallographic examinations, x-ray diffraction analyses, alpha and beta autoradiography, and post-irradiation corrosion evaluations.

VI. ANALYSES OF POST-IRRADIATION DATA

Relationships between grain growth, thermal conductance, fission gas release, swelling and burnup are discussed.

SUMMARY

PHASE RELATIONSHIPS

An extensive single phase, face centered cubic region was found in the ZrO_2 rich portion of the UO_2 - ZrO_2 - CaO system for powder compacts sintered at 1700°C (3090°F) or higher in vacuum, argon or hydrogen. Long-time isothermal heat treatments at temperatures from 1000 to 2000°C (1830 to 3630°F) restricted the thermally stable single phase cubic structures to compositions containing up to 12 m/o UO_2 and from 15 to 25 m/o CaO . Two phase fields, face centered cubic plus CaZrO_3 and face centered cubic plus monoclinic bound the upper and lower limits of the single phase cubic region. The high CaO , high UO_2 compositions developed complex structures by reaction of CaZrO_3 with the face centered cubic matrix during the isothermal heat treatments.

Single phase, face centered cubic solid solutions were obtained by air firing UO_2 - CeO_2 compositions containing up to 21 m/o UO_2 . These single phase structures were stable after extended heat treatments in argon at temperatures of 1500°C (2730°F). Two distinct face centered cubic phases were found after air firing samples containing 50 m/o UO_2 or greater. Extrapolation of lattice parameter data indicated that the two phase structure originated at compositions between 21 and 30 m/o UO_2 . The lattice parameter of one of these phases changed with variation in UO_2 content whereas the lattice constant of $5.427 \text{ \AA}$ for the second phase was invariant with UO_2 content.

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

EX-REACTOR PROPERTY EVALUATIONS

Thermal Conductivity

Measurements of thermal conductivity by the steady state comparative method in the temperature range of 200 to 950°C (390 to 1740°F) 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 $0.0045 \text{ cal/cm-sec}^{-1}\text{-cm}^{-2}\text{-}^\circ\text{C}^{-1}$ 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 $\text{cal/cm-sec}^{-1}\text{-cm}^{-2}\text{-}^\circ\text{C}^{-1}$ over the same temperature range.

Thermal conductivity data for zirconia base fuel compositions were extended to 2400°C (4350°F). A gradual decrease in conductivity was observed at temperatures up to 1500°C , followed by an increase in conductivity at temperatures above 1500°C (2730°F).

Melting Point

The melting point apparatus constructed for these evaluations were 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 and 2685°C (4775 and 4865°F) were measured for the 4 m/o UO_2 -stabilized ZrO_2 samples, whereas values of 2630 and 2670°C (4766 and 4838°F) were found for the 12 m/o UO_2 composition. Liquidus temperatures of 2420 and 2335°C (4388 and 4235°F) were measured for the 7 m/o and 21 m/o $\text{UO}_2\text{-CeO}_2$ compositions, respectively. As a result of difficulties encountered in obtaining reliable solidus temperatures for the ceria base compositions, the solidus, used as a base for the irradiation program, was established as 100°C (180°F) below the liquidus for each composition.

Thermal Expansion

The thermal expansion coefficients for two compositions in the $\text{UO}_2\text{-CaO-ZrO}_2$ system can be best described by the following relationships for the temperature range of 20 to 1000°C (68 to 1830°F).

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

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

where

$$t = ^\circ\text{C}$$

Corrosion

Unclad pellets of four fuel compositions (7 and 21 m/o $\text{UO}_2\text{-CeO}_2$ and 4 and 12 m/o $\text{UO}_2\text{-CaO-ZrO}_2$) showed corrosion penetrations of less than 0.002 cm (0.001 inch) following 700 days of exposure to 650°C (1200°F) flowing steam and 480 days in 360°C (680°F) static degassed water.

FABRICATION OF IRRADIATION TEST SAMPLES

Pellets for irradiation testing were prepared by cold pressing and sintering to densities of 89 to 90 percent of theoretical density for the zirconia base compositions and 92 to 95 percent of theoretical density for the ceria base compositions. The four compositions selected for irradiation testing were as follows:

Zirconia base:

4 m/o UO_2 - 77 m/o ZrO_2 - 19 m/o CaO: Designated Z10

10.2 m/o UO_2 - 72.2 m/o ZrO_2 - 17.6 m/o CaO: Designated Z22

Ceria base:

7 m/o UO_2 - 93 m/o CeO_2 : Designated C10

17.5 m/o UO_2 - 82.5 m/o CeO_2 : Designated C25

After completion of x-ray diffraction, metallographic and chemical analyses of selected pellets from each batch, pellets of one composition were assembled into stainless steel cladding tubes approximately 2-1/2 inches long. Final closures were made by heliarc welding of end plugs. Five clad irradiation samples each were assembled into six capsules, together with three zirconia base and two ceria base samples of comparable UO_2 content.

Compromises had to be made to permit the irradiation testing of ceria base and zirconia base samples in the same capsule. Reference burnup and temperature conditions were provided for the zirconia base samples. The differences in accrued burnup between the zirconia and ceria base samples were estimated as 5 to 10 percent.

Nuclear mockup experiments confirmed the W. B. Lewis method for calculating perturbation factor as a function of burnup for these fuels.

IRRADIATION PROGRAM

Six instrumented capsules, each containing five stainless steel clad specimens, three with ZrO_2 base fuels and two with CeO_2 base fuels, were irradiated in the ETR and the MTR. Capsule relocations were, in general, successful in maintaining target maximum fuel temperatures close to 2200°C and 1870°C for the ZrO_2 base and the CeO_2 base fuels, respectively. Outages of 14 out of the 72 thermocouples during in-reactor residence left at least one thermocouple for continuous monitoring the temperature of each fuel specimen in the six capsules. Burnups ranged from 4.4×10^{20} and 6.5×10^{20} f/cm³ for the Z10 and C10 fuels and up to 18.5×10^{20} and 28.4×10^{20} f/cm³ for the Z22 and C25 fuels.

POST-IRRADIATION EXAMINATION

Post-irradiation examination consisted of visual inspection, gamma scanning, burnup analysis, dimensional and density measurements, fission gas sampling and analysis, metallographic examination, x-ray diffraction analysis and alpha and beta autoradiography. Pertinent results of some of these examinations are summarized below:

- 1) None of the samples showed significant dimensional changes. There was no evidence of either corrosive attack on the cladding or severe distortion.
- 2) Fission gas release ranged from 22 to 32 percent of the theoretical amounts formed for the lower burnup C10 and Z10 fuels to 84 to 96 percent for the highest burnup Z22 and C25 fuels. The fractional release increased with increasing burnup for each fuel composition.
- 3) Fuel microstructures of the ZrO_2 base fuels at all burnup levels resembled high burnup UO_2 structures; that is, central void formation, columnar grains, equiaxed grain growth and essentially unaffected grains were observed with decreasing radial temperature. A filament-like structure near the fuel surface was not identified. The CeO_2 base fuels contained a porous, large equiaxed grain structure surrounding the central void. Microstructural changes in the CeO_2 system were, in general, less pronounced than in the case of the ZrO_2 base fuels.
- 4) All irradiated fuels retained the single phase, face centered cubic crystal structure.

5) Irradiation to burnup of 25×10^{20} f/cm³ did not adversely affect the corrosion resistance of these fuels.

6) As expected, diametrical changes were almost insignificant. Two types of axial dimensional changes were observed. One was a small change of the fuel column or pellet length in the cooler operating outer fuel regions and the other was a much larger length change which occurred in some samples along the fuel centerline and which was characterized by localized swelling at the top center of the fuel column.

ANALYSES OF POST-IRRADIATION DATA

Decided trends in the post-irradiation relationship between percent grain growth and burnup for both zirconia base and ceria base fuels provide more than subtle indications that the thermal conductance of the fuel rods decreased with increasing burnup. The slope and width of the trend bands relating percent grain growth and burnup for the zirconia base and ceria base fuels are almost identical.

For burnups above approximately 8×10^{20} f/cm³, fission gas release appears to increase linearly with burnup for both the zirconia and ceria base fuels. The following relationship appears to represent the bulk of the data for these two fuel systems for burnups in excess of 8×10^{20} f/cm³:

$$R_z = \frac{B + 14.4 (\pm 2.5)}{0.44}$$

$$R_c = \frac{B + 15.5 (\pm 1.8)}{0.43}$$

where

R_z = Percent gas release from zirconia base fuels

R_c = Percent gas release from ceria base fuels

B = Burnup (f/cm³ $\times 10^{20}$)

Most of the swelling observed in these fuels was characterized by small increases in the fuel column length in the outer regions of the fuel and, in some cases, by more severe swelling at the top center of the fuel column.

Fuel swelling values fall below the value of 0.7 percent ΔV per 10^{20} f/cm³ found for UO₂. With only a few exceptions, swelling values were below 0.2 percent ΔV per 10^{20} f/cm³ which is indicative of good swelling accommodation within the hot plastic center of the fuel column.

I. PHASE RELATIONSHIPS

A. SUMMARY

An extensive single phase, face centered cubic region was found in the ZrO_2 rich portion of the UO_2 - ZrO_2 -CaO system for powder compacts sintered at 1700°C (3090°F) or higher in vacuum, argon or hydrogen. Long-time isothermal heat treatments at temperatures from 1000 to 2000°C (1830 to 3630°F) restricted the thermally stable single phase cubic structures to compositions containing up to 12 m/o UO_2 and from 15 to 25 m/o CaO. Two phase fields, face centered cubic plus CaZrO_3 and face centered cubic plus monoclinic bound the upper and lower limits of the single phase cubic region. The high CaO, high UO_2 compositions developed complex structures by reaction of CaZrO_3 with the face centered cubic matrix during the isothermal heat treatments.

Single phase, face centered cubic solid solutions were obtained by air firing UO_2 - CeO_2 compositions containing up to 21 m/o UO_2 . These single phase structures were stable after extended heat treatments in argon at temperatures of 1500°C (2730°F). Two distinct face centered cubic phases were found after air firing samples containing 50 m/o UO_2 or greater. Extrapolation of lattice parameter data indicated that the two phase structure originated at compositions between 21 and 30 m/o UO_2 . The lattice parameter of one of these phases changed with variation in UO_2 content whereas the lattice constant of $5.427 \text{ \AA}$ for the second phase was invariant with UO_2 content.

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

B. SAMPLE PREPARATION AND SINTERABILITY TESTS

The composition, purity and source of the oxide starting materials used in this investigation are shown in Table I-1. The samples were prepared by conventional powder metallurgy methods of cold pressing and sintering. The need for organic binders such as Carbowax 4000 was eliminated by improved

TABLE I-1

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	2μ	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 _f 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								
Bulk 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

compaction methods which provided samples that were free of cracks and of adequate green strength for handling. For these studies all samples were pressed at 5 or 10 tsi to avoid lamination cracks that developed at the higher compaction pressure.

An extensive sinterability study was conducted on two compositions in each of the ceria and zirconia base fuel systems exhibiting single phase, face centered cubic structures. High density homogeneous samples 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 (3270°F) for one hour in vacuum (5×10^{-6} mm Hg). The sintered compacts were crushed to -200 mesh powder using a mortar and pestle and then milled for 8 to 16 hours in rubber lined steel jars using Burundum grinding cylinders. No binder or lubricant additions to the powder were necessary because suitable crack-free samples could be readily prepared. The samples were pressed at 5 tsi and sintered at 1800°C (3270°F) in purified argon over periods ranging from 2 to 144 hours. The effects of milling for 8 and 16 hours, respectively, and of sintering times at 1800°C (3270°F) upon the bulk densities of samples of the two compositions are shown graphically in Figure I-1. An increase in milling time from 8 to 16 hours resulted in significantly improved densities for samples of both compositions.

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 (2730°F) for 4 or 16 hours to geometric densities of 96 to 98 percent of theoretical density. A second series of samples attained bulk densities of 88 to 90 percent of theoretical density by air sintering at 1450°C (2640°F) for one hour. The desired value of 94-95 percent of theoretical density for the irradiation investigations was obtained by air sintering at 1475°C (2687°F) for one-half hour. As the CeO_2 base samples are highly sensitive to thermal stress

FIG. I-1 EFFECT OF SINTERING TIME AT 1800°C (3270°F) 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)

slow heating and cooling rates of at least 100°C (180°F) 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. 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 sintering techniques described in the foregoing.

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 to develop special techniques for the preparation of a variety of shapes required to determine the physical and thermal properties of these oxide compositions. The tests were conducted in oxidizing (air), reducing (hydrogen) and inert (vacuum or argon) environments at temperatures to 2100°C (3810°F). 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 $\text{UO}_2\text{-ZrO}_2\text{-CaO}$ system were prepared by sintering in vacuum at temperatures from 1500 to 1900°C (2730 to 3450°F). The vacuum sintering cycle involved heating to the sintering temperature during a 3 to 4 hour period, holding at temperature from 2 to 16 hours, and cooling to room temperature within a 3 to 4 hour period. The furnace pressure was maintained at 5×10^{-3} micron or better during sintering.

Due to the high sample losses by volatilization at the elevated temperatures in vacuum, the furnace was modified to allow sintering in inert gases. The argon gas was purified by means of a zirconium chip gettering furnace. The samples were initially heated in vacuum to about 1000°C (1830°F) to remove volatile constituents in the samples and container. Following

the out-gassing process, argon was introduced 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 sintering both in vacuum or argon led to the formation of identical structures for the same compositions. However, lower losses resulted during sintering in the latter and subsequent phase relationship 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, and contained in a molybdenum or tantalum boat for sintering in vacuum or in argon at temperatures to 1700°C (3090°F). All of the CeO_2 base samples were highly reactive above 1500°C (2730°F) with the container materials constructed from beryllia, zirconia, thoria, tungsten, molybdenum, tantalum and rhodium. As a result of high sample losses by volatilization above 1500°C (2730°F) 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 (2460 to 2730°F) in these furnace environments.

2. Oxidizing Atmosphere

A limited series of ZrO_2 base samples were air sintered at temperatures to 1550°C (2820°F) in the silicon carbide element resistance furnace. Equivalent weights of U_3O_8 were substituted for UO_2 in the preparation of powder mixtures to avoid crumbling of the pellets by oxidation of UO_2 to U_3O_8 during heating. The samples were heated slowly to the sintering temperature over 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 (2730°F) and air quenched by rapid removal of 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 bulk of the phase relationship samples of the UO_2 - CeO_2 compositions was prepared by air sintering at temperatures of 1400 to 1500°C (2550 to 2730°F). The urania starting material was U_3O_8 . The CeO_2 base samples were extremely thermal-stress sensitive and slow heating and cooling rates were required to prevent cracking and fragmentation.

3. Reducing Atmosphere

CaO stabilized $\text{ZrO}_2\text{-UO}_2$ (or U_3O_8) 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 to 45 ft^3/hr of hydrogen. The majority of the sintering runs utilized as-bottled hydrogen gas. Several runs were made for which the hydrogen was prepurified to a dew point of -51°C (-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 to 1200°C (2010 to 2190°F) to minimize thermal stress cracking of the samples. The furnace temperature was increased at the rate of about 100°C (180°F) per hour to the sintering temperature, held for 12 to 16 hours at temperature and cooled at the rate of 100 to 300°C (180 to 540°F) per hour to room temperature. Four experiments were conducted at 1425, 1525, 1675, and 1750°C (2600, 2780, 3045, and 3180°F). Sintering time at each of the four temperatures was 12 hours. All samples were furnace cooled to room temperature in hydrogen.

Sintering data at 1425°C (2600°F) indicated that densification increased both with increasing UO_2 contents and with decreasing CaO contents. All compositions containing up to about 20 m/o UO_2 densified only slightly above the green densities. Compositions containing more than about 20 m/o UO_2 showed improved sinterability with increasing UO_2 contents, probably as a result of increasing concentrations of the highly sinterable UO_2 . Shrinkage showed similar trends with UO_2 content.

At 1525°C (2780°F) marked improvement in densification was obtained for the 10 m/o CaO series. This effect was most pronounced for the low UO_2 compositions which had shown little or no densification at 1425°C (2600°F). Sinterability behavior at 1675°C (3045°F) was examined as a function of bulk densities containing fixed UO_2 and variable CaO contents. Samples containing 4 m/o and 12 m/o UO_2 showed either no change or a slight decrease in density with increasing CaO content. This was expected in view 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 .

At 1750°C (3180°F) sinterability trends similar to those observed for the 1675°C (2780°F) samples were obtained. The low UO_2 compositions of the 10 and 20 m/o CaO series densified at lower rates at 1750°C (3180°F) than at 1675°C (2780°F). 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.

A limited hydrogen sintering study was conducted on samples of two CeO_2 base compositions containing 7 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 (2780°F) 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 (180°F) per hour. A second series of duplicate samples with UO_2 and U_3O_8 , respectively, was sintered at 1700°C (3090°F) for 16 hours in hydrogen. The heating and cooling rates were reduced to 50 to 75°C (90 to 135°F) per hour. Though all samples were cracked, they were 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 to a deep blue, probably due to Ce_2O_3 vapor deposition.

3. 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.

C. PHASE RELATIONSHIPS IN THE UO_2 -CaO- ZrO_2 SYSTEM

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 was completed on samples with compositions as shown in Table I-2. Data obtained by x-ray diffraction and microscopy were used to establish phase boundaries resulting from each isothermal heat treatment.

Suitable etchants were 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 2 to 30 minutes, depending upon the composition and microstructure of the samples.

1. 1000°C Heat Treatment

Two series of samples were utilized for the phase relationship studies involving 1000°C (1830°F) heat treatments for compositions located in the ZrO₂ rich ternary region. Duplicate samples of the first series initially were prepared by sintering in vacuum or in argon at 1800°C (3270°F) for four hours prior to isothermal heat treatment. The phases developed by argon or vacuum sintering are shown in Figure I-2. One group of samples was heat treated at 1000°C for 28 days in argon. The second group of the same series was heated in air at 1000°C for 28 days in order to compare structural changes developed in an inert atmosphere with changes following heating in air. The second series of samples which were of the same compositions as the first series, were sintered in hydrogen at 1750°C (3180°F) for 16 hours, furnace cooled to room temperature, and then reheated in argon at 1000°C (1830°F) for 28 days. The phases formed by hydrogen sintering are shown in Figure I-3. The relationships based on samples sintered in vacuum, argon or hydrogen and then reheated in argon will be discussed jointly since very similar structures were formed by all three 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.

a. Heat Treatments in Argon

The general appearance of the phase fields for the ZrO₂ corner for vacuum or argon sintered and 1000°C (1830°F) argon reheated samples is shown in Figure I-4.

TABLE I-2

COMPOSITIONS IN THE $\text{UO}_2\text{-ZrO}_2\text{-CaO}$ SYSTEM UNDER INVESTIGATION

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

LEGEND

- O - FCC
- - FCC + CaZrO_3

FIG. I-2 PHASES PRESENT AT ROOM TEMPERATURE IN THE UO_2 - ZrO_2 - CaO SYSTEM FOR COMPOSITIONS SINTERED AT 1800°C (3270°F) IN ARGON OR IN VACUUM

LEGEND

O - FCC

□ - FCC + CaZrO_3

FIG. I-3 PHASES PRESENT AT ROOM TEMPERATURE IN THE UO_2 - ZrO_2 - CaO SYSTEM FOR COMPOSITIONS SINTERED AT 1750°C (3180°F) IN HYDROGEN

FIG. I-4 PHASES PRESENT AT ROOM TEMPERATURE IN THE UO_2 - ZrO_2 - CaO SYSTEM FOR COMPOSITIONS SINTERED AT 1800°C (3270°F) IN ARGON AND THEN REHEATED AT 1000°C (1830°F) IN ARGON FOR 28 DAYS

Similar phase fields for hydrogen sintered at 1000°C argon reheated samples are shown in Figure I-5. The high CaO, high UO_2 region formed complex structures consisting of CaUO_4 and face centered cubic solid solutions.

A typical microstructure of the single phase cubic compositions is shown in Figure I-6a. These structures are highly resistant to chemical attack and required up to 30 minutes immersion in the $\text{HNO}_3\text{-Hf-H}_2\text{O}$ solution to delineate the grain boundaries. There was no evidence of impurity or decomposition phases for UO_2 contents up to 12 m/o UO_2 as a result of the 1000°C (1830°F) heat treatment in argon. A feather-like grain boundary phase was observed in the 15 m/o UO_2 sample prepared with 20 m/o CaO stabilized ZrO_2 (Figure I-6b). At high magnification, the feather-like phase consisted of a very fine precipitate. This phase was identified by x-ray diffraction to be monoclinic ZrO_2 solid solution. The quantity of this phase increased by inward growth toward the center of the grains in the high UO_2 samples (Figure I-6c). At the highest composition (38 m/o UO_2) investigated for this series, the monoclinic phase was the major structure and contained islands of the cubic phase (Figure I-6d). 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 I-7a, 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 I-7b. The quantity and size of the CaZrO_3 decreased with increasing UO_2 content. There was no evidence of decomposition of this phase 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 I-4 and I-5. A small amount of a fine precipitate for the 38 m/o UO_2 —22 m/o CaO at the grain boundaries

LEGEND

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

FIG. I-5 PHASES PRESENT AT ROOM TEMPERATURE IN THE UO_2 - ZrO_2 - CaO SYSTEM FOR COMPOSITIONS SINTERED AT 1750°C (3180°F) IN HYDROGEN AND THEN REHEATED AT 1000°C (1830°F) IN ARGON FOR 28 DAYS

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

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

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

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

NOTE
ALL MAGNIFICATIONS ARE 500 X

FIG. 1-6 MICROSTRUCTURES OF UO_2 - ZrO_2 - CaO COMPOSITIONS FOLLOWING ANNEALING
HEAT TREATMENT AT 1000°C (1830°F) IN ARGON FOR 28 DAYS

MAG 500 X

(a) VIEW OF TWINNED STRUCTURE OF THE CaZrO_3 PHASE FOR THE TWO PHASE UO_2 - ZrO_2 - CaO COMPOSITIONS

MAG 500 X

(b) VIEW OF STRUCTURE SHOWN IN (a) FOLLOWING SEVERE ETCHING TO OUTLINE THE MATRIX 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, but again this could not be confirmed by x-ray diffraction.

b. Heat Treatment in Air

The phase fields based on 1800°C (3270°F) argon sintered and then 1000°C (1830°F) air reheated samples are shown in Figure I-8. The same group of 12 samples was removed from the furnace after accumulative heat treatments of 4, 7, 17, and 28 days for visual examination and weight and dimensional measurements. All samples had remained intact during the 28 day heat treatment.

Figure I-8 indicates 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 the complete absence of minor phases under 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, 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:

CaUO_4 (major phase)
 CaZrO_3 (minor phase)
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:

LEGEND

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

FIG. I-8 PHASES PRESENT AT ROOM TEMPERATURE IN THE UO_2 - ZrO_2 - CaO SYSTEM FOR COMPOSITIONS SINTERED AT 1800°C (3270°F) IN ARGON AND THEN REHEATED AT 1000°C (1830°F) IN AIR FOR 28 DAYS

Monoclinic solid solution (major phase)

Hexagonal U_3O_8 (minor phase)

Unknown minor phase indexed as BCC with an approximate lattice constant of 10.7 Å.

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

2. 1300°C Heat Treatment

The phase relationships for samples sintered in argon or in hydrogen, and then reheated at 1300°C (2370°F) in argon, are shown in Figures I-9 and I-10. In general, the phase fields resemble those observed for the 1000°C heat treated argon atmosphere samples. The first evidence of thermal instability for the high CaO compositions is noted in the 12 m/o UO_2 samples which were hydrogen sintered and contained 25 and 31 m/o CaO, respectively. Figure I-11 shows the partial decomposition of the $CaZrO_3$ phase by reaction with the face centered cubic matrix. The fine precipitate surrounding the $CaZrO_3$ phase was identified as $CaUO_4$ by x-ray diffraction. The higher CaO compositions containing from about 13 to 35 m/o UO_2 are grouped in a single region for which unidentified multiphase structures were observed microscopically. The structure of the 15 m/o UO_2 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 I-12). The structure of the 29 m/o UO_2 sample consisted of a fine precipitate within the grains of the single phase matrix (Figure I-13). 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 I-14) for the adjacent 38 and 52 m/o UO_2 .

LEGEND

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

FIG. I-9 PHASES PRESENT AT ROOM TEMPERATURE IN THE UO_2 - ZrO_2 - CaO SYSTEM FOR COMPOSITIONS SINTERED AT 1800°C (3270°F) IN ARGON AND THEN REHEATED AT 1300°C (2370°F) IN ARGON FOR 28 DAYS

LEGEND

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

FIG. I-10 PHASES PRESENT AT ROOM TEMPERATURE IN THE UO_2 - ZrO_2 - CaO SYSTEM FOR COMPOSITIONS SINTERED AT 1750°C (3180°F) IN HYDROGEN AND THEN REHEATED AT 1300°C (2370°F) IN ARGON FOR 28 DAYS

MAG 500 X

ETCHED

FIG. I-11 STRUCTURE OF THE 12 M/O UO_2 , HIGH CaO COMPOSITIONS SHOWING THE DECOMPOSITION PRODUCT, CaUO_4

MAG 500 X

ETCHED

FIG. I-12 MULTIPHASE STRUCTURE FOR THE
HIGH CaO COMPOSITIONS
CONTAINING 21 M/O UO_2

MAG 500 X

ETCHED

FIG. I-13 MULTIPHASE STRUCTURE FOR THE HIGH CaO
COMPOSITIONS CONTAINING 29 M/O UO_2

MAG 500 X

ETCHED

FIG. I-14 TWO PHASE STRUCTURE, FACE CENTERED CUBIC PLUS MONOCLINIC, FOR THE HIGH CaO COMPOSITIONS CONTAINING 38 M/O TO 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 relationships based on samples sintered in 1800°C (3270°F) argon and then reheated in argon at 1500°C (2730°F), Figure I-15, shows an interesting departure from the 1000°C (1830°F) and 1300°C (2370°F) diagrams in 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 (1830°F) isotherms. There was no evidence of decomposition of CaZrO_3 for any of the samples and there was a 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 which received the 1500°C argon heat treatment showed evidence of CaUO_4 or other decomposition products by either 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 was sintered at 1800°C (3270°F) in argon and then reheated at 1700°C (3090°F) in argon for seven days. The phase field is shown in Figure I-16. The heat treatment extended the single phase cubic region to include all compositions containing less than about 15 m/o CaO. The only two

LEGEND

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

FIG. I-15 PHASES PRESENT AT ROOM TEMPERATURE IN THE UO_2 - ZrO_2 - CaO SYSTEM FOR COMPOSITIONS SINTERED AT 1800°C (3270°F) IN ARGON AND THEN REHEATED AT 1500°C (2730°F) IN ARGON FOR 28 DAYS

FIG. I-16 PHASES PRESENT AT ROOM TEMPERATURE IN THE UO_2 - ZrO_2 - CaO SYSTEM FOR COMPOSITIONS SINTERED AT 1800°C (3270°F) IN ARGON AND THEN REHEATED AT 1700°C (3040°F) IN ARGON FOR 7 DAYS

phase field of face centered cubic plus CaZrO_3 is of the same magnitude as observed for the 1500°C (2730°F) isotherm. No other second phases were detected in any other sample 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 (2910°F). Heating above this temperature resulted in single phase cubic structures regardless of 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 I-17 and I-18 are based upon argon or hydrogen sintered samples which were reheated at 1800°C (3270°F) for 30 hours in argon. Both diagrams contain identical phase fields of face centered cubic and face centered cubic plus CaZrO_3 . They resemble very closely the diagrams determined from the as-sintered samples shown in Figures I-2 and I-3. The essential difference between the 1700°C (3090°F) and 1800°C (3270°F) isotherms 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 (3270°F) argon sintered samples were reheated at 2000°C (3630°F) for 24 hours in argon. Phase relationships based on these samples are shown in Figure I-19. 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 further confirm the thermal stability of the low CaO , single phase cubic structures at temperatures above approximately 1600°C (2900°F) in argon.

LEGEND

- - FCC
- - FCC + CaZrO_3

FIG. I-17 PHASES PRESENT AT ROOM TEMPERATURE IN THE $\text{UO}_2\text{-ZrO}_2\text{-CaO}$ SYSTEM FOR COMPOSITIONS SINTERED AT 1750°C (3180°F) IN HYDROGEN AND THEN REHEATED AT 1800°C (3270°F) IN ARGON FOR 30 HOURS

FIG. I-18 PHASES PRESENT AT ROOM TEMPERATURE IN THE UO_2 - ZrO_2 - CaO SYSTEM FOR COMPOSITIONS SINTERED AT 1800°C (3270°F) IN ARGON AND THEN REHEATED AT 1800°C IN ARGON FOR 30 HOURS

LEGEND

- — FCC
- — FCC + CaZrO_3

FIG. I-19 PHASES PRESENT AT ROOM TEMPERATURE IN THE UO_2 - ZrO_2 - CaO SYSTEM FOR COMPOSITIONS SINTERED AT 1800°C (3270°F) IN ARGON AND THEN REHEATED AT 2000°C (3630°F) IN ARGON FOR 24 HOURS

7. Conclusions

These investigations show 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 .

D. PHASE RELATIONSHIPS IN THE UO_2 - CeO_2 SYSTEM

A limited investigation was undertaken to determine the effect of various sintering and heat treating parameters on the phases found in the UO_2 - 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 aspects is discussed below.

1. Initial Investigation

The initial part of the program was concentrated on investigations of 14 and 30 m/o UO_2 - 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 to 1550°C (2460 to 2820°F). Results of x-ray diffraction analyses indicated single phase, face centered cubic crystal structures for both compositions after air firing at 1375 to 1550°C (2510 to 2820°F) for three and four hours, respectively, and after vacuum sintering at 1350°C for three hours. These results were confirmed by microscopic examination, see Figure I-20. Samples of both compositions which were vacuum sintered at 1500°C (2730°F) for three hours, or argon sintered at 1400°C (2550°F) for three hours, exhibited two face centered cubic crystal structures. The lattice parameters for these two face centered cubic phases are 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 possibility of an incomplete reaction is difficult to assume because these structures were also found after

MAG 500 X

ETCHED

FIG. I-20 SINGLE PHASE STRUCTURE TYPICAL FOR THE
 $\text{UO}_2 - \text{CeO}_2$ COMPOSITIONS UNDER
INVESTIGATION

sintering in vacuum at 1500°C for the same length of time over which a single phase, face centered cubic structure was formed in the same environment at 1350°C.

2. Hydrogen Sintering

Samples containing 7 and 21 m/o UO_2 (or equivalent U_3O_8) were sintered in hydrogen at 1700°C (3090°F) for 16 hours with heating and cooling rates of 50 to 75°C (90 to 125°F) per hour. Even at these low heating and cooling rates, all samples exhibited a strong tendency to fracture, probably as a result of the volume changes induced by the formation of lower oxides of cerium as a result of hydrogen sintering. Samples containing U_3O_8 exhibited higher geometric densities than those containing UO_2 , most likely because of a greater inhibition to form 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 I-21 to I-23. The microstructure (Figure I-21) 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 investigation⁽¹⁾ 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 apparently single phase solid solution. However, x-ray diffraction results indicate small remnants of substoichiometry resulting in wide diffraction lines. 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 which indicate less volume transformation to lower oxides with increasing UO_2 content.

The following conclusions were based upon this investigation:

- a) In sufficient concentrations, UO_2 (or U_3O_8) 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)

MAG 500 X

ETCHED

FIG. I-21 STRUCTURE OF CERIUM OXIDE CONTROL SPECIMEN
SINTERED AT 1700°C (3090°F) IN HYDROGEN

MAG 500 X

ETCHED

FIG. I-22 STRUCTURE OF 7 M/O UO_2 (AS U_3O_8) - 93 M/O CeO_2
COMPOSITION DEVELOPED BY SINTERING AT 1700°C
(3090°F) IN HYDROGEN

MAG 500 X

UNETCHED

FIG. I-23 STRUCTURE OF 21 M/O UO_2 (AS U_3O_8) - 79 M/O CeO_2
COMPOSITION SINTERED AT 1700°C (3090°F) IN
HYDROGEN

FIG. I-24 LATTICE CONSTANT COMPOSITION RELATIONSHIPS IN THE $\text{UO}_2\text{-CeO}_2$ SYSTEM

FIG. I-25 LATTICE CONSTANT COMPOSITION RELATIONSHIPS IN THE UO_2 - CeO_2 SYSTEM

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 (1830°F). Pellets of both compositions were sintered at 1400, 1600, 1700, and 1800°C (2550, 2910, 3090, and 3270°F), respectively, for four hours in a flowing prepurified argon atmosphere. X-ray diffraction photograms for samples which were sintered in the range between 1400 to 1700°C revealed a series of doublet lines typical of those described earlier 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 Å reported⁽²⁾ 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.

4. Air Sintering

Pellets of the compositions shown in Table I-3 were prepared by air firing compacts containing equivalent weights of U_3O_8 for UO_2 at 1500 to 1550°C (2730 to 2820°F). A series of isothermal heat treatments in argon was conducted with the air fired compacts at 1300 and 1500°C (2370 and 2730°F), respectively, for 28 days and at 1700°C (3090°F) for four days. Results of x-ray diffraction analyses shown on Table I-3 are plotted in Figure I-24, 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 I-24. Hund, Wagner and Peetz⁽³⁾ 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 Å 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 which 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 content. Further evaluation of the data indicates a high probability that the two phase structure originates

TABLE I-3

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

Heat Treatment	Number of Phases	Appearance of X-Ray Pattern	Lattice Constant-A
1500°C - 8 hours - air	1 FCC	Sharp	5.416
1500°C - 8 hours - air	1 FCC	Slightly diffused	5.420
1500°C - 8 hours - air	1 FCC	Slightly diffused	5.430
1500°C - 8 hours - air	1 FCC	Slightly diffused	5.443
1500°C - 8 hours - air	1 FCC	Highly diffused	5.455
1500°C - 36 hours - air	1 FCC	Sharp	5.417
1500°C - 36 hours - air	1 FCC	Slightly diffused	5.423
1500°C - 36 hours - air	1 FCC	Slightly diffused	5.430
1500°C - 36 hours - air	1 FCC	Slightly diffused	5.438
1500°C - 36 hours - air	1 FCC	Highly diffused	-----*
1500°C - 130 hours - air	1 FCC	Sharp	5.415
1500°C - 130 hours - air	1 FCC	Slightly diffused	5.420
1500°C - 130 hours - air	2 FCC	Slightly diffused	(5.427
			(5.430
1500°C - 130 hours - air	2 FCC	Slightly diffused	(5.427
			(5.440
1500°C - 130 hours - air	2 FCC	Highly diffused	-----*
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
	1	Sharp	5.424
	1	Sharp	5.430
	1	Sharp	5.442
	1	Sharp	5.452

*Lines too diffused for determination of lattice constants.

between 21 and 30 m/o UO_2 . The data for the 30 m/o sample are probably an average of two lattice constants, one at 5.425 Å and another at a value slightly higher than the 5.432 Å noted on Figure I-24 for this composition. It is significant that extreme broadening of the back reflection lines was found for this particular sample, which is indicative of the presence of two face centered cubic structures of almost identical lattice constants.

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.

In an attempt to assess the influence of oxygen rich and oxygen deficient (argon) atmospheres on phase equilibria in the UO_2 - 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 of x-ray diffraction analyses after each of the first two firings. The total sintering time was 12 hours and the third sinter was followed by an argon anneal at 1500°C, with x-ray diffraction analyses before and after annealing.

Data pertinent to this series of samples are included in Table I-4 and lattice constants as a function of UO_2 content are plotted in Figure I-25. 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 periods in air. Further substantiation of this assumption was obtained during triple sintering and crushing investigations in which x-ray diffraction patterns became more diffuse with each successive sinter. Subsequent heat treatment at the same

TABLE I-4

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

Composition		History	Phases	Lattice Parameter
m/o UO_2^*	m/o CeO_2			
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 plus 28 days in Argon at 1300°C	FCC	5.413
7	93	Air Fired 1500°C - 24 hours plus 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 plus 28 days in Argon at 1000°C	FCC	5.418
14	86	Air Fired 1550°C - 4 hours plus 28 days in Argon at 1300°C	FCC	5.419
14	86	Air Fired 1500°C - 4 hours plus 28 days in Argon at 1500°C	FCC	5.418
14	86	Air Fired 1500°C - 4 hours plus 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 plus 28 days in Argon at 1300°C	FCC	5.421
21	79	Air Fired 1500°C - 24 hours plus 4 days in Argon at 1700°C	FCC**	5.427
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 plus 28 days in Argon at 1000°C	FCC	5.424
30	70	Air Fired 1550°C - 4 hours plus 28 days in Argon at 1300°C	FCC	5.428
30	70	Air Fired 1500°C - 4 hours plus 28 days in Argon at 1500°C	FCC	5.427
30	70	Air Fired 1500°C - 4 hours plus 4 days in Argon at 1700°C	FCC**	5.432
				(5.425)
50	50	Air Fired 1500°C - 16 hours	2 FCC	(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.

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 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 for the air fired samples, in which two phases 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 little oxygen pickup to permit the ternary composition to enter the two phase field. However, even after eight 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.

5. Conclusions

These investigations have shown that a 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). The long term thermal stability of this single phase, face centered cubic structure was demonstrated for temperatures up to 1500°C and for times up to 28 days in argon.

II. EX-REACTOR PROPERTY EVALUATIONS

A. THERMAL CONDUCTIVITY

1. Summary

Measurements of thermal conductivity by the steady state comparative method in the temperature range of 200 to 950°C (390 to 1740°F) 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 $\text{cal/cm-sec}^{-1}\text{-cm}^{-2}\text{-}^\circ\text{C}^{-1}$ 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 $\text{cal/cm-sec}^{-1}\text{-cm}^{-2}\text{-}^\circ\text{C}^{-1}$ over the same temperature range.

Thermal conductivity data for zirconia base fuel compositions were extended to 2400°C (4350°F). A gradual decrease in conductivity was observed at temperatures up to 1500°C, followed by an increase in conductivity at temperatures above 1500°C (2730°F).

2. General

Two sets of thermal conductivity data were obtained. Low temperature data (up to about 900°C (1650°F)) were obtained by Materiadyn Corporation with a steady state comparative type apparatus⁽⁴⁾ modified⁽⁵⁾ to permit controlled atmosphere testing at elevated temperatures. Data up to 2400°C were obtained through use of a radial heat flow unit.

3. Low Temperature Data

Details of sample preparation and test methods are reported in CEND-158. Results of these investigations are shown in Figure II-1. Figure II-2 shows the size of the samples required for this investigation.

4. High Temperature Data

a. Test Apparatus

Techniques and apparatus developed at Combustion Engineering,⁽⁶⁻⁹⁾ as part of a Joint United States - Euratom Research and Development Program

FIG. II-1 THERMAL CONDUCTIVITY VS. TEMPERATURE

FIG. II-2 THERMAL CONDUCTIVITY SAMPLE IN THE AS-SINTERED CONDITION (LEFT) AND AS A FINISHED GROUND ONE INCH CUBE (RIGHT)

have been utilized in this investigation. The major features of the test equipment are shown schematically in Figure II-3.

(1) Test Element

The test element configuration is shown in Figure II-4. The cladding was 1.270 cm (0.5 inch) OD stainless steel tubing with an 0.0508 cm (0.020 inch) thick wall. Thirteen 0.635 cm (0.250 inch) stainless steel standpipes were brazed to the cladding to provide optical paths within the pellets to selected depths for temperature measurements. Temperatures were measured optically at three radial locations within the ZrO_2 base fuels as well as at the surface of the heater rod.

The fuel pellets were ground to OD and bore tolerances of less than ± 0.003 cm (± 0.001 inch) to provide zero clearance between pellets, the cladding and the tungsten-rhenium heater at test temperatures. After assembly, each test element was radiographed to verify proper positioning of the pellets within the cladding.

The pellets were prepared by cold compaction and sintering techniques as described in Reference 10. Densities ranged from 90 to 92 percent of theoretical.

(2) Cooling Jacket

The cooling jacket, Figure II-5, was a brass cylinder, flanged at both ends to permit easy insertion and removal of the test element. The row of 13 standpipes extended through the side wall of the jacket where they were sealed with O-rings. Both ends of the test element were also sealed with O-rings to the flanged ends of the cooling jacket. The annulus between the test element and the cooling jacket contained flowing deionized water for heat removal. This water was recirculated and purified in an ion exchange column and cooled in a heat exchanger.

(3) Test Chamber

The cooling jacket test element assembly was contained within a stainless steel chamber approximately 30.48 cm (12 inches) long, 15.24 cm (6 inches)

FIG. II-3 TEST APPARATUS

FIG. II-4 ARRANGEMENT OF COMPONENTS
1/2 IN. TEST ELEMENT

FIG. II-5 THIRTEEN STANDPIPE COOLING JACKET WITH TEST ELEMENT INSERTED

wide and 12.70 cm (5 inches) deep. The chamber cover containing the viewing window was removed for insertion and removal of the test element. Liberal use of O-rings permitted quick access into the chamber and provided adequate hermetic sealing. The leak rate of the chamber, blanked off from the pumps, was less than 0.5×10^{-3} Torr/min. A vacuum level of about 10^{-5} Torr was attained within 30 minutes from a cold start.

Power terminals at both ends of the chamber consisted of water cooled copper bellows with a split copper clamp to provide quick coupling to the tungsten-rhenium heater. This design provided high current capacity while accommodating axial thermal expansion of the heater. The terminals were electrically insulated from the stainless steel chamber by plexiglass plates and hermetically sealed by O-rings.

All tests were conducted in inert gas at pressures slightly above atmospheric.

The atmosphere control system included a diffusion pump with an associated cold trap and mechanical pump; a second mechanical pump for preliminary pumpdown; gas purification furnaces containing zirconium chips; and a pressure relief system to prevent pressure buildup in the test chamber. Appropriate high vacuum valves provided good operational flexibility.

Fuel temperature measurements were made with a laboratory-type optical pyrometer equipped with a prism at the objective end to permit sighting in a vertical direction. Reproducibility of temperature measurement from operator to operator was found to be within 2°C (3.5°F). Corrections for specimen emittance and optical path transmission were obtained by comparison of optical pyrometer readings with thermocouple readings. No evidence of sight glass degradation due to vapor deposition was observed. Cladding temperatures were measured with chromel-alumel thermocouples spot welded to the outer surface of the cladding.

b. Test Conditions

Pellet preparation, assembly, thermal cycling and examination procedures for the test elements were important functions in the overall test program.

Caution had to be exercised during grinding and assembly to maintain the close tolerances required to minimize temperature drops at the heater—pellet and pellet—clad interfaces.

Three test elements were evaluated for thermal performance, as follows:

<u>Element Designation</u>	<u>Fuel Composition*</u>
IRRAD No. 1	Z-10
IRRAD No. 2	Z-22
IRRAD No. 3	Z-10

Pellet preparation, element assembly, thermal cycling and examination procedures are described in the following.

(1) Pellet Preparation

The outside diameter of the pellets was finish-ground to provide a cold clearance of less than 0.003 cm (0.001 inch) with the stainless steel clad. The bore of the pellets was similarly ground to provide intimate pellet—heater rod contact during assembly. All pellets were end faced to a length of 0.635 cm (0.250 inch). The compositions and dimensions of the various components of the test elements were as follows:

<u>Component</u>	<u>Material</u>	<u>Dimensions (cm)</u>
Clad	304 Stainless Steel	1.270 OD x 1.168 ID
Pellet	Z-10 or Z-22	1.266 OD x 0.231 ID
Heater	W-26 Re	0.229 OD

Thirteen of the 32 pellets in each element were slotted axially for temperature measurements, Figure II-4 and II-6. Initially, slots 0.038 cm (0.015 inch) in width were cut radially into the pellets to the desired depths. After measurements were made to confirm the depth of the slots, a second axial

* Z-10-- CaO stabilized ZrO_2 containing 10 w/o UO_2 .

Z-22-- CaO stabilized ZrO_2 containing 22 w/o UO_2

cut widened the slot to 0.102 cm (0.040 inch) to a depth of 0.254 cm (0.100 inch) from the pellet ID in order to minimize obstruction of the optical path by pellet cracking during test. The depths of sight holes for various positions along the length of each test element are shown in Figure II-6.

(2) Element Assembly

The fuel pellet column was assembled by inserting each pellet individually over the heater rod, which was positioned in the center of the clad. Each slotted pellet was positioned beneath its standpipe and then aligned by a shaped pin which was inserted through the standpipe and into the slot in the pellet. Retention of the alignment pins within the pellet slots during assembly prevented rotational displacement of the slotted pellets in relation to the standpipes. The assembled test element was radiographed to establish proper assembly of the pellet column within the clad. Prior to the test, the assembly was vacuum dried at 125°C (257°F) for 8 to 10 hours. The test element was inserted into the cooling jacket and the assembly installed into the test chamber for evacuation to a pressure of about 10^{-5} Torr. The system was back-filled to atmospheric pressure with inert gas and the test element outgassed further by increasing the temperature of the heater to about 300°C (570°F). Several cycles of evacuation, followed by backfill of inert gas, were performed to ensure complete removal of moisture prior to the start of the high temperature tests.

(3) Thermal Cycling

The test element was considered ready for thermal cycle tests upon attainment of a constant pressure of about 10^{-5} Torr within the test chamber. The thermal history of each test element follows.

Test Element, IRRAD No. 1 — The temperature cycle history for element No. 1 is shown graphically in Figure II-7. After successful completion of the first cycle (heater rod temperature of about 1850°C (3360°F) for two hours), a longer, higher temperature cycle was initiated at 1900°C (3450°F). One end of the element formed a hot spot after 15 hours at temperature. Attempts to stabilize the temperature fluctuation by reduction in power were unsuccessful and burnout of the heater occurred near sight hole No. 12. The test was terminated and the element was sectioned for microstructural examination in accordance with the plan shown in Figure II-6.

Test Element, IRRAD No. 2 — Test element No. 2 was held at about 2400°C (4350°F) for 4-1/2 hours. A second cycle to 2400°C resulted in failure of the heater rod at sight hole No. 10 after about 1-1/2 hours at temperature, terminating the test. The sectioning plan for this element is also shown in Figure II-6.

Test Element, IRRAD No. 3 — Because of the failures of test elements Nos. 1 and 2 in the same general location, the axial temperature variation was reduced by installing diffusers on the inlet and outlet lines of the cooling jacket. A somewhat more uniform coolant velocity was obtained along the length of the test element.

Test element No. 3 was cycled with more success than element Nos. 1 and 2. After a slow heatup, it was maintained at 2100°C (3810°F) for one hour and then the temperature was decreased to 1000°C (1830°F) where it was held overnight. During the second cycle, element temperature was increased to 2550°C (4080°F). After about three hours at this temperature, a fluctuation in the power supply caused the equipment to trip out and the temperature to drop suddenly. The element was quickly restored to 1000°C where it was again held overnight. During the third cycle, the element was brought to 2400°C and held there for 4-1/2 hours before being slowly cooled to room temperature.

It was found that as a result of the change in cooling jacket design the axial temperature variations were much smaller than those for element Nos. 1 and 2. In addition, the element has already completed three cycles at high temperature without failure. A fourth cycle was conducted in order to cause failure. After reaching 2500°C (4530°F) temperatures could no longer be measured because the sight hole was closed by what is believed to be a vaporization deposition of the fuel. The element failed shortly after the last temperature readings were made. The complete cycle history for element No. 3 is shown in Figure II-7. After completion of the thermal cycling, the element was sectioned for metallographic examination, Figure II-6.

c. Test Results

(1) Thermal Conductivity

The thermal conductivities of the ZrO_2 base fuels were calculated on the basis of the following assumptions:

IRRAD No. 1

IRRAD No. 2

IRRAD No. 3

LEGEND

* = THIS SURFACE PREPARED FOR METALLOGRAPHY

FIG. II-6 SIGHT HOLES AND POST-TEST SECTIONS

IRRAD No. 1
Z 10

IRRAD No. 2
Z 22

IRRAD No. 3
Z 10

FIG. II-7 CENTERLINE TEMPERATURE HISTORY

The fuel pellets were in intimate contact with both the tungsten-rhenium heater rod and the cladding at the test temperatures.

The heater rod—fuel pellet gap conductance was a constant value of 2 watts/cm⁻²-°C⁻¹.

The contribution of cracks to the thermal resistance of the fuel was insignificant at operating temperatures.

The fuel pellets were homogeneous, isotopic bodies. (Actually, the pellets were continuous single phase structures with uniformly distributed porosity.)

The temperature at the inner surface of the fuel pellets was calculated from the average heater rod temperature, the geometry of the element, and the power required to maintain a given temperature within the element.

Values of thermal conductivity as a function of temperature were calculated by applying the integrated form of Fournier's law for heat transmission by conduction across a homogeneous material.

$$k = \frac{Q \ln \frac{R_2}{R_1}}{2\pi L (T_1 - T_2)} \frac{\text{watts}}{\text{cm} \cdot ^\circ\text{C}}$$

where

k = Thermal conductivity at a temperature $\frac{T_1 + T_2}{2}$

Q = Heat flux

R_1 and R_2 = Radial distances (cm)

L = Length of heat transfer surface (cm)

T_1 and T_2 = Temperatures at radial distances R_1 and R_2 (°C)

The calculated values for thermal conductivity were corrected to 100 percent theoretical density by the simplified Loeb⁽¹¹⁾ expression

$$k_s = \frac{k_m}{1 - P_v} = k_m \frac{\rho T}{\rho_m}$$

where

- k_s = Thermal conductivity of solid (100% dense) fuel
- k_m = Measured thermal conductivity
- P_v = Pore volume fraction
- ρ_T = Theoretical density of fuel
- ρ_m = Actual density of the fuel

Thermal conductivity data are presented in Figure II-8. Although test element Nos. 1 and 3 were both of Z-10 composition, results of element No. 3 were selected as representative of that fuel composition because of the early failure and erratic behavior of test element No. 1. The conductivity data obtained from the innermost radial segment ($R_1 - R_2$) of element No. 3 were totally unreliable and erratic due to the deterioration of the heater rod and, therefore, are not included in Figure II-8. This, in effect, reduced the ΔT of the $R_1 - R_2$ segment and increased the calculated k value for that radial segment.

The Z-10 data presented in Figure II-8 resulted from temperature observations at three radial positions. A high degree of correlation among the data points exists, resulting in a rather narrow scatter band. The conductivity values for this composition remained within a relatively constant region between 0.0175 to 0.0225 watts/cm⁻¹°C⁻¹ up to 1400°C (2550°F). Above 1500°C, the conductivity slowly increased and values at 1850°C (3360°F) were between 0.0200 to 0.0275 watts/cm⁻¹°C⁻¹. The conductivity values for this composition remained within this region over three successive temperature cycles, a result which indicates that there is no permanent influence of prior high temperature treatment on conductivity.

The thermal conductivity values for the Z-22 composition also remained within a relatively constant region between 0.0150 to 0.0200 watts/cm⁻¹°C⁻¹ up to about 1600°C (2190°F). Above this temperature, a slow rise was observed to values between 0.0225 to 0.0275 watts/cm⁻¹°C⁻¹ at 2200°C (3990°F). These values are for one cycle only, since early failure of the test element prevented additional determinations.

FIG. II-8 THERMAL CONDUCTIVITY DATA

Figure II-9 presents a comparison of results in this program with those obtained by Combustion Engineering, Inc., for Phillips Petroleum Company as part of their Power Burst Program.

A comparison of thermal conductivity data reported previously⁽¹⁰⁾ with the present data for similar compositions of these homogeneous ZrO_2 base fuels shows good agreement between the low temperature and high temperature test methods. The thermal conductivity up to about $800^\circ C$ ($1470^\circ F$) was determined by Materiatyne Corporation with a steady state comparative method, while the thermal conductivity between 900 to $2200^\circ C$ (1650 to $3990^\circ F$) was determined at Combustion Engineering using a high thermal gradient radial heat flow method.

(2) Effective Thermal Conductivity

The calculated pellet inside surface temperature and the exterior cladding temperature were used in making calculations of the effective thermal conductivity of the test elements. The results of these calculations as a function of pellet inside surface temperature are presented in Figure II-10. Density corrections were not made. The shape of the k_{eff} curves is similar to that of the thermal conductivity curves shown in Figures II-8 and II-9. The lower values for k_{eff} , which were expected, are a result of the interface resistance between the fuel pellets and the cladding. The increase in k_{eff} at elevated temperatures reflects the influence of higher conductivities noted for these fuels at such temperatures.

The values for k_{eff} are slightly higher than those reported for 4 and 12 m/o UO_2 fuels in Reference 10. The difference can be attributed to the following two factors:

The present values of the k_{eff} were determined from the pellet inside surface temperature and clad temperature and plotted against pellet inside surface temperature, whereas the values of k_{eff} in Reference 10 were determined from heater surface temperature and clad temperature and plotted against heater rod temperature. This produces a lower ΔT for any given heat flux, thus increasing the k_{eff} .

FIG. II-9 COMPARISON OF THERMAL CONDUCTIVITY DATA

FIG. II-10 EFFECTIVE THERMAL CONDUCTIVITY,
COMPARISON OF Z-10 AND Z-22 COMPOSITION

The present elements had cold diametral clearances between heater and pellet and pellet and clad of less than 0.003 cm (0.001 inch). Earlier test elements had diametral clearances of about 0.015 cm (0.006 inch) between heater rod and pellets and about 0.010 cm (0.004 inch) between pellets and clad. The higher interfacial conductivity in the present series of tests is reflected in a greater k_{eff} .

(3) Microstructural Changes

Upon completion of thermal cycle testing, the fuel elements were impregnated with a commercial sealant which locked all fragments in place and permitted sectioning in accordance with details shown in Figure II-6.

Descriptions of microstructures developed in these thermal test elements are discussed in the following:

Element 1: Z-10 Composition -- The appearance of the samples from element 1 indicated a microstructural change in the form of grain growth, densification of the fuel or pore distribution. Since the maximum fuel temperature was about the same as the sintering temperature of the fuel, this test demonstrated that high thermal gradients at maximum fuel temperatures in the range of 1800 to 1850°C (3270 to 3360°F) for short periods of time do not alter the as-sintered microstructure. Figure II-11 shows the appearance of a typical microstructure from element 1 of the Z-10 composition. Evidence of intimate contact between fuel and heater rod at test temperatures is visible. A small amount of deterioration of the heater rod as well as migration of fine metallic particles into the fuel can also be observed. The uniform grain size and pore distribution of this region very closely resembles the as-sintered Z-10 fuel microstructure.

Element 2: Z-22 Composition -- Maximum fuel temperatures achieved in this element were about 2300°C (4170°F) for both test cycles. Microscopic examinations showed a very narrow band adjacent to the heater rod where a limited amount of grain growth had occurred (Figure II-12).

Grain size measurements and the technique for determining onset of grain growth described for UO_2 microstructures in Reference 12 were used in the analysis of these microstructures.

The change in grain size is abrupt, as indicated by a sharp delineation between the as-sintered and growth region. Of particular interest is the high density and pore redistribution in the growth region as compared to the microstructure in the colder regions of the pellet, which resembles that of the

AS SINTERED

100 X

ELEMENT #1 SECTION 8
POST-TEST

100 X

FIG. II-11 TYPICAL AS-SINTERED AND POST-TEST Z-10 COMPOSITION MICROSTRUCTURES FROM THERMAL PERFORMANCE SPECIMENS

AS SINTERED

100 X

ELEMENT #2 SECTION 7
POST-TEST

100 X

FIG. II-12 TYPICAL AS-SINTERED AND POST-TEST Z-22 COMPOSITION MICROSTRUCTURES FROM THERMAL PERFORMANCE SPECIMENS

as-sintered microstructure, Figure II-12. From the appearance of these microstructures, Figures II-11 and II-12, it is evident that grain growth (and associated redistribution of voids and densification) under brief, high thermal gradient conditions does not occur unless fuel temperatures greater than 2000°C (3630°F) are attained. When this temperature is exceeded, a growth region is formed which is essentially free of voids.

The microstructure shown in Figure II-13 was produced at maximum fuel temperatures within 50 to 100°C of the melting point (2635°C) (4775°F)⁽¹⁰⁾ of the Z-10 composition. An analysis of the end-of-life thermal history and the post test microstructure⁽¹²⁾, established the radial temperature isotherm of about 1900°C (3450°F) as the onset of grain growth. The large, blocky columnar grains produced under these conditions are almost completely free of voids. These changes in microstructure further substantiates the earlier observation that temperatures in excess of 2000°C are required to initiate discontinuous grain growth in these fuels under thermal gradient conditions.

B. MELTING POINT DETERMINATIONS

1. Summary

The melting point apparatus constructed for these evaluations were 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 and 2685°C (4775 and 4865°F) were measured for the 4 m/o UO₂-stabilized ZrO₂ samples, whereas values of 2630 and 2670°C (4766 and 4838°F) were found for the 12 m/o UO₂ composition. Liquidus temperatures of 2420 and 2335°C (4388 and 4235°F) were measured for the 7 m/o and 21 m/o UO₂-CeO₂ 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 (180°F) below the liquidus for each composition.

2. Equipment and Test Conditions

An accurate determination of the melting points for these solid solution fuels was an essential prerequisite to establishing the maximum temperatures

Z-10 COMPOSITION

100 X

FIG. II-13 MICROSTRUCTURES FROM Z-10 COMPOSITION
THERMAL PERFORMANCE SPECIMEN SHOWING
GRAIN GROWTH

which could be used in the design of specimens and capsules for the irradiation test program.

Initial attempts to establish the melting points for the homogeneous ceramic fuels studied were based on the utilization of a tungsten ribbon filament apparatus similar to that used for UO_2 .⁽¹³⁾ This technique required intimate contact between sample and tungsten.

The original method provided for a sintered pellet fragment to be placed on a tungsten ribbon which was then resistance heated. Prepurified 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 had indicated a need for a flowing helium system because of the vapor deposition of intermediate oxides of tungsten on the surface of the bell jar containing the test unit. The deposit had resulted in erroneous temperature measurements by optical pyrometry.

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, yielding substantially lower melting values for ZrO_2 than those reported in the literature. As a result, 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 a V-shaped trough in the tungsten ribbon without touching it. 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.

When some problems were encountered with sample and heater sagging, which resulted in contact or severe heat loss, further modifications to the test apparatus were made. The unit which finally evolved, Figure II-14, was found to be extremely successful for this program. The heater was 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. Both heater and thermal shields were fabricated from 0.002 inch thick tantalum sheet. Water cooled, stainless steel electrode posts supported the heater and thermal shields

FIG. II-14 MELTING POINT APPARATUS

and provided 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 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 prepurified argon gas was maintained in the test chamber at a pressure slightly above atmospheric.

An optical pyrometer, focussed on the end face of the sample inside the furnace, provided means for temperature measurements as well as visual observations. The temperature at which a slight rounding of the corners and edges of the sample tip was observed was taken as the solidus; the liquidus was established as the temperature of 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 proper corrections for emissivity and absorption through the window of the pyrex enclosure and for calibration of the optical pyrometer. Some indication of the sensitivity of the test technique is demonstrated in Table II-1; solidus and liquidus points were measured with the optical pyrometer even when the spread in temperature was as little as 40°C (70°F) in the temperature range of up to 2700°C (4900°F).

3. Results

The test apparatus developed in this program was used to establish 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. Six to 10 samples of each composition were melted. All samples were heated rapidly to within 200 to 300°C (360 to 540°F) of their anticipated melting points and then at a reduced rate to the solidus and the liquidus points. Melting point data are presented in Table II-1.

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 $\pm 10^\circ\text{C}$ (18°F) based on a series of six to 10 measurements.

CeO_2 base samples exhibited extensive volatilization at temperatures above 2000°C (3630°F) and erroneous indications of sample tip rounding occurred due to this volatilization as the melting point was approached. The heating procedure

Table II-1
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) W. A. Lambertson and F. H. Gunzel, "Refractory Oxide Melting Points", AECD-3465

(2) Handbook of Chemistry and Physics, 42nd Edition, Chemical Rubber Publishing Company

for the CeO₂ base samples was altered to provide for slow heating to 1500°C (2730°F), a rapid rate to 2300°C (4170°F) to reduce vaporization, and again a slow heating up to the first sign of melting. It was not possible to pinpoint the solidus and liquidus in this system, and the first sign of liquation at the sample tip was reported at the liquidus.

These data were utilized in the design of the irradiation program. The maximum fuel temperatures during irradiation were established as just below the solidus for the ZrO₂ base compositions and 100°C (180°F) below the liquidus for the CeO₂ base compositions. The latter value is believed to be a very conservative estimate of the solidus, base upon an analysis of other binary phase diagrams with CeO₂.

C. THERMAL EXPANSION

1. Summary

The thermal expansion coefficients for two compositions in the UO₂-CaO-ZrO₂ system can be best described by the following relationships for the temperature range of 20 to 1000°C (68 to 1830°F):

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

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

where

$$t = ^\circ\text{C}$$

2. General

Early in the program, it was demonstrated that identical single phase structures can be developed by either very rapid cooling (20,000°C/hour) or by slow cooling (100°C/hour) in the furnace from the sintering temperature of 1800°C (3270°F). A series of isothermal sections from 1000 to 2000°C (1830 to 3630°F) was constructed, on 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 sample holder were designed and constructed.

3. Sample Holder Test Experiment

A view of the furnace and the housing is shown in Figure II-15. The system was attached to a standard diffractometer head which contained 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, contained a series of water channels for internal cooling during elevated temperature operation. A hollow spindle extended through the rotating center shaft of the diffractometer and served the dual purpose of supporting the housing and furnishing an air evacuation line to the housing. Two circumferential beryllium windows, 0.010 inch in thickness, covered about 90 degrees of arc each. The furnace was constructed as a single removable unit and consisted of an inner resistance element and two heat shields of tantalum sheet. The sample holder was a cantilever paddle machined from high density stabilized ZrO_2 , and was located within the furnace. The flat plate sample, 3/8 inch by 3/4 inch by 1/8 inch, was contained in a pocket at the free end of the paddle.

FIG. II-15 VIEW OF HIGH TEMPERATURE X-RAY DIFFRACTOMETER SAMPLE HOLDER

The root of the paddle was attached to a shaft extending through the rear of the housing. A lever attached to the shaft provided for mechanical alignment of the sample. An axial tube located in the front cover of the housing contained a sight port with a magnetically operated rotating shutter. Temperature measurements with an optical pyrometer and direct observation of the sample were made by sighting through a telescope mounted to the base table which supported the diffractometer.

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

Alignment techniques for the high temperature x-ray diffraction specimen holder were developed which permitted accurate alignment while the sample was at temperature. Small misalignments, either as parallel displacements from diffractometer geometry from the axis of rotation of the sample or 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 (2730°F) without incidents as a check on performance 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 (1470°F) yielded lattice constants of 3.923 and 3.954 Å, respectively. An

average thermal expansion coefficient of 9.0×10^{-6} per $^{\circ}\text{C}$ was calculated, which compared favorably with a value of 8.9×10^{-6} per $^{\circ}\text{C}$ quoted in literature. (14)

4. Temperature Measurement

Accurate temperature measurement by optical means through the sighting telescope was difficult because of the necessity of making absorption and emissivity corrections. These corrections were dependent upon exact knowledge of emissivity values for solid solutions under study and on the assumption that volatilization did not occur such as to influence absorption factors. Since neither factor could be accurately obtained an internal standard to provide accurate temperature data appeared to be attractive. 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.

5. Results

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 (2460°F) to provide sufficient strength for handling. X-ray diffraction and metallographic examination of these compacts, as well as of samples which were run in the high temperature diffractometer unit up to 1400°C (2550°F), revealed no evidence of interaction between platinum and the ZrO_2 base solid solution fuels.

Figure II-16a and b shows the calibration curve used for platinum to obtain accurate temperature data and 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>
4.0	9.83
10.2	10.00
12.0	10.00

The expansion coefficients in the range of 20 to 1000°C (68 to 1830°F) can best be described by the following equation for the 4 and 12 m/o UO₂ compositions:

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

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

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 II-16 only single phase, face centered cubic solid solution structures were observed.

D. CORROSION TESTS

1. Summary

Unclad pellets of four fuel compositions of interest (7 and 21 m/o UO₂-CeO₂ and 4 and 12 m/o UO₂-CaO-ZrO₂) showed corrosion penetrations of less than 0.002 cm (0.001 inch) following 700 days of exposure to 650°C (1200°F) flowing steam and 480 days in 360°C (680°F) static degassed water.

2. General

An evaluation of corrosion behavior is necessary in the event of a cladding failure and subsequent exposure of the fuel to coolant environment. A description of sample preparation methods was given in Reference 10; results of earlier corrosion tests were reported both in Reference 10 and 15. The latter values were obtained following exposures of 300 days in static degassed water at 360°C and 420 days in flowing steam at 650°C. Weight gain measurements indicated corrosion penetrations of less than one mil per year. Visual and metallographic examinations indicated that none of the pellets had developed severe cracks. In addition, no heavy surface corrosion products were evident.

Corrosion testing was terminated after 480 days in 360°C degassed water and to 700 days in flowing 650°C steam. Detailed results are reported in Reference 16.

THERMAL EXPANSION OF PLATINUM

(a)

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

(b)

FIG. II-16 THERMAL EXPANSION COEFFICIENTS FOR ZrO_2 BASE COMPOSITIONS

3. Results

Tables II-2 and II-3 show the composition of samples used in this evaluation. The long term stability of both the ZrO_2 base and CeO_2 base fuel pellets in degassed water at 360°C and steam at 650°C is demonstrated in Figures II-17 and II-18. Data for all fuel compositions indicate decreasing corrosion rates with increasing time. Continued exposure to the test environments did not alter the corrosion behavior or the physical appearance of the samples. The previously reported⁽¹⁵⁾ corrosion penetration of less than one mil per year (based on weight change) was not exceeded even after prolonged exposures to the same conditions. These results are especially significant in the case of pellets exposed to flowing steam, where the combination of elevated temperature and a dynamic environment constitutes a more severe test condition. The corrosion behavior of these solid solution oxide fuels compares favorably with reported data for sintered UO_2 pellets exposed to high temperature water and steam.

TABLE II-2

COMPOSITION OF STEAM CORROSION TEST SAMPLES

Pellet Type	UO ₂	Mole Percent CaO Stabilized 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 II-3

COMPOSITION OF WATER CORROSION TEST SAMPLES

Pellet Type	UO ₂	Mole Percent CaO Stabilized 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

FIG. II-17 WATER CORROSION DATA AT 360°C

FIG. II-18 STEAM CORROSION DATA AT 650°C

III ✓ FABRICATION OF IRRADIATION TEST SAMPLES

A. SUMMARY

Pellets for irradiation testing were prepared by cold pressing and sintering to densities of 89 to 90 percent of theoretical density for the zirconia base compositions and 92 to 95 percent of theoretical density for the ceria base compositions. The four compositions selected for irradiation testing were as follows:

4 m/o UO_2 - 77 m/o ZrO_2 - 19 m/o CaO

Zirconia base

10.2 m/o UO_2 - 72.2 m/o ZrO_2 - 17.6 m/o CaO

7 m/o UO_2 - 93 m/o CeO_2

Ceria base

17.5 m/o UO_2 - 82.5 m/o CeO_2

After completion of x-ray diffraction, metallographic and chemical analysis of selected pellets from each batch, pellets of one composition were assembled into stainless steel cladding tubes approximately 2-1/2 inches long. Final closures were made by heliarc welding of end plugs. Five clad irradiation samples each were assembled into six capsules, together with three zirconia base and two ceria base samples of comparable UO_2 content.

Compromises had to be made to permit the irradiation testing of ceria base and zirconia base samples in the same capsule. Reference burnup and temperature conditions were provided for the zirconia base samples. The differences in accrued burnup between the zirconia and ceria base samples were estimated as 5 to 10 percent.

Nuclear mockup experiments confirmed the W. B. Lewis method for calculating perturbation factor as a function of burnup for these fuels.

B. PELLET PREPARATION

The fuel samples for the irradiation program contained cylindrical pellets of the four compositions prepared by cold pressing and sintering techniques.

On the basis of earlier work on this program, process outlines were prepared for the preparation of the irradiation pellets. Figures III-1 and III-2 show these process outlines for the two zirconia base and two ceria base fuel compositions.

The properties of the starting materials, UO_2 and U_3O_8 (93 percent enriched), ceria and zirconia stabilized with 20 m/o CaO , are shown in Table III-1. The ceria and zirconia were from lots of the oxides which were used in the earlier phases of the program. A portion of the enriched UO_2 powder was oxidized to U_3O_8 for use in the preparation of the ceria base pellets.

Preliminary sinterability tests were performed on several pellets of each composition. These tests were useful in refining the preparation techniques involving the handling of highly enriched uranium oxide powders and contributed confirmatory data on sinterability, crystal structure, bulk density, and general quality of the sintered pellets. The first group of 14 pellets of the Z-10 composition (4 m/o UO_2 -77 m/o ZrO_2 -19 m/o CaO) was sintered at 1800°C (3270°F) for 66 hours in prepurified argon to develop a bulk density of 92 percent of theoretical density. All pellets of this group had sintered to a low density of 4.81 to 4.84 gm/cm^3 (84.2 to 84.4 percent of theoretical). A reevaluation of the powder preparation methods indicated that a milling time of 16 hours of the sintered and crushed briquettes may have been insufficient to provide a uniformly fine particle size. Accordingly, the remaining powder of this composition was milled for an additional 8 hours, or a total of 24 hours, and used in the preparation of 50 pellets which were argon sintered at 1800°C for 70 hours to a bulk density of 5.16 to 5.20 gm/cm^3 (89.9 to 90.5 percent of theoretical). This density level is still significantly lower than the 92 percent value which was obtained on a routine basis for pellets of the same composition prepared with UO_2 of depleted enrichment. It was felt that variations in the processing of UO_2 powder of depleted and high enrichments by the vendor were factors affecting the sinterability of these powder mixtures.

A single powder batch of the Z-22 composition (10.2 m/o UO_2 -72.2 m/o ZrO_2 -17.6 m/o CaO) was prepared in the same manner as the Z-10 composition with a milling time of 24 hours for the sintered and crushed briquettes. A group of 50 pellets was sintered at 1800°C for 70 hours in prepurified argon to a bulk

TABLE III-1

PROPERTIES OF THE OXIDE STARTING MATERIALS

Uranium Oxides - United Nuclear Corporation			CeO ₂ -High Purity, Calcined		ZrO ₂ **--Hafnium Free Zirconium Corporation of America				
	Dioxide (UO ₂) 93% Enriched ² Lot K07GA	Oxide (U ₃ O ₈) 93% Enriched Sample A-833	Heavy Minerals Company		0 m/o CaO(%)	10 m/o CaO(%)	20 m/o CaO(%) ***	28 m/o CaO(%)	35 m/o CaO(%)
U	87.7%	84.5%	Other Rare	0.1%	SiO ₂ 0.015*	0.017*	0.021*	--	--
H ₂ O	0.11%	0.15%	Earths		Fe ₂ O ₃ 0.02	0.019	0.018	0.017	0.016
Ag	0.1 ppm	1.0 ppm	Fe ₂ O ₃	0.1%	Al ₂ O ₃ 0.02	0.02	0.02	0.02	0.02
Al	5.0 ppm	--	CaO	0.05%*	BaO --	0.001	0.001	0.002	0.003
B	<0.1 ppm	0.1 ppm	SiO ₂	0.1%*	MgO 0.01	0.054	0.09	0.13	0.18
Ca	5.0 ppm	8.0 ppm	Average	2μ	CaO 0.05	5.1	10.2	15.2	20.2
Cd	--	0.2 ppm	Particle Size		H _f O ₂ 0.006	0.006	0.006	0.005	0.005
Co	<1.0 ppm	1.0 ppm			* Maximum **Measured Impurity Levels in ZrO ₂ -CaO Mixtures ***This composition was used in the preparation of irradiation samples				
Cr	30.0 ppm	30.0 ppm							
Cu	4.0 ppm	8.0 ppm							
F	<50.0 ppm	30.0 ppm							
Fe	80.0 ppm	80.0 ppm							
Mg	10.0 ppm	--							
Mn	4.0 ppm	15.0 ppm							
Mo	11.0 ppm	20.0 ppm							
Ni	70.0 ppm	120.0 ppm							
Pb	8.0 ppm	10.0 ppm							
Si	30.0 ppm	20.0 ppm							
Sn	8.0 ppm	20.0 ppm							
Ti	--	2.0 ppm							
V	--	<1.0 ppm							
W	<8.0 ppm	<5.0 ppm							
N	--	50.0 ppm							

* Maximum

**Measured Impurity Levels in ZrO₂-CaO Mixtures

***This composition was used in the preparation of irradiation samples

(4 m/o UO_2 - 77 m/o ZrO_2 - 19 m/o CaO) Z10
 (10.2 m/o UO_2 - 72.2 m/o ZrO_2 - 17.6 m/o CaO) Z22

FIG. III-1 FLOW SHEET FOR THE PREPARATION OF FULLY ENRICHED ZrO_2 BASE PELLETS FOR THE IRRADIATION PROGRAM

(7 m/o UO_2 - 93 m/o CeO_2) C10
 (17.5 m/o UO_2 - 82.5 m/o CeO_2) C25

FIG. III-2 FLOW SHEET FOR THE PREPARATION OF FULLY ENRICHED CERIA BASE PELLETS FOR IRRADIATION PROGRAM

density of 5.58 to 5.60 gm/cm³ (89.7 to 90.1 percent of theoretical). Additional heating of the sintered pellets at 1840°C (3340°F) for 55 hours in prepurified argon did not cause further densification of the pellets. These results are in agreement with previous sinterability data⁽¹⁰⁾ for these compositions which demonstrated that optimum densities of 90 to 91 percent of theoretical were attained after 60 hours at 1800°C in argon.

The prior sinterability studies on ceria rich compositions in the UO₂-CeO₂ system⁽¹⁰⁾ had demonstrated that a high degree of homogeneity was attained when powders milled for eight hours and air sintered at 1475°C for one-half hour to a density of 94 percent of theoretical density were used. Evaluations by x-ray diffraction and microscopy had indicated completely single phase, face centered cubic structures. The first groups of highly enriched pellets of the C-10 composition (7 m/o UO₂-93 m/o CeO₂) and of the C-25 composition (17.5 m/o UO₂-82.5 m/o CeO₂) were prepared in accordance with the previously established procedures. The C-10 pellets were air fired at 1475°C (2690°F) for one-half hour to a density of 7.03 to 7.07 gm/cm³ (94.2 to 94.7 percent of theoretical) and the required number of C-10 pellets for the irradiation program were prepared by this procedure. However, considerable difficulty was experienced in the preparation of crack free pellets of the required density of the C-25 composition. The first two groups of pellets fragmented due to thermal shock even when the furnace heating and cooling rates were controlled to about 100°C (180°F) per hour. The third and fourth groups of C-25 pellets, air sintered at 1475°C and 1450°C for one-half hour, developed densities of 98.8 to 99.0 percent and 98.4 to 98.7 percent of theoretical density, respectively. This high density was due to the longer time within sintering range as a result of decreased heating and cooling rates to about 75°C (135°F) per hour. Reduction of the sintering temperature to 1400°C for one-half hour still developed densities of 97.0 to 97.5 percent of theoretical. Further reductions in the sintering temperature to 1325°C (2420°F) provided the desired density of 93.5 to 94.0 percent of theoretical density. A second batch of enriched U₃O₈ was obtained to complete the preparation of the C-25 pellets. On the basis of sinterability tests established for the enriched C-25 pellets to attain 94 percent of theoretical density, this group, prepared with the new U₃O₈, was air sintered at 1325°C for

one-half hour. Two batches consisting of 58 pellets were air-sintered in two furnaces with very closely similar heating and cooling rates. As for the zirconia base pellet density, the only plausible explanation is that the characteristics of each batch of uranium oxide are sufficiently different in terms of particle size distribution, particle surface area, and surface activity to significantly influence sinterability even though the oxide was present as a minor constituent, in quantities up to 17.5 m/o, of the total powder mixtures. The sintered pellets were reheated for an additional one-half hour at 1400°C in air to a density of 91.8 to 92.9 percent of theoretical.

The sintered pellets of the four compositions were visually examined for cracks and other defects, dimensioned, weighed, and chemically analyzed for UO_2 content. Some of the data are summarized in Table III-2.

Table III-2
DATA ON AS-SINTERED PELLETS

Composition	Bulk Density (% TD)	Pellet Diameter (In.)	UO_2 Content		
			Nominal		Actual w/o
			m/o	w/o	
Z-10	89.9 - 90.5	0.4620 $\pm$ 0.005	4.0	10	9.97
Z-22	89.7 - 90.1	0.2940 $\pm$ 0.005	10.2	22	21.76
C-10	94.2 - 94.7	0.3420 $\pm$ 0.003	7.0	10	9.77
C-25	91.8 - 92.9	0.2715 $\pm$ 0.003	17.5	25	24.10

The final step in the preparation of the pellets for the irradiation program involved finish-grinding to the required diameter and length. On the basis of thermal conductivity measurements and melting points from Reference 10,

and of nuclear mockup experiments conducted in the shielding facility of the Battelle Research Reactor, the diameters of the pellets were established, as follows:

<u>Composition</u>	<u>Pellet Diameter (In.)</u>
Z-10	0.350
Z-22	0.250
C-10	0.300
C-25	0.190

Groups of 50 pellets of each of the four compositions were centerless-ground to ± 0.0005 inch of the established diameters at NUMEC (Nuclear Materials and Equipment Corporation). The finish-ground pellets were end-ground to 0.5000 ± 0.0005 inch in length at Combustion Engineering prior to final inspection and assembly into the stainless steel cladding.

C. CLADDING AND ASSEMBLY

The design of the irradiation samples required a fuel column 1-1/2 inches in length (3 pellets) and contained in Type 347 SS cladding. Disks of the oxide diluent (stabilized ZrO_2 or CeO_2 , depending on fuel composition) served as insulators between the fuel ends and the cladding. Each sample contained a coiled spring of 0.015 inch diameter tungsten wire in the gas collection space to secure intimate contact between the pellets during fabrication and shipping of the samples. For details of the sample design and the basis of the design, see Reference 10. A typical irradiation sample is shown in Figure III-3.

A cold diametral clearance of 0.0005 inch maximum was provided between the fuel and the cladding to ensure high contact conductance. The wall thickness of the cladding was 0.030 inch for all samples. One end of the cladding tubes was end capped by inert gas shielded tungsten arc welding. The integrity of the welds was established by radiographic, liquid penetrant, and visual (5 to 20 magnifications) inspections and helium leak testing.

FIG. III-3 DESIGN FOR IRRADIATION SAMPLES

Selected groups of pellets, oxide insulators and the tungsten spring were assembled in the cladding tubes. The spring had a slightly larger diameter turn at the top end so that it would be retained in place by friction with the clad wall. Figure III-4 shows exploded views of the irradiation sample components of Z-10 and C-25 fuel compositions. The assembled samples were radiographed prior to end cap welding to confirm proper positioning of the components. Welding of the second end cap was performed in the miniature welding chamber shown in Figure III-5. The sample was positioned in the welding chamber but the top end cap was not inserted into the cladding tube. A stainless steel trough was positioned in the groove of the copper chill block so that the end cap was in line with the open end of the cladding tube but not fitted into it. The system was evacuated to 10 microns and purged with purified helium. The welding electrode was advanced to push the end cap into the clad and welding was completed. The samples were machined in the area of the weld and inspected by radiographic and liquid penetrant techniques, weighed, dimensioned and gamma scanned. The appearance of typical fabricated fuel samples as well as radiographic views of the internal components are shown in Figures III-6 and III-7.

D. PROPERTY DETERMINATIONS

X-ray diffraction and metallographic examinations were conducted on finish-ground pellets of the four compositions to verify the existence of the single phase, face centered cubic structures of the solid solution enriched fuels. Unclad pellets as well as two defective clad samples (C-10 and C-25 compositions) were corrosion tested at Battelle Memorial Institute (BMI) for compatibility with sodium at 345°C and at 430°C (650°F and 800°F), respectively.

1. X-Ray Diffraction

X-ray diffractometer traces were taken of pellets of the four fuels by scanning at high speed, $1^\circ (2\theta)/\text{min}$, through the entire spectrum to determine the presence of minor phases, and at slow speed, $1/8^\circ (2\theta)/\text{min}$, through the back reflection region to provide data for the calculation of lattice constants.

(a)

MAG. $1\frac{1}{8} \times$

(b)

MAG. $1\frac{1}{8} \times$

FIG. III-4 EXPLODED VIEWS OF Z-10 (a) AND C-25 (b) FUELED SAMPLES

FIG. III-5 END CAP WELDING CHAMBER

FIG. III-6 COMPLETED SAMPLES OF THE FOUR FUEL COMPOSITIONS

(a) Z-10

(b) C-25

FIG. III-7 RADIOGRAPHS SHOWING ASSEMBLED COMPONENTS OF Z-10 (a) AND C-25 (b) FUELED SAMPLES

The x-ray radiation was characteristic copper K^α . The diffraction maxima in the back reflection region were sharp, indicating that equilibrium structures had been developed by sintering heat treatments. The lattice constants are as follows:

<u>Composition</u>	<u>Lattice Constant (A)</u>
Z-10	5.149
Z-22	5.173
C-10	5.415
C-25	5.421

2. Metallography

Microstructural examinations were conducted to establish the single phase nature of the enriched fuels more conclusively. The pellets were mounted in an epoxy resin which sets at room temperature (Hysal Company, Olean, New York) and prepared by routine metallographic techniques of polishing on successively finer grade of emery papers using a kerosene-paraffin mixture as lubricant. Final polishing was performed on Buehler Microcloth covered wheels using 6 micron and 0.25 micron diamond paste as the abrasives. The specimens were automatically polished for up to eight hours to remove the roughened surface resulting from the coarser polishing operations.

Both the zirconia base and the ceria base fuels are highly resistant to chemical attack by the common inorganic acids. A suitable etchant consisting of 50 v/o HNO_3 - 10 v/o HF - 40 v/o H_2O was used successfully to delineate the structures of the zirconia based compositions. The ceria base fuels were unaffected by this etchant for immersion times up to eight hours. A combination of a fluoride salt (NH_4F), an oxidant (H_2O_2) and an oxidizing acid (H_2SO_4) was found to be an effective chemical etchant for the ceria base fuels. The composition of the etchant included the following:

NH_4F	20 vol %
60% H_2O_2	30 vol %
Conc. H_2SO_4	50 vol %

The microstructures of ceria (CeO_2) and the ceria base fuels were delineated by immersion of the specimens in the etchant at 60°C (140°F) for 2 to 10 minutes.

The microstructures of the Z-10 and Z-22 fuel compositions are shown in Figures III-8 and III-9. The structures are completely single phased, consisting of uniformly equiaxed grains free of minor or impurity phases. The large grain size of the two specimens is the result of extended sintering times of 66 hours and 125 hours at 1800°C (3270°F) for the Z-10 and Z-22 fuels, respectively.

The etching characteristics of the ceria base fuels were highly dependent upon the UO_2 content. Air fired pellets of ceria, without UO_2 additions, exhibited an equiaxed grain structure with sharply defined boundaries. A minor phase, globular in appearance, was evident within the grains (Figure III-10). X-ray diffraction analyses of this starting material had indicated a completely single phased, face centered cubic structure for samples prior to and following heating at 1500°C in air. The microstructure contains an estimated one volume percent of the second phase, and accordingly, is not detectable by the x-ray techniques utilized. Air sintered pellets of C-10 composition were attacked preferentially at the grain boundaries, as shown in Figure III-11. This grain boundary attack appeared to be associated with a fine precipitate (Figure III-12). It was not established whether the grain boundary phase was of the same composition and structure as the globular phase observed in all three ceria specimens. These phases were not detectable by x-ray diffraction.

An examination of the C-25 fuel microstructure indicated the formation of an adherent surface stain during the etching process. The partly obscured structure exhibited fine equiaxed grains containing clusters of a globular second phase. The appearance and the distribution of this constituent were very similar to those observed for the ceria starting material and the C-10 fuel specimens. In all cases, the second phase showed an isotropic behavior under polarized light and might have been ceria rich impurity phase containing small amounts of other oxides. The appearance of the unetched structure of the C-25 fuel pellets is shown in Figure III-13.

FIG. III-8 MICROSTRUCTURE OF Z-10 FUEL

MAG 250 X

FIG. III-9 MICROSTRUCTURE OF Z-22 FUEL

MAG 250 X

MAG 500 X

FIG. III-10 MICROSTRUCTURE OF CERIA WITHOUT UO_2 ADDITIONS

MAG 500 X

FIG. III-11 MICROSTRUCTURE OF C-10 FUEL

MAG 1500 X

FIG. III-12 HIGHER MAGNIFICATION VIEW OF PORTION OF STRUCTURE
IN FIGURE III-11

MAG 500 X

FIG. III-13 UNETCHED APPEARANCE OF C-25 FUEL MICROSTRUCTURE

3. Sodium Corrosion Study

Out-of-pile corrosion tests in water at 325°C and in steam at 650°C had demonstrated the excellent resistance of bare pellets of the four compositions to these environments. Their performance in a water reactor under conditions of a defective clad is expected to be similar to that for sintered UO_2 pellets. Since sodium rather than water would be the heat transfer medium in the irradiation capsules, the corrosion resistance of these fuels to sodium at 345 and 430°C (655 and 805°F), respectively, was studied.

The results of these studies indicate the following:

- a) The zirconia base fuels (Z-10 and Z-22) are not subject to corrosive attack by sodium at 430°C for exposures up to 150 hours. There were no dimensional or weight changes for these pellets.
- b) The ceria base fuels (C-10 and C-25) suffer severe corrosive attack by sodium at 430°C for exposures as short as 2 hours.
- c) The sodium-ceria fuel reaction is sufficient to cause severe swelling in a defective clad specimen of the type used in the irradiation program.
- d) The sodium reaction with bare fuel pellets does not seem to be altered by reduction of the fuel enrichment (to depleted) or of the temperature (to 345°C), but it does appear to be slowed down in defective clad specimens.

Additional details are provided in Reference 15.

The significance of these sodium corrosion test results are discussed in Section IV-A and resulted in a realignment of sample positions within some of the capsules.

IV. IRRADIATION PROGRAM

A. GENERAL

The objective of the irradiation program was to determine the performance of fuels containing UO_2 in solid solution in stabilized zirconia and ceria, respectively, at fission burnups of 40, 55, and 70% of the U-235 atoms, and at temperatures just below the melting point of these fuels.* Details of melting point determinations for these fuels were presented in CEND-158.⁽¹⁰⁾ As a result of the inherent uncertainties in irradiation experiments, target maximum fuel temperatures of 2200°C (4000°F) and 1870°C (3400°F) were established for the zirconia base and ceria base samples as a precaution against melting.

The program provided for scheduled capsule moves to permit all capsules to operate at their maximum heat generation rates consistent with the requirement that the melting point not be exceeded. The general scheme was to move a capsule to a higher flux position when the center temperature of the fuel was less than 540°C (1000°F) below the target temperatures established for each fuel type.

Post-irradiation examination included visual inspection and macrographs of fuel cladding, collection and identification of fission gas from punctured fuel samples, measurement of swelling, metallography of representative regions, x-ray diffraction analyses to determine whether the single phase, face-centered cubic structure has been retained, burnup analyses, and corrosion testing.

* Sample designations used in this report are:

	<u>w/o</u>	<u>m/o</u>	<u>w/o</u>	<u>m/o</u>
	<u>in CaO Stabilized ZrO_2</u>		<u>in CeO_2</u>	
Z-10	10	4	--	--
C-10	--	--	10	7
Z-22	22	10.2	--	--
C-25	--	--	25	17.5

Six instrumented capsules, each containing three stainless steel clad samples of zirconia base compositions and two stainless steel clad samples of ceria base compositions were irradiated. Capsule identifications, together with a description of the samples in each capsule and target burnups, are presented in Table IV-1. The original intent has been to intersperse ceria base samples with zirconia base compositions to provide a comparison of performance under nearly identical flux conditions. Three capsules, 43-1, 43-4, and 43-6 contained this arrangement and were the first three capsules fabricated and inserted in the test reactor. However, as a result of the incompatibility of the ceria base compositions with sodium, a realignment of sample positions within later capsules was made. The sodium interaction with the ceria base samples was unexpected and not predictable from thermodynamic relationships. This incompatibility would become important only if a sample cladding failure occurred during irradiation, as a failure of this kind could lead to the accumulation of a sodium-ceria fuel slurry within the capsule. An analysis of the potential problems induced by such a failure indicated the following:

a) If all of the $\text{CeO}_2\text{-UO}_2$ were released and remained suspended in the sodium, the temperature increase in the sodium would be less than 40°C (104°F).

b) If $\text{CeO}_2\text{-UO}_2$ particles collected at a particular locations, except at the bottom of the inner capsule wall, damage to the inner wall of the capsule would be unlikely.

c) If a significant quantity of $\text{CeO}_2\text{-UO}_2$ particles collected at the bottom of the inner capsule wall, damage to the inner capsule wall might occur. However, overall capsule integrity would not be impaired.

d) The relative volumes and helium gas pressures within the inner capsule wall and between the inner and outer capsule walls were such that the specimens would remain covered by sodium even if sodium entered the space between the two capsule walls.

e) If $\text{CeO}_2\text{-UO}_2$ and sodium entered the space between the two capsule walls, the outer cladding wall would not be damaged due to water cooling on the outside wall. Although the local heat flux might increase, burnout was not possible as long as sodium was present in the capsule annulus.

TABLE IV-1
SUMMARY OF CAPSULE CONDITIONS

Capsule Number	Sample Identification and Sequence*	Target Fission Burnup a/o	Reactor
43-1	Z-10 C-10 Z-10 Z-10 C-10	40	ETR
43-2	Z-10 Z-10 Z-10 C-10 C-10**	55	ETR
43-3	Z-10 Z-10 Z-10 C-10 C-10**	70	ETR
43-4	Z-22 C-25 Z-22 Z-22 C-25	40	MTR
43-5	Z-22 Z-22 Z-22 C-25 C-25**	70	ETR
43-6	Z-22 C-25 Z-22 Z-22 C-25	55	ETR

* The sample order given is from the top to the bottom of the capsule.

** The original configuration in the first three capsules inserted into the reactor was altered as a result of interaction of sodium with ceria-base compositions. Changes in position assured that zirconia-base samples were always above the ceria-base samples.

On the basis of this analysis, it was concluded that interaction of the ceria-base fuels with sodium, in the unlikely event of rupture of the cladding on the sample, would not impair the safety of the capsules. It was further concluded that a clad failure in the ceria-base samples, with resultant interaction between sodium and ceria, could produce particles in the sodium. As a result of the location of sample supports within the capsules, there was a reasonable probability that fuel particles could become lodged in areas adjacent to the zirconia base samples, thus perturbing the heat generation for these samples and leading to inconclusive data. Although this sequence of events was believed to be unlikely, precautions were taken in capsules 43-2, 43-3, and 43-5

to prevent it. The sample arrangement, as noted in Table IV-1, placed the three zirconia-base samples above the ceria-base samples. The other three capsules had already been inserted in MTR and ETR and contained the original configuration.

An interchange in target burnups was effected between capsule 43-6, inserted with the alternating zirconia-ceria configuration, and capsule 43-5, containing the new configuration, to provide as low a burnup as possible within the framework of program objectives for the capsules containing the alternating sample configuration. Table IV-1 reflects the result of all changes and presents the target burnups and sample sequence of all capsules as inserted in the reactor.

Table IV-2 indicates the sample identification sequence in each capsule.

TABLE IV-2
SPECIMEN LOADING
(From Top to Bottom in Capsule)

Capsule Number	Top					Bottom				
BMI 43-1	Z-10-A	C-10-A	Z-10-B	Z-10-C		C-10-B				
BMI 43-2	Z-10-D	Z-10-E	Z-10-F	C-10-C		C-10-D				
BMI 43-3	Z-10-G	Z-10-H	Z-10-J	C-10-E		C-10-F				
BMI 43-4	Z-22-M	C-25-M	Z-22-N	Z-22-O		C-25-O				
BMI 43-5	Z-22-T	Z-22-X	Z-22-Y	C-25-N		C-25-S				
BMI 43-6	Z-22-P	C-25-P	Z-22-R	Z-22-Z		C-25-R				

B. CAPSULE DESIGN AND FABRICATION

Capsule design and fabrication were performed by Battelle Memorial Institute as part of their subcontract with Combustion Engineering, Inc.

The stainless steel clad samples were fabricated and tested by Combustion Engineering. Fabrication procedures and data pertinent to these fuel samples are presented earlier in this report.

1. Evaluation of Irradiation Conditions Resulting from Two Different Fuels in the Same Capsule

Each capsule contained five stainless steel clad fuel samples, three of which contained zirconia base fuel and two ceria base fuel. It was desired to optimize the operation of each capsule for each fuel type, and the following series of relationships were evaluated to determine the extent to which such optimization could be achieved.

1. Fission heat generation rate is proportional to $k\Delta T$;
 $k\Delta T$ is proportional to $d^2 N_o (1-B_t) \phi_e$
2. Burnup rate is proportional to $\phi_e \alpha_u P$
3. Perturbation factor is proportional to $f [dN_o (1-B_t)]$

where

- k = Effective thermal conductivity
 ΔT = Specimen cladding to centerline temperature difference
 d = Specimen diameter
 N_o = Initial volumetric loading of U-235
 B_t = Total burnup of U-235
 ϕ_e = Effective thermal neutron flux
 ϕ_u = Unperturbed thermal neutron flux
 P = Perturbation factor derived from the Lewis⁽¹⁸⁾ empirical relations.

The fuel parameters considered as a basis for the irradiation program are presented in Table IV-3. The influence of changes in specimen diameters and flux conditions for the two fuels in each capsule was assessed by means of these relationships. It was concluded that it was not possible to provide the desired sample thermal gradient for the two fuels if equal rates of burnup were required simultaneously.

It was decided to provide reference burnup and temperature conditions for the zirconia base samples and to compromise test conditions for the ceria base samples. Further analyses indicated that differences in accrued burnup between the ceria and zirconia base samples would be in the range of 5 to 10 percent. Furthermore, the fairly large difference between target and actual centerline temperatures for the ceria base compositions would decrease as higher burnups were attained. The compromises necessary to permit irradiation of both materials in the same capsule were not believed to be limiting, and the irradiation program proceeded on this basis.

TABLE IV-3
FUEL PARAMETERS

Fuel	U-235 Content (grams/cm ³)	Effective Thermal Conductivity*		Target Sample Temperature (°C)		Fuel Diam. (in.)
		w/cm-°C	Btu/hr-ft-°F**	Clad. Surf.	Center- line	
Z-10	5.2	0.0175	1.01	315	2200	0.35
C-10	7.2	0.0230	1.33	315	1870	0.30
Z-22	5.7	0.0138	0.80	315	2200	0.25
C-25	7.3	0.0152	0.88	315	1870	0.19

* Fuel centerline to cladding surface

** Values are based on Reference 10

2. Nuclear Mockup Data

The shielding facility in the Battelle Research Reactor was used to conduct nuclear mockup experiments aimed at verifying use of the Lewis flux perturbation factors as a function of fuel composition, specimen diameter, and fuel depletion. Values obtained were relative perturbation factors rather than absolute perturbations for MTR and ETR.

In the mockup experiments, which utilized 0.25 inch and 0.34 inch diameter specimens containing 3 to 7.5% enriched UO₂ and natural uranium, the influence of burnup was assessed by changing the ratio of enrichments to cover the range from 11 to 80% total burnup of the U-235 atoms. All samples were contained in a 1 inch outside diameter shell to provide capsule simulation. Exposures were about eight minutes in a thermal neutron flux of approximately 10⁸ nv.

Typical data obtained from this series of experiments are presented in Figure IV-1. The Lewis relationship was derived from

$$\frac{\phi_e}{\phi_u} = 0.7 f \exp(-\Sigma_a X)$$

where

f = Lewis perturbation factor

$\exp(-\Sigma_a X)$ = Capsule attenuation factor based on slab calculation
(approximately 0.8 for these design conditions)

0.7 = Experience factor based on irradiations in MTR and ETR

As demonstrated in Figure IV-1, the slope of the curve of $\frac{\phi_e}{\phi_u}$ obtained through nuclear mockup experiments closely approximates that of the Lewis calculation. The difference in absolute values for these curves is related to the difference in reactors for the generation and utilization of the nuclear mockup data. The slope of curves relating effective flux to fuel surface flux and capsule surface flux also closely approximates the Lewis relationship. On this basis, utilization of the Lewis relationship in capsule and sample design was justified.

3. Capsule Design

Details of the irradiation capsule used for all six capsules are shown in Figure IV-2, and individual capsule components in Figure IV-3. The basic capsule design incorporated a double capsule wall fabricated from Type 316 stainless steel. The inner capsule contained the five fueled specimens immersed in sodium and stacked end to end in the array described in Table IV-1. They were aligned both axially and radially by Type 304 stainless steel spacers. Radial fins were machined on the outside of the inner shell to provide heat transfer paths to the outer shell at axial positions corresponding to fuel sample locations. These contact fins were eliminated in regions

FIG. IV-1 SUMMARY OF NUCLEAR MOCKUP DATA

FIG. IV-2 CAPSULE DESIGN

FIG. IV-3. CAPSULE COMPONENTS

which were not opposite fuel samples to minimize uncertainties associated with nonradial heat flow. The fin surface of the inner shell was ground and the fin surface contact area of the outer shell was honed to close tolerances to provide a contact fit at room temperature and a 0.0008 inch interference fit at operating temperature. The amount of fin contact with the outer shell per unit axial length was similar for both fuels in a given capsule for the Z-10 and C-10 compositions. Different fin ratios were required for the Z-22 and C-25 samples in the same capsule. The parameter controlling the fin ratios was the expected fission heat production rate for each sample. The fins were slotted to permit evacuation and filling of the annulus with helium at atmospheric pressure. The inner and outer shells were welded at the top to the header assembly and, at the bottom, to end caps. All of these components were fabricated from Type 316 stainless steel.

The inner shell was filled with sufficient sodium to provide a sodium level 5/8 inch above the top sample at room temperature. A sodium expansion space was provided at the top of the inner shell and filled with helium at atmospheric pressure at room temperature. An analysis of the stresses in the welded regions of the capsule and on the inner capsule wall resulting from internal pressure buildup was calculated to be less than 2 percent of the yield strength of Type 316 stainless steel at 315°C (600°F). Stresses on the headers indicated values of well below 2 percent of the yield strength of the material at temperature. A further calculation, assuming 100% release of all fission gas from the fuel from simultaneous ruptures of all five samples within a given capsule after the highest burnup had been achieved, indicated maximum stresses in any component in the capsule structure of less than 4 percent of the yield strength of the material.

Twelve 0.062 inch OD, end closed, Type 316 stainless steel sheathed, chromel-alumel thermocouples were assembled in each capsule. Two thermocouples were attached at the axial midpoint of each sample cladding at radial positions 180° apart. The junction ends of the thermocouples were fixed to the sample surfaces by means of small thermocouple clips shown in Figure IV-2.

Two thermocouples were placed on the inner wall of the inner shell to provide additional data on the heat transfer of the capsule. All thermocouples were double sealed into the header assembly by means of high temperature Coast-50 braze.

Calculated relationships between fuel sample clad thermocouple reading and fission heat generation, fuel centerline temperature, and clad surface temperature are shown in Figures IV-4 to IV-6 for each of the four different fuel compositions in each of the capsules. These fission heat generation rates were important considerations in the capsule design, and both relationships were significant for the interpretation of in-pile performance.

C. IRRADIATION HISTORY

Irradiation commenced in November 1962 with the insertion of capsule 43-4 in MTR and capsules 43-1 and 43-6 in ETR. Irradiation of the remaining three capsules in ETR was initiated in April 1963.

The target irradiation conditions for the capsules are given in Table IV-4.

Target temperature levels were to be maintained by relocating the capsules periodically into progressively higher neutron fluxes as the fission heat production decreased with fuel burnout. The selection of reactor space was governed by three considerations:

- 1) That a particular area of the reactor be selected for each capsule where initial and terminal flux conditions could be met without extensive lateral movement of the equipment;
- 2) For the initial part of the irradiation, that each capsule was to be located in a reactor facility having a flux level slightly lower than the design flux level to check out the thermal design;
- 3) As the irradiation progressed, that each capsule was to be re-located into progressively higher fluxes in order to minimize the decrease in specimen centerline temperature with fuel burnout.

FIG. IV-4 FISSION HEAT GENERATION AS A FUNCTION OF CLAD THERMOCOUPLE TEMPERATURE

FIG. IV-5 FUEL CENTERLINE TEMPERATURE AS A FUNCTION OF CLAD THERMOCOUPLE TEMPERATURE

FIG. IV-6 SPECIMEN CLAD TEMPERATURE AS A FUNCTION OF CLAD THERMOCOUPLE TEMPERATURE FOR ALL SAMPLES IN ALL CAPSULES

Tables IV-5 through IV-10 present the summaries of capsule performance during irradiation. Information presented in these tables was obtained by use of a data reduction system which operated as follows:

- 1) The multipoint recorders were connected in parallel with the ETR data logger and these were operated simultaneously. (This step does not apply to BMI 43-4, which was irradiated at the MTR.)
- 2) The data logger scanned each thermocouple every five minutes and punched out a scan on tape every 30 seconds.
- 3) The punched tapes were converted to IBM cards at Battelle and used, in conjunction with a computer program developed for the irradiation, to obtain the desired irradiation data.
- 4) For the MTR capsule, daily temperature averages obtained directly from the recorder charts were used, in conjunction with the same computer program.

Various capsule relocations were carried out during the irradiations in an effort to maintain the specimen clad surface temperatures near 315°C (600°F) as fuel burnout progressed. The following is a comparison of the number of actual relocations per capsule (not including the initial facility) with the number which had been anticipated at the start of irradiations.

Capsule Number	Actual Number of Relocations	Number of Relocations Anticipated at Start of Program
BMI 43-1	3	3
BMI 43-2	5	4
BMI 43-3	12	6
BMI 43-4	4	1
BMI 43-5	7	2
BMI 43-6	7	4

In general, the capsule relocations were successful. However, in some instances the temperatures did not increase as anticipated and in others it was necessary to relocate the capsule to a previous facility because of uncertainties in reactor flux levels as a result of abnormal reactor core loadings.

TABLE IV-4

TARGET IRRADIATION CONDITIONS FOR BMI 43 SERIES CAPSULES

Capsule Number	Type Fuel ^(a)	Target Specimen Temperature				a/o By Fission	Target Burnup	
		Cladding		Centerline			Fission/cc x 10 ²⁰	
		F	C	F	C			
BMI 43-1	Z-10	600	315	4000	2200	40	4.4	
	C-10	600	315	3000	1650		5.7	
BMI 43-2	Z-10	600	315	4000	2200	55	6.1	
	C-10	600	315	3000	1650		7.8	
BMI 43-3	Z-10	600	315	4250	2340	70	7.8	
	C-10	600	315	3200	1760		10.0	
BMI 43-4	Z-22	600	315	4000	2200	40	10.1	
	C-25	600	315	3200	1760		15.1	
BMI 43-5	Z-22	600	315	4000	2200	70	17.7	
	C-25	600	315	3200	1760		26.4	
BMI 43-6	Z-22	600	315	4000	2200	55	13.9	
	C-25	600	315	3200	1760		20.8	

(a) Each capsule contains 3 "Z" and 2 "C" fuel specimens.

Z-10 and C-10 fuels contain 10 w/o UO₂.

Z-22 and C-25 fuels contain 22 w/o and 25 w/o UO₂, respectively.

TABLE IV-5

IRRADIATION HISTORY FOR CAPSULE BMI 43-1

ETR Irradiation Facility	ETR Cycle Number	Specimen Number	Estimated Temperatures, C				Estimated Accumulated Burnup, Fissions/cc x 10 ²¹
			Cladding		Fuel		
			Surface	Avg	Centerline	Avg	
			Maximum		Maximum		
P-13-SE	51	Z-10-A	265	260	1760	1705	0.32
		C-10-A	295	280	1510	1455	0.44
		Z-10-B	305	300	2065	2010	0.37
		Z-10-C	305	295	2065	1955	0.37
		C-10-B	275	270	1425	1400	0.43
P-13-NE	52	Z-10-A	315	280	2150	1900	0.67
		C-10-A	330	315	1760	1650	0.94
		Z-10-B	340	310	2345	2095	0.77
		Z-10-C	350	310	2425	2095	0.77
		C-10-B	305	275	1595	1425	0.86
P-13-NE	53	Z-10-A	300	275	2010	1845	1.17
		C-10-A	320	300	1675	1540	1.62
		Z-10-B	340	305	2345	2065	1.32
		Z-10-C	320	305	2175	2065	1.32
		C-10-B	280	270	1455	1400	1.44
P-13-NE	54	Z-10-A	305	295	2065	1954	1.53
		C-10-A	325	315	1730	1650	2.12
		Z-10-B	340	310	2345	2095	1.70
		Z-10-C	325	310	2230	2095	1.71
		C-10-B	295	275	1510	1425	1.86
P-13-NE	55	Z-10-A	290	260	1925	1705	1.86
		C-10-A	315	280	1650	1455	2.57
		Z-10-B	320	280	2175	1900	2.07
		Z-10-C	305	280	2065	1900	2.08
		C-10-B	270	255	1400	1290	2.26
P-13-NE	56	Z-10-A	270	255	1790	1650	2.26
		C-10-A	305	280	1595	1455	3.12
		Z-10-B	310	270	2095	1790	2.50
		Z-10-C	295	280	1955	1900	2.53
		C-10-B	270	250	1400	1260	2.74
P-13-NE	57	Z-10-A	245	230	1565	1480	2.56
		C-10-A	265	255	1345	1290	3.53
		Z-10-B	275	250	1845	1620	2.83
		Z-10-C	265	255	1760	1650	2.87
		C-10-B	250	230	1260	1150	3.14

TABLE IV-5 (Continued)

ETR Irradiation Facility	ETR Cycle Number	Specimen Number	Estimated Temperatures, C				Estimated Accumulated Burnup, Fissions/cc x 10 ²¹
			Cladding		Fuel		
			Surface		Centerline		
			Maximum	Avg	Maximum	Avg	
P-12-SE	58	Z-10-A	260	255	1705	1650	2.86
		C-10-A	295	280	1510	1455	3.94
		Z-10-B	305	270	2065	1790	3.15
		Z-10-C	295	280	1955	1900	3.20
		C-10-B	270	265	1400	1345	3.52
P-12-SE	59	Z-10-A	255	245	1650	1565	3.21
		C-10-A	275	265	1430	1345	4.45
		Z-10-B	280	275	1900	1845	3.56
		Z-10-C	280	265	1900	1760	3.60
		C-10-B	260	245	1315	1230	3.95
P-12-SE	60	Z-10-A	250	245	1620	1565	3.62
		C-10-A	275	270	1425	1400	5.01
		Z-10-B	280	270	1900	1790	4.04
		Z-10-C	280	265	1900	1760	4.05
		C-10-B	260	250	1315	1260	4.46
P-12-SE	61	Z-10-A	250	230	1620	1480	3.99
		C-10-A	270	260	1400	1315	5.56
		Z-10-B	280	265	1900	1760	4.48
		Z-10-C	270	260	1790	1705	4.48
		C-10-B	250	240	1260	1175	4.95
P-12-NE	62	Z-10-Z	270	250	1790	1620	4.40
		C-10-A	295	210	1510	1010	5.97
		Z-10-B	295	265	1955	1760	4.92
		Z-10-C	270	255	1790	1650	4.91
		C-10-B	250	230	1260	1150	5.40
Capsule Discharged							

TABLE IV-6

IRRADIATION HISTORY FOR CAPSULE BMI 43-2

ETR Irradiation Facility	ETR Cycle Number	Specimen Number	Estimated Temperatures, C				Estimated Accumulated Burnup, Fissions/cc x 10 ²¹
			Cladding		Fuel		
			Surface		Centerline		
			Maximum	Avg	Maximum	Avg	
Q-6-SW	54	Z-10-D	260	250	1705	1620	0.31
		Z-10-E	270	250	1790	1620	0.32
		Z-10-F	265	250	1760	1620	0.32
		C-10-C	260	245	1315	1230	0.39
		C-10-D	240	215	1175	1040	0.31
P-6-SE	55	Z-10-D	310	280	2095	1900	0.68
		Z-10-E	330	300	2290	2010	0.71
		Z-10-F	345	315	2370	2150	0.74
		C-10-C	340	315	1790	1650	0.90
		C-10-D	305	270	1595	1400	0.74
P-6-SE	56	Z-10-D	340	290	2345	1925	1.14
		Z-10-E	360	300	2510	2010	1.18
		Z-10-F	365	315	2565	2150	1.23
		C-10-C	365	315	1955	1650	1.55
		C-10-D	315	270	1650	1400	1.27
P-6-SE	57	Z-10-D	330	305	2290	2065	1.56
		Z-10-E	340	315	2345	2150	1.63
		Z-10-F	360	330	2510	2290	1.71
		C-10-C	365	325	1955	1730	2.12
		C-10-D	315	295	1650	1510	1.77
P-6-SE	58	Z-10-D	295	265	1955	1760	1.82
		Z-10-E	305	275	2065	1845	1.95
		Z-10-F	315	295	2150	1955	2.06
		C-10-C	325	295	1730	1510	2.55
		C-10-D	280	260	1455	1315	2.14
P-6-SE	59	Z-10-D	280	270	1900	1790	2.28
		Z-10-E	295	275	1955	1845	2.37
		Z-10-F	300	280	2010	1900	2.49
		C-10-C	300	280	1540	1455	3.09
		C-10-D	255	250	1290	1260	2.62
P-6-SE	60	Z-10-D	315	295	2150	1955	2.80
		Z-10-E	325	305	2230	2065	2.92
		Z-10-F	340	315	2345	2150	3.05
		C-10-C	340	315	1790	1650	3.79
		C-10-D	295	280	1510	1455	3.22

TABLE IV-6 (Continued)

ETR Irradiation Facility	ETR Cycle Number	Specimen Number	Estimated Temperatures, C				Estimated Accumulated Burnup, Fissions/cc x 10 ²¹
			Cladding		Fuel		
			Surface		Centerline		
			Maximum	Avg	Maximum	Avg	
P-6-SE	61	Z-10-D	280	270	1900	1790	3.26
		Z-10-E	295	280	1955	1900	3.39
		Z-10-F	305	280	2065	1900	3.48
		C-10-C	315	280	1650	1455	4.36
		C-10-D	260	255	1315	1290	3.73
P-6-SE	62	Z-10-D	280	265	1900	1760	3.68
		Z-10-E	295	270	1955	1790	3.84
		Z-10-F	300	255	2010	1650	3.90
		C-10-C	300	280	1540	1455	4.95
		C-10-D	260	250	1315	1260	4.24
P-6-SE	63	Z-10-D	270	265	1790	1760	4.20
		Z-10-E	280	270	1900	1790	4.35
		Z-10-F	280	270	1900	1790	4.43
		C-10-C	290	270	1480	1400	5.59
		C-10-D	245	240	1230	1175	4.79
P-5-SW	64	Z-10-D	270	255	1790	1650	4.53
		Z-10-E	275	265	1845	1760	4.70
		Z-10-F	280	270	1900	1790	4.76
		C-10-C	280	270	1455	1400	6.01
		C-10-D	245	240	1200	1175	5.15
P-5-SW	65	Z-10-D	260	255	1705	1650	4.80
		Z-10-E	270	265	1790	1760	4.99
		Z-10-F	280	270	1900	1790	5.05
		C-10-C	280	270	1455	1400	6.38
		C-10-D	245	230	1230	1150	5.46
P-6-NW	66	Z-10-D	245	240	1565	1510	5.17
		Z-10-E	245	240	1565	1510	5.35
		Z-10-F	255	250	1650	1620	5.46
		C-10-C	260	250	1315	1260	6.88
		C-10-D	215	210	1040	1010	5.84
P-6-NW	67	Z-10-D	205	200	1290	1230	5.51
		Z-10-E	210	205	1315	1280	5.20
		Z-10-F	215	205	1345	1290	5.80
		C-10-C	205	195	980	925	7.26
		C-10-D	190	180	870	815	6.24

TABLE IV-6 (Continued)

ETR Irradiation Facility	ETR Cycle Number	Specimen Number	Estimated Temperatures, C				Estimated Accumulated Burnup, Fissions/cc x 10 ²¹
			Cladding Surface		Fuel Centerline		
			Maximum	Avg	Maximum	Avg	
0-5	68	Z-10-D	225	205	1425	1290	5.77
		Z-10-E	225	215	1425	1345	5.99
		Z-10-F	250	230	1620	1480	6.11
		C-10-C	245	225	1230	1120	7.67
		C-10-D	210	205	1010	980	6.58
0-6	69	Z-10-D	195	190	1205	1175	5.96
		Z-10-E	215	205	1345	1290	6.20
		Z-10-F	240	225	1510	1425	6.36
		C-10-C	250	240	1260	1175	7.98
		C-10-D	225	215	1120	1040	6.86
0-6	70	Z-10-D	215	205	1345	1290	6.15
		Z-10-E	240	215	1510	1345	6.41
		Z-10-F	270	260	1790	1705	6.63
		C-10-C	270	260	1400	1315	8.32
		C-10-D	240	225	1175	1120	7.13
Capsule Discharged							

TABLE IV-7

IRRADIATION DATA FOR BMI 43-3

ETR Irradiation Facility	ETR Cycle Number	Specimen Number	Estimated Temperatures, C				Estimated Accumulated Burnup, Fissions/cc x 10 ²¹
			Cladding		Fuel		
			Surface		Centerline		
			Maximum	Avg	Maximum	Avg	
G-16-SW*	54	Z-10-G	395		3010		
		Z-10-H	405		3095		
		Z-10-J	405		3095		
		C-10-E	400		2290		
		C-10-F	395		2260		
* Capsule initially inserted into G-16-SW for Cycle 54. Excessive temperatures achieved at 170 Mw. Reactor was shutdown and capsule moved to F-17-C for rest of cycle.							
F-17-C	54	Z-10-G	205	190	1315	1175	0.22
		Z-10-H	205	195	1315	1205	0.23
		Z-10-J	210	200	1345	1260	0.24
		C-10-E	205	195	1040	980	0.29
		C-10-F	200	195	1040	980	0.29
G-16-SW*	55	Z-10-G	345		2565		
		Z-10-H	330		2455		
		Z-10-J	360		2705		
		C-10-E	328		1870		
		C-10-F	325		1845		
* Capsule reinserted into G-16-SW for Cycle 55. Temperatures at 150 Mw were at design levels. Consequently the reactor was shutdown and the capsule moved to F-17-NE for the rest of the cycle.							
F-17-NE	55	Z-10-G	225	180	1480	1095	0.43
		Z-10-H	225	175	1480	1065	0.44
		Z-10-J	240	205	1540	1315	0.51
		C-10-E	240	205	1260	1065	0.62
		C-10-F	220	170	1175	815	0.56
F-17-NE	56	Z-10-G	245	200	1595	1260	0.75
		Z-10-H	240	200	1540	1260	0.75
		Z-10-J	250	225	1650	1480	0.87
		C-10-E	250	220	1315	1175	1.01
		C-10-F	225	205	1205	1065	0.96
G-17-NE	57	Z-10-G	270	240	1925	1615	1.10
		Z-10-H	270	245	1925	1705	1.10
		Z-10-J	300	265	2175	1870	1.26
		C-10-E	295	260	1620	1425	1.55
		C-10-F	280	245	1540	1315	1.40

TABLE IV-7 (Continued)

ETR Irradiation Facility	ETR Cycle Number	Specimen Number	Estimated Temperatures, C				Estimated Accumulated Burnup, Fissions/cc x 10 ²¹
			Cladding		Fuel		
			Surface		Centerline		
			Maximum	Avg	Maximum	Avg	
F-16-SE	58	Z-10-G	300	245	2175	1705	1.41
		Z-10-H	295	240	2120	1650	1.40
		Z-10-J	315	265	2315	1870	1.61
		C-10-E	295	205	1620	1065	1.85
		C-10-F	300	250	1650	1345	1.80
F-16-SE	59	Z-10-G	305	270	2230	1925	1.86
		Z-10-H	305	280	2230	2040	1.86
		Z-10-J	340	305	2510	2230	2.12
		C-10-E	315	295	1760	1620	2.46
		C-10-F	320	300	1790	1650	2.43
F-16-SE	60	Z-10-G	295	250	2120	1730	2.32
		Z-10-H	305	260	2230	1845	2.34
		Z-10-J	340	295	2510	2120	2.68
		C-10-E	325	280	1845	1540	3.14
		C-10-F	300	300	1870	1650	3.14
F-16-SE	61	Z-10-G	295	260	2110	1845	2.78
		Z-10-H	295	265	2110	1870	2.83
		Z-10-J	330	300	2455	2175	3.23
		C-10-E	325	300	1850	1845	3.82
		C-10-F	340	305	1900	1705	3.85
F-16-SE	62	Z-10-G	265	255	1870	1790	3.24
		Z-10-H	270	260	1925	1730	3.30
		Z-10-J	310	295	2260	2095	3.78
		C-10-E	305	290	1705	1650	4.50
		C-10-F	315	295	1760	1620	4.52
F-16-SE	63	Z-10-G	280	240	2040	1650	3.74
		Z-10-H	280	245	2040	1705	3.80
		Z-10-J	320	275	2370	1980	4.38
		C-10-E	315	270	1760	1480	5.20
		C-10-F	310	275	1730	1510	5.22
G-16-SE	64	Z-10-G	325	300	2425	2175	4.17
		Z-10-H	315	300	2315	2175	4.24
		Z-10-J	360	325	2705	2425	4.86
		C-10-E	325	300	1845	1650	5.74
		C-10-F	300	290	1650	1595	5.75

TABLE IV-7 (Continued)

ETR Irradiation Facility	ETR Cycle Number	Specimen Number	Estimated Temperatures, C				Estimated Accumulated Burnup, Fissions/cc x 10 ²¹
			Cladding		Fuel		
			Surface		Centerline		
			Maximum	Avg	Maximum	Avg	
G-16-SW	65	Z-10-G	290	260	2095	1845	4.41
		Z-10-H	275	265	1980	1870	4.53
		Z-10-J	310	300	2260	2175	5.20
		C-10-E	290	265	1595	1455	6.11
		C-10-F	270	260	1480	1400	6.12
G-16-SW	66	Z-10-G	280	270	2040	1925	4.89
		Z-10-H	270	265	1925	1870	5.01
		Z-10-J	300	290	2175	2095	5.74
		C-10-E	270	260	1480	1400	6.68
		C-10-F	255	245	1370	1315	6.65
G-16-C	67	Z-10-G	315	300	2315	2175	5.48
		Z-10-H	310	295	2260	2120	5.61
		Z-10-J	345	315	2565	2315	6.38
		C-10-E	305	280	1705	1540	7.39
		C-10-F	295	270	1620	1480	7.34
G-16-C	68	Z-10-G	340	300	2510	2175	5.94
		Z-10-H	330	295	2455	2120	6.06
		Z-10-J	370	315	2790	2315	6.86
		C-10-E	325	280	1845	1540	7.91
		C-10-F	325	275	1845	1510	7.86
G-16-C	69	Z-10-G	315	300	2315	2175	6.32
		Z-10-H	300	295	2175	2120	6.41
		Z-10-J	320	315	2370	2315	7.27
		C-10-E	300	290	1650	1595	8.39
		C-10-F	275	260	1510	1400	8.30
G-16-C	70	Z-10-G	245	230	1705	1595	6.57
		Z-10-H	240	220	1650	1480	6.67
		Z-10-J	260	240	1845	1650	7.55
		C-10-E	250	215	1345	1120	8.66
		C-10-F	225	210	1205	1095	8.56
G-16-NE	71	Z-10-G	345	290	2565	2095	6.93
		Z-10-H	340	290	2510	2095	7.01
		Z-10-J	360	305	2705	2205	7.90
		C-10-E	325	290	1845	1595	9.10
		C-10-F	300	260	1650	1400	8.95

TABLE IV-7 (Continued)

ETR Irradiation Facility	ETR Cycle Number	Specimen Number	Estimated Temperatures, C				Estimated Accumulated Burnup, Fissions/cc x 10 ²¹
			Cladding		Fuel		
			Surface		Centerline		
			Maximum	Avg	Maximum	Avg	
G-16-NE	72	Z-10-G	270	220	1925	1650	7.21
		Z-10-H	255	230	1790	1595	7.30
		Z-10-J	275	250	1980	1730	8.21
		C-10-E	250	230	1345	1230	9.44
		C-10-F	250	210	1345	1095	9.25
G-16-NE	73	Z-10-G	260	220	1845	1650	7.63
		Z-10-H	260	220	1845	1650	7.70
		Z-10-J	270	245	1925	1705	8.65
		C-10-E	255	230	1370	1230	9.94
		C-10-F	230	210	1230	1095	9.70
F-15-C	74	Z-10-G	345	315	2565	2315	8.11
		Z-10-H	345	315	2565	2315	8.18
		Z-10-J ^(a)	-	-	-	-	-
		C-10-E	350	320	1980	1790	10.55
		C-10-F	325	300	1845	1650	10.28
G-16-NE	75	Z-10-G	230	213	1595	1425	8.39
		Z-10-H	215	205	1455	1370	8.45
		Z-10-J ^(a)	-	-	-	-	-
		C-10-E	205	193	1455	980	10.84
		C-10-F	195	173	980	870	10.53
G-16-NE	76	Z-10-G	250	220	1730	1480	8.57
		Z-10-H	240	213	1650	1425	8.61
		Z-10-J ^(a)	-	-	-	-	-
		C-10-E	220	198	1150	1010	11.05
		C-10-F	200	178	1095	900	10.70
F-15-C	77	Z-10-G	395	340	2980	2510	9.10
		Z-10-H	390	325	2925	2425	9.11
		Z-10-J ^(a)	-	-	-	-	-
		C-10-E	370	310	2120	1730	11.63
		C-10-F	345	300	1955	1650	11.24
Capsule Discharged							

(a) Validity of temperature and burnup data as determined from thermocouple data for specimen Z-10-J in question.

TABLE IV-8

IRRADIATION HISTORY FOR CAPSULE BMI 43-4

ETR Irradiation Facility	ETR Cycle Number	Specimen Number	Estimated Temperatures, C				Estimated Accumulated Burnup, Fissions/cc x 10 ²¹
			Cladding		Fuel		
			Surface		Centerline		
			Maximum	Avg	Maximum	Avg	
A-29-NW	183	Z-22-M	270	265	1815	1790	0.35
		C-25-M	275	265	1510	1425	0.57
		Z-22-N	320	305	2230	2095	0.40
		Z-22-O	330	310	2345	2150	0.40
		C-25-O	280	265	1540	1425	0.57
A-29-NW	184	Z-22-M	260	255	1730	1675	0.73
		C-25-M	255	250	1370	1315	1.09
		Z-22-N	270	265	1815	1790	0.81
		Z-22-O	300	295	2065	2010	0.86
		C-25-O	305	295	1675	1595	1.20
A-29-SE	185	Z-22-M	350	330	2455	2315	1.14
		C-25-M	330	315	1870	1730	1.65
		Z-22-N	370	340	2650	2370	1.24
		Z-22-O	380	350	2730	2455	1.31
		C-25-O	350	320	1955	1790	1.80
A-29-SE	186	Z-22-M	340	330	2370	2345	1.59
		C-25-M	305	305	1675	1675	2.25
		Z-22-N	345	325	2400	2290	1.67
		Z-22-O	360	340	2565	2370	1.74
		C-25-O	320	305	1790	1675	2.40
A-29-SE	187	Z-22-M	325	320	2290	2230	2.07
		C-25-M	295	295	1595	1595	2.88
		Z-22-N	325	320	2290	2230	2.12
		Z-22-O	340	325	2370	2290	2.22
		C-25-O	310	300	1705	1650	3.04
A-29-SE	188	Z-22-M	320	315	2230	2205	2.32
		C-25-M	295	290	1595	1565	3.23
		Z-22-N	310	305	2150	2095	2.38
		Z-22-O	315	310	2205	2150	2.48
		C-25-O	295	290	1595	1565	3.38
A-29-SE	189	Z-22-M	320	310	2230	2150	2.86
		C-25-M	295	280	1595	1540	3.94
		Z-22-N	310	295	2150	2010	2.88
		Z-22-O	320	305	2230	2095	3.02
		C-25-O	305	295	1675	1595	4.13

TABLE IV-8 (Continued)

ETR Irradiation Facility	ETR Cycle Number	Specimen Number	Estimated Temperatures, °C				Estimated Accumulated Burnup, Fissions/cc x 10 ²¹
			Cladding		Fuel		
			Surface		Centerline		
			Maximum	Avg	Maximum	Avg	
A-29-SE	190	Z-22-M	320	310	2230	2150	3.22
		C-25-M	315	310	1730	1705	4.47
		Z-22-N	320	315	2230	2205	3.24
		Z-22-O	310	300	2150	2065	3.34
		C-25-O	305	300	1675	1650	4.62
A-29-SE	191	Z-22-M	320	310	2230	2150	3.67
		C-25-M	280	275	1540	1510	4.62
		Z-22-N	295	290	2010	1980	3.67
		Z-22-O	315	305	2205	2095	3.80
		C-25-O	305	300	1675	1650	5.28
A-29-SE	192	Z-22-M	310	300	2150	2065	4.18
		C-25-M	275	265	1510	1425	5.28
		Z-22-N	290	280	1980	1925	4.13
		Z-22-O	305	300	2095	2065	4.30
		C-25-O	300	295	1650	1595	6.04
A-29-SE	193	Z-22-M	320	310	2230	2150	4.58
		C-25-M	295	280	1595	1540	6.26
		Z-22-N	315	300	2205	2065	4.50
		Z-22-O	340	320	2370	2230	4.70
		C-25-O	340	325	1900	1815	6.68
A-29-SE	194	Z-22-M	310	300	2150	2065	5.08
		C-25-M	290	275	1565	1510	6.94
		Z-22-N	305	295	2095	2010	4.98
		Z-22-O	315	305	2205	2095	5.22
		C-25-O	310	300	1705	1650	7.39
A-29-SE	195	Z-22-M	315	305	2205	2095	5.54
		C-25-M	290	280	1565	1540	7.54
		Z-22-N	300	295	2065	2010	5.42
		Z-22-O	315	305	2205	2095	5.67
		C-25-O	310	300	1705	1650	8.07
A-29-SE	196	Z-22-M	275	250	1870	1650	5.90
		C-25-M	265	250	1425	1345	8.07
		Z-22-N	295	280	2010	1925	5.82
		Z-22-O	310	295	2150	2010	6.10
		C-25-O	310	295	1705	1620	8.70

TABLE IV-8 (Continued)

ETR Irradiation Facility	ETR Cycle Number	Specimen Number	Estimated Temperatures, C				Estimated Accumulated Burnup, Fissions/cc x 10 ²¹
			Cladding Surface		Fuel Centerline		
			Maximum	Avg	Maximum	Avg	
A-29-SE	197	Z-22-M	315	310	2205	2150	6.38
		C-25-M	295	280	1595	1540	8.70
		Z-22-N	305	280	2095	1925	6.25
		Z-22-O	315	300	2205	2065	6.56
		C-25-O	315	300	1730	1650	9.38
A-29-SE	198	Z-22-M	315	305	2205	2095	6.84
		C-25-M	275	270	1510	1480	9.31
		Z-22-N	295	275	2010	1870	6.68
		Z-22-O	305	295	2095	2010	7.02
		C-25-O	305	295	1675	1595	10.05
A-29-SE	199	Z-22-M	280	270	1925	1815	7.19
		C-25-M	260	255	1400	1370	9.79
		Z-22-N	280	275	1925	1870	7.04
		Z-22-O	300	290	2065	1980	7.40
		C-25-O	295	280	1595	1540	10.61
A-29-SE	200	Z-22-M	265	255	1790	1675	7.62
		C-25-M	255	245	1370	1290	10.39
		Z-22-N	275	265	1870	1790	7.50
		Z-22-O	300	280	2065	1925	7.86
		C-25-O	300	280	1650	1540	11.31
A-29-SE	201	Z-22-M	295	275	2010	1870	8.02
		C-25-M	275	260	1510	1400	10.96
		Z-22-N	265	255	1790	1675	7.85
		Z-22-O	260	245	1730	1595	8.20
		C-25-O	250	230	1315	1230	11.82
A-28-NE	202	Z-22-M	295	275	2010	1870	8.40
		C-25-M	280	270	1540	1480	11.51
		Z-22-N	280	270	1925	1815	8.23
		Z-22-O	275	260	1870	1730	8.33
		C-25-O	260	250	1400	1315	12.30
A-28-NE	203	Z-22-M	270	260	1815	1730	8.81
		C-25-M	260	250	1400	1315	12.09
		Z-22-N	265	255	1790	1675	8.64
		Z-22-O	265	255	1790	1675	8.96
		C-25-O	260	245	1400	1290	12.87

TABLE IV-8 (Continued)

ETR Irradiation Facility	ETR Cycle Number	Specimen Number	Estimated Temperatures, C				Estimated Accumulated Burnup, Fissions/cc x 10 ²¹
			Cladding		Fuel		
			Surface		Centerline		
			Maximum	Avg	Maximum	Avg	
A-28-NE	204	Z-22-M	260	245	1730	1595	9.04
		C-25-M	255	245	1730	1290	12.60
		Z-22-N	255	250	1675	1650	8.96
		Z-22-O	250	245	1650	1595	9.29
		C-25-O	240	230	1260	1400	13.37
A-28-NE	205	Z-22-M	260	255	1730	1675	9.54
		C-25-M	245	240	1290	1260	13.12
		Z-22-N	240	225	1540	1455	9.32
		Z-22-O	220	210	1400	1345	9.61
		C-25-O	210	200	1065	980	13.78
A-2-NE	206	Z-22-M	305	300	2095	2065	9.90
		C-25-M	315	310	1730	1705	13.73
		Z-22-N	325	315	2290	2205	9.72
		Z-22-O	310	300	2150	2065	10.0
		C-25-O	295	280	1595	1540	14.30
A-2-NE	207	Z-22-M	275	270	1870	1815	10.22
		C-25-M	295	290	1595	1565	14.28
		Z-22-N	300	295	2065	2010	10.08
		Z-22-O	280	275	1925	1870	10.32
		C-25-O	270	265	1480	1425	14.78
Capsule Discharged							

TABLE IV-9
IRRADIATION DATA FOR BMI 43-5

ETR Irradiation Facility	ETR Cycle Number	Specimen Number	Estimated Temperatures, C				Estimated Accumulated Burnup, Fissions/cc x 10 ²¹
			Cladding		Fuel		
			Surface		Centerline		
			Maximum	Avg	Maximum	Avg	
I-2-C	54	Z-22-T	325	290	2290	1980	0.58
		Z-22-X	325	290	2290	1980	0.58
		Z-22-Y	355	310	2510	2150	0.63
		C-25-N	340	300	1900	1650	0.90
		C-25-S	315	265	1760	1425	0.86
I-2-C	55	Z-22-T	270	260	1845	1760	1.09
		Z-22-X	290	255	1980	1705	1.09
		Z-22-Y	305	275	2095	1870	1.16
		C-25-N	305	280	1675	1540	1.72
		C-25-S	295	265	1620	1425	1.65
I-2-C	56	Z-22-T	245	240	1620	1565	1.64
		Z-22-X	250	240	1650	1565	1.64
		Z-22-Y	270	260	1845	1760	1.79
		C-25-N	280	270	1540	1480	2.70
		C-25-S	270	250	1480	1315	2.55
I-2-SW	57	Z-22-T	295	270	2010	1845	2.22
		Z-22-X	305	270	2095	1845	2.20
		Z-22-Y	305	295	2095	2010	2.42
		C-25-N	320	305	1790	1675	3.67
		C-25-S	280	275	1540	1510	3.38
I-2-SW	58	Z-22-T	280	275	1925	1870	2.70
		Z-22-X	280	265	1925	1790	2.68
		Z-22-Y	295	290	2010	1980	2.93
		C-25-N	325	300	1815	1650	4.50
		C-25-S	270	270	1510	1480	4.13
I-2-SW	59	Z-22-T	315	290	2205	1980	3.39
		Z-22-X	320	300	2260	2065	3.36
		Z-22-Y	320	300	2260	2065	3.64
		C-25-N	325	305	1815	1675	5.58
		C-25-S	300	275	1650	1510	5.06
I-2-SW	60	Z-22-T	315	280	1760	1925	4.12
		Z-22-X	295	280	2010	1925	4.12
		Z-22-Y	295	290	2010	1980	4.40
		C-25-N	310	300	1730	1650	6.74
		C-25-S	280	275	1540	1510	6.15

TABLE IV-9 (Continued)

ETR Irradiation Facility	ETR Cycle Number	Specimen Number	Estimated Temperatures, C				Estimated Accumulated Burnup, Fissions/cc x 10 ²¹
			Cladding		Fuel		
			Surface		Centerline		
			Maximum	Avg	Maximum	Avg	
I-2-SW	61	Z-22-T	315	265	2205	1790	4.81
		Z-22-X	260	245	1760	1620	4.73
		Z-22-Y	265	255	1790	1705	5.03
		C-25-N	275	265	1510	1425	7.76
		C-25-S	260	250	1400	1315	7.09
I-3-NW	62	Z-22-T	330	310	2345	2150	5.36
		Z-22-X	345	325	2425	2290	5.34
		Z-22-Y	350	325	2455	2290	5.92
		C-25-N	350	330	1980	1870	9.11
		C-25-S	325	310	1815	1705	8.33
I-2-SW	63	Z-22-T	295	260	2010	1760	6.38
		Z-22-X	280	260	1925	1760	6.35
		Z-22-Y	270	265	1845	1790	6.68
		C-25-N	280	265	1540	1425	10.28
		C-25-S	260	250	1400	1315	9.37
I-3-NW	64	Z-22-T	315	260	2205	1760	6.87
		Z-22-X	275	245	1870	1620	6.80
		Z-22-Y	315	270	2205	1845	7.20
		C-25-N	345	300	1925	1650	11.18
		C-25-S	305	290	1675	1595	10.28
I-3-NW	65	Z-22-T	275	245	1870	1595	7.28
		Z-22-X	275	240	1870	1565	7.18
		Z-22-Y	275	245	1870	1595	7.61
		C-25-N	280	265	1540	1425	11.80
		C-25-S	265	245	1425	1290	10.84
I-3-NW	66	Z-22-T	270	230	1845	1510	7.82
		Z-22-X	270	225	1845	1480	7.72
		Z-22-Y	270	230	1845	1510	8.14
		C-25-N	275	275	1510	1400	12.73
		C-25-S	250	220	1315	1150	11.62
I-3-C	67	Z-22-T	280	275	1925	1760	8.55
		Z-22-X	275	255	1870	1705	8.40
		Z-22-Y	280	260	1925	1760	8.90
		C-25-N	300	280	1650	1540	13.94
		C-25-S	265	245	1425	1290	12.60

TABLE IV-9 (Continued)

ETR Irradiation Facility	ETR Cycle Number	Specimen Number	Estimated Temperatures, C				Estimated Accumulated Burnup, Fissions/cc x 10 ²¹
			Cladding		Fuel		
			Surface		Centerline		
			Maximum	Avg	Maximum	Avg	
I-3-SW	68	Z-22-T	275	240	1870	1565	9.05
		Z-22-X	270	225	1845	1480	8.88
		Z-22-Y	255	240	1675	1565	9.38
		C-25-N	260	255	1400	1370	14.73
		C-25-S	225	210	1175	1095	13.22
I-3-SW	69	Z-22-T	270	255	1790	1705	9.38
		Z-22-X	240	225	1565	1480	9.20
		Z-22-Y	240	215	1565	1370	9.74
		C-25-N	225	240	1370	1260	15.32
		C-25-S	230	220	1230	1150	13.70
I-3-SW	70	Z-22-T	320	300	2230	2065	9.81
		Z-22-X	300	280	2065	1925	9.64
		Z-22-Y	290	280	1980	1925	10.12
		C-25-N	300	295	1650	1595	16.00
		C-25-S	250	245	1315	1290	14.13
I-3-SW	71	Z-22-T	330	295	2345	2010	10.29
		Z-22-X	325	290	2290	1980	10.11
		Z-22-Y	315	280	2205	1925	10.62
		C-25-N	340	300	1900	1650	16.76
		C-25-S	270	240	1480	1260	14.74
I-3-SW	72	Z-22-T	340	315	2370	2205	10.90
		Z-22-X	330	315	2345	2205	10.70
		Z-22-Y	325	300	2290	2065	11.18
		C-25-N	360	325	2040	1815	17.65
		C-25-S	290	270	1565	1480	15.42
I-3-SW	73	Z-22-T	345	305	2425	2095	11.67
		Z-22-X	340	295	2370	2010	11.43
		Z-22-Y	340	295	2370	2010	11.88
		C-25-N	350	305	1955	1675	18.80
		C-25-S	300	255	1650	1370	16.38
I-3-SW	74	Z-22-T	320	280	2230	1925	12.29
		Z-22-X	320	270	2230	1845	12.04
		Z-22-Y	320	270	2230	1845	12.50
		C-25-N	343	290	1925	1595	19.75
		C-25-S	275	230	1510	1230	17.10

TABLE IV-9 (Continued)

ETR Irradiation Facility	ETR Cycle Number	Specimen Number	Estimated Temperatures, C				Estimated Accumulated Burnup, Fissions/cc x 10 ²¹
			Cladding		Fuel		
			Surface		Centerline		
			Maximum	Avg	Maximum	Avg	
I-3-SW	75	Z-22-T	290	275	1980	1870	12.81
		Z-22-X	275	260	1870	1760	12.52
		Z-22-Y	275	260	1870	1760	12.97
		C-25-N	295	270	1620	1480	20.28
		C-25-S	245	240	1290	1260	17.72
I-3-SW	76	Z-22-T	190	175	1175	1065	13.00
		Z-22-X	175	160	1095	930	12.70
		Z-22-Y	170	154	1040	900	13.14
		C-25-N	180	165	900	790	20.80
		C-25-S	180	165	900	790	18.00
I-3-SW	77	Z-22-T	210	205	1375	1290	13.35
		Z-22-X	195	190	1205	1150	13.02
		Z-22-Y	195	190	1205	1150	13.48
		C-25-N	205	195	1040	985	21.3
		C-25-S	205	195	1040	985	18.5
I-3-SW	78	Z-22-T	250	225	1650	1480	13.90
		Z-22-X	230	210	1540	1345	13.50
		Z-22-Y	220	200	1425	1260	13.92
		C-25-N	230	215	1205	1095	22.1
		C-25-S	170	160	815	760	19.0
I-3-SW	79	Z-22-T	230	215	815	1370	14.24
		Z-22-X	210	200	1375	1260	13.80
		Z-22-Y	205	195	1290	1205	14.20
		C-25-N	215	200	1120	1010	22.6
		C-25-S	175	154	870	705	19.8
I-3-SW	80	Z-22-T	230	210	1540	1345	14.70
		Z-22-X	215	190	1370	1150	14.20
		Z-22-Y	195	180	1205	1120	14.60
		C-25-N	215	195	1120	985	23.2
		C-25-S	160	149	760	650	19.8
I-3-SW	81	Z-22-T	210	205	1375	1290	15.18
		Z-22-X	190	180	1150	1120	14.58
		Z-22-Y	190	175	1150	1095	15.00
		C-25-N	200	190	1010	930	23.8
		C-25-S	165	160	790	760	20.3

TABLE IV-9 (Continued)

ETR Irradiation Facility	ETR Cycle Number	Specimen Number	Estimated Temperatures, C				Estimated Accumulated Burnup, Fissions/cc x 10 ²¹
			Cladding		Fuel		
			Surface		Centerline		
			Maximum	Avg	Maximum	Avg	
I-3-SW	82	Z-22-T	190	180	1150	1120	15.50
		Z-22-X	175	170	1095	1040	14.93
		Z-22-Y	175	165	1095	985	15.32
		C-25-N	190	180	930	900	24.4
		C-25-S	149	138	650	620	20.7
E-4-C	83	Z-22-T	225	220	1480	1425	16.05
		Z-22-X	210	205	1375	1290	15.42
		Z-22-Y	200	195	1260	1205	15.78
		C-25-N	210	205	1095	1040	25.1
		C-25-S	154	149	705	650	21.1
Capsule Discharged							

TABLE IV-10
IRRADIATION DATA FOR BMI 43-6

ETR Irradiation Facility	ETR Cycle Number	Specimen Number	Estimated Temperatures, C				Estimated Accumulated Burnup, Fissions/cc x 10 ²¹
			Cladding		Fuel		
			Surface		Centerline		
			Maximum	Avg	Maximum	Avg	
Q-12-NW	51	Z-22-P	265	250	1790	1650	0.48
		C-25-P	280	270	1540	1480	0.79
		Z-22-R	295	280	2010	1925	0.56
		Z-22-Z	290	280	1980	1925	0.56
		C-25-R	270	265	1480	1425	0.75
Q-12-SW	52	Z-22-P	300	295	2065	2010	1.04
		C-25-P	315	305	1760	1675	1.65
		Z-22-R	340	315	2370	2205	1.16
		Z-22-Z	325	305	2290	2095	1.14
		C-25-R	305	295	1675	1595	1.58
Q-12-SW	53	Z-22-P	305	295	2095	2010	1.82
		C-25-P	305	295	1675	1620	2.88
		Z-22-R	325	305	2290	2095	2.00
		Z-22-Z	325	295	2290	2010	1.95
		C-25-R	305	280	1675	1540	2.74
Q-12-SW	54	Z-22-P	320	295	2260	2010	2.40
		C-25-P	325	295	1815	1595	3.75
		Z-22-R	340	305	2370	2095	2.60
		Z-22-Z	340	295	2370	2010	2.53
		C-25-R	305	230	1675	1205	3.38
Q-12-SW	55	Z-22-P	305	290	2095	1980	2.98
		C-25-P	315	290	1760	1595	4.60
		Z-22-R	315	290	2205	1980	3.16
		Z-22-Z	315	270	2205	1845	3.06
		C-25-R	275	195	1480	1205	3.90
Q-12-SW	56	Z-22-P	320	270	2260	1845	3.62
		C-25-P	325	270	1815	1480	5.55
		Z-22-R	315	280	2205	1925	3.87
		Z-22-Z	295	260	2010	1760	3.67
		C-25-R	270	240	1480	1260	4.76
Q-12-SW	57	Z-22-P	270	255	1845	1705	4.15
		C-25-P	270	250	1480	1315	6.34
		Z-22-R	280	255	1925	1705	4.35
		Z-22-Z	270	250	1845	1650	4.17
		C-25-R	240	220	1260	1150	5.44

TABLE IV-10 (Continued)

ETR Irradiation Facility	ETR Cycle Number	Specimen Number	Estimated Temperatures, C				Estimated Accumulated Burnup, Fissions/cc x 10 ²¹
			Cladding		Fuel		
			Surface		Centerline		
			Maximum	Avg	Maximum	Avg	
P-12-NE*	58	Z-22-P	350		2455	-	-
		C-25-P	360		2040	-	-
		Z-22-R	360		2540	-	-
		Z-22-Z	365		2595	-	-
		C-25-R	350		1980	-	-
* Capsule initially inserted into P-12-NE for Cycle 58. During startup temperatures were higher than desired, and reactor was shutdown and capsule was moved to Q-12-NW for rest of Cycle.							
Q-12-NW	58	Z-22-P	270	255	1845	1705	4.60
		C-25-P	270	250	1480	1315	7.00
		Z-22-R	250	215	1650	1370	4.73
		Z-22-Z	255	250	1705	1650	4.60
		C-25-R	225	215	1205	1120	6.00
Q-12-NW	59	Z-22-P	260	250	1760	1650	5.16
		C-25-P	260	250	1400	1315	7.83
		Z-22-R	240	225	1565	1480	5.23
		Z-22-Z	245	240	1620	1565	5.13
		C-25-R	215	205	1120	1040	6.68
P-13-NE	60*	Z-22-P	350	320	2480	2260	6.02
		C-25-P	355	325	2010	1815	9.18
		Z-22-R	320	310	2260	2150	6.07
		Z-22-Z	320	310	2260	2150	5.97
		C-25-R	295	290	1620	1595	7.80
* Capsule reached maximum levels in P-13-SW at 122 Mw during startup for Cycle 60. Reactor was shutdown and capsule was moved to P-13-NE for rest of Cycle.							
P-13-NE	61	Z-22-P	355	325	2510	2290	6.88
		C-25-P	360	330	2040	1870	10.50
		Z-22-R	300	290	2065	1980	6.88
		Z-22-Z	325	280	2290	1925	6.78
		C-25-R	305	290	1675	1595	8.93
P-13-NE	62	Z-22-P	355	320	2510	2260	7.74
		C-25-P	360	325	2040	1815	11.80
		Z-22-R	355	310	2510	2150	7.68
		Z-22-Z	315	295	2205	2010	7.53
		C-25-R	295	265	1620	1425	9.94

TABLE IV-10 (Continued)

ETR Irradiation Facility	ETR Cycle Number	Specimen Number	Estimated Temperatures, C				Estimated Accumulated Burnup, Fissions/cc x 10 ²¹
			Cladding		Fuel		
			Surface		Centerline		
			Maximum	Avg	Maximum	Avg	
P-13-NE	63	Z-22-P	373	325	2650	2290	8.73
		C-25-P	370	325	2120	1815	13.28
		Z-22-R	370	320	2650	2260	8.67
		Z-22-Z	325	300	2290	2065	8.45
		C-25-R	290	270	1595	1480	11.11
P-13-NE	64	Z-22-P	310	280	2150	1925	9.31
		C-25-P	305	280	1675	1540	14.12
		Z-22-R	305	280	2095	1925	9.23
		Z-22-Z	270	260	1845	1760	8.95
		C-25-R	240	230	1260	1205	11.80
P-13-NE	65	Z-22-P	300	280	2040	1925	9.76
		C-25-P	295	275	1620	1510	14.82
		Z-22-R	295	275	2010	1870	9.68
		Z-22-Z	260	255	1760	1705	9.35
		C-25-R	240	230	1260	1230	12.38
P-13-NE	66	Z-22-P	325	295	2290	2010	10.50
		C-25-P	320	290	1790	1565	15.90
		Z-22-R	300	280	2040	1925	10.38
		Z-22-Z	275	250	1870	1650	9.96
		C-25-R	260	230	1400	1230	13.18
P-12-SE	67	Z-22-P	315	295	2205	2010	11.32
		C-25-P	305	290	1675	1595	17.10
		Z-22-R	270	250	1845	1650	11.08
		Z-22-Z	270	255	1845	1705	10.68
		C-25-R	255	225	1370	1175	14.05
P-12-SW	68	Z-22-P	370	345	2650	2425	12.10
		C-25-P	355	340	2010	1900	18.20
		Z-22-R	350	320	2455	2260	11.82
		Z-22-Z	320	305	2260	2095	11.32
		C-25-R	305	270	1675	1480	14.92
P-12-SW	69	Z-22-P	355	330	2510	2345	12.72
		C-25-P	330	320	1870	1790	19.12
		Z-22-R	315	310	2205	2150	12.38
		Z-22-Z	300	280	2040	1925	11.84
		C-25-R	275	265	1510	1425	15.62

TABLE IV-10 (Continued)

ETR Irradiation Facility	ETR Cycle Number	Specimen Number	Estimated Temperatures, C				Estimated Accumulated Burnup, Fissions/cc x 10 ²¹
			Cladding		Fuel		
			Surface		Centerline		
			Maximum	Avg	Maximum	Avg	
P-12-SW	70	Z-22-P	370	355	2650	2510	13.30
		C-25-P	360	340	2040	1900	19.95
		Z-22-R	345	320	2425	2260	12.90
		Z-22-Z	310	280	2150	1925	12.30
		C-25-R	290	260	1565	1400	18.24
P-12-SW	71	Z-22-P	345	310	2425	2150	13.84
		C-25-P	330	305	1870	1675	20.7
		Z-22-R	315	290	2205	1980	13.38
		Z-22-Z	275	265	1870	1790	12.72
		C-25-R	265	260	1425	1400	16.9
P-12-SW	72	Z-22-P	350	325	2455	2290	14.42
		C-25-P	340	320	1900	1790	21.6
		Z-22-R	325	305	2290	2095	13.95
		Z-22-Z	290	280	1980	1925	13.24
		C-25-R	270	250	1510	1315	17.6
P-12-SW	73	Z-22-P	320	305	2260	2095	15.22
		C-25-P	320	310	1790	1730	22.8
		Z-22-R	305	290	2095	1980	14.67
		Z-22-Z	280	270	1925	1845	13.90
		C-25-R	270	260	1510	1400	18.6
P-12-SW	74	Z-22-P	315	290	2205	1980	15.8
		C-25-P	325	295	1815	1620	23.7
		Z-22-R	305	270	2095	1845	15.2
		Z-22-Z	290	260	1980	1760	14.5
		C-25-R	270	245	1480	1290	19.4
P-12-SW	75	Z-22-P	310	295	2150	1675	16.4
		C-25-P	315	295	1760	1620	24.6
		Z-22-R	290	265	1980	1790	15.7
		Z-22-Z	270	250	1845	1650	14.9
		C-25-R	260	245	1400	1290	20.0
P-12-NW	76	Z-22-P	255	230	1705	1540	17.4
		C-25-P	260	240	1400	1260	25.0
		Z-22-R	245	190	1620	1175	15.9
		Z-22-Z	225	210	1480	1345	15.1
		C-25-R	245	190	1290	925	20.3
Capsule Discharged							

The thermocouple performance during irradiation was good. The number of thermocouple outages which occurred out of the total of 12 per capsule is as follows:

Capsule Number	Thermocouple Outages
BMI 43-1	2
BMI 43-2	0
BMI 43-3	0
BMI 43-4	5
BMI 43-5	2
BMI 43-6	5

It should be noted that several other thermocouple outages occurred during the irradiations, but the thermocouples were repaired. Even though these outages occurred, there was always at least one thermocouple for monitoring the temperature of each fuel specimen in the capsules.

A summary of the highlights of each of the irradiations follows.

1. BMI 43-1

Capsule BMI 43-1 was inserted in ETR Position P-13-SE for Cycle 51 (beginning November 26, 1962). Since the temperatures were slightly lower than desired for this cycle, the capsule was moved to P-13-NE for Cycle 52 (beginning January 7, 1963). Design temperatures were maintained in this position through Cycle 54. During Cycle 55, a significant decrease in temperature was noted. Since such a sudden drop is not normally expected, it was decided to leave the capsule in the same position until all of the data from Cycle 56 could be fully evaluated. This was completed during the early part of Cycle 57, at which time it was decided to move the capsule to P-12-SE for Cycle 58 (beginning September 16, 1963). Temperatures were increased slightly in the new position but were still lower than desired. As there was no other facility available which had a high flux in the same area of the reactor, it was necessary to leave the capsule in P-12-SE until Cycle 62, when it was moved to P-12-NE. Temperatures in the new position for Cycle 62 were not changed significantly over those in the

P-12-SE facility during the previous cycle. However, it was decided to discharge the capsule at the end of Cycle 62 (April 13, 1964) even though reference temperature conditions were not achieved during the last cycle of irradiation since other moves were not available in the foreseeable future.

2. BMI 43-2

Capsule BMI 43-2 was inserted in ETR Position Q-6-SW for Cycle 54 (beginning April 1, 1963). As anticipated, the temperatures were low, and it was moved to P-6-SE for Cycle 55 (beginning May 13, 1963) where design temperatures were maintained through Cycle 58. By Cycle 59, temperatures had decreased below desired levels, but the capsule was left in the same position for Cycle 60 to determine whether the lower temperatures would continue or if the conditions for Cycle 59 were unique as a result of perturbations in surrounding experiments. As it turned out, the temperatures for Cycle 60 were again at satisfactory levels. During Cycles 61 and 62, design temperature levels were achieved only during the initial part of each reactor cycle; however, a relocation to a higher flux facility could not be made until Cycle 64. At this time the capsule was moved to P-5-SW. Temperatures during Cycles 64 and 65 in this position were essentially unchanged, and the capsule was moved to P-6-NW where a flux increase of up to 25 percent was anticipated for Cycle 66. However, capsule temperatures during Cycles 66 and 67 were even lower than in P-5-SW, indicating abnormal reactor flux conditions. Consequently, it was decided to relocate the capsule in 0-5, for which a flux increase of 30 percent was indicated. However, temperatures for Cycle 68 in 0-5 remained unchanged from the previous cycle, and a move to 0-6 for Cycle 69 was made in an effort to achieve design temperatures prior to discharge, which had originally been scheduled for the end of Cycle 69 (February 15, 1965). Capsule temperatures in the new facility for Cycle 69 were essentially unchanged, but the irradiation was extended by one cycle in view of the increase in flux which was anticipated for the zone of the reactor occupied by this experiment. A slight increase in capsule performance for Cycle 70 was noted; however, temperatures were still well below design levels. The irradiation was terminated at the end of Cycle 70 (ending March 29, 1965).

3. BMI 43-3

Capsule BMI 43-3 was inserted in ETR Position G-16-SW for Cycle 54 (beginning April 1, 1963). On reactor startup, the specimens (cladding surface) attained temperatures in excess of 370°C (700°F) while the reactor was still operating at a partial power level. The reactor was subsequently scrammed and the capsule relocated in Position F-17-C for the remainder of the cycle; temperatures in this location were far below design levels. For Cycle 55, the capsule was relocated into Position F-17-NE without any significant change in capsule temperatures. During Cycle 55, a scram occurred which provided an opportunity to relocate the capsule into G-16-SW, the position tried for the initial insertion, since no other positions were available. Again temperatures reached the maximum allowable limit while the reactor was at partial power, and the reactor was scrammed and the capsule returned to F-17-NE for the remainder of Cycle 55 and for all of Cycle 56. For Cycle 57 (beginning August 5, 1963), Position G-17-NE became available and the capsule was relocated into this facility. Cladding temperatures for Cycle 57 were increased about 21°C, but were still below the desired irradiation temperature; a relocation to F-16-SE for Cycle 58 (beginning September 16, 1963) did not improve temperatures appreciably. At the end of Cycle 58, a high absorber experiment was removed from a facility on the core side of Position F-16-SE. Therefore, the capsule was left in this facility for Cycle 59 with good results since temperatures were near design levels. The capsule remained in F-16-SE until Cycle 64 (beginning May 25, 1964) when it was relocated in Position G-16-SW. Temperatures through Cycle 65 in G-16-SW were satisfactory. However, temperatures during Cycle 66 (beginning August 17, 1964) were below par and the capsule was relocated into G-16-C for Cycle 67 (beginning September 28, 1964), where design temperature levels were achieved until Cycle 70 (beginning February 15, 1965). During Cycle 70, temperatures were below par and the capsule was relocated into G-16-NE for Cycle 71 (beginning March 29, 1965); however, design temperatures were achieved for this cycle only. Since no other facilities with the required flux were available, the capsule had to remain in G-16-NE until Cycle 74 (beginning August 2, 1965), when it was relocated into the beryllium reflector Position F-15-C. Design temperatures were achieved in this facility for Cycle 74 but it became necessary to move back into the lower flux facility G-16-NE for Cycles 75 and 76 because ETRC flux information indicated

a flux increase was expected which would produce excessive capsule temperatures in the F-15 facility. Temperatures were well below desired levels for both cycles. The capsule was moved back into F-15-C for Cycle 77 where high temperatures were again attained. The capsule was discharged at the end of Cycle 77 (January 17, 1966).

4. BMI 43-4

Capsule BMI 43-4 was inserted in MTR Position A-29-NW for Cycle 183 (beginning November 19, 1962). It operated at satisfactory temperatures in this location, but during Cycle 184 the temperatures fell off slightly and the capsule was moved to A-29-SE for the next cycle. On January 11, 1963, during initial operation at full reactor power for Cycle 185, a temperature excursion occurred which lasted approximately three hours. During this period the cladding temperature for the Z-22-0 specimen reached 382°C (714°F) which was about 11°C higher than the cladding temperature level which had been established by design criteria as limiting so as to minimize the possibility of centerline melting. The other four specimens in the capsule did not exceed the preset cladding temperature limit. Capsule performance was satisfactory for the remainder of Cycle 185 as well as over the next 10 cycles (through Cycle 198). During Cycles 199 through 201, temperatures were lower than desired but no other facilities possessing a higher flux were available. At the end of Cycle 201 (ending December 23, 1963), A-28-NE became available and the capsule was re-located in this facility. Temperature levels were only slightly improved in the new facility during Cycle 202, and since no other facilities were available at this time it was necessary to accept the lower temperatures until Cycle 206. At this time A-2-NE became available, and the capsule was moved to this facility for the remainder of the irradiation. Temperatures were maintained at design levels for Cycle 206 but decreased slightly for Cycle 207. The capsule was discharged at the end of Cycle 207 (April 27, 1965).

5. BMI 43-5

Capsule BMI 43-5 was inserted into Position I-2-C for ETR Cycle 54 (beginning April 1, 1963) where it operated at design temperatures for this cycle only. The temperature dropped during Cycles 55 and 56 and a relocation to I-2-SW was made

for Cycle 57 (beginning August 5, 1963) where the capsule operated at satisfactory temperatures through Cycle 60. Temperatures were below par during Cycle 61 and a relocation was made to Position I-3-NW for Cycle 62 (beginning March 2, 1964), where satisfactory temperatures were achieved for this cycle only. Results of critical mockup studies of the anticipated core loading for Cycle 63 indicated a probable 20 percent increase in the reactor flux in the I-3 position and surrounding facilities. Since the capsule temperatures in the I-3-NW facility during Cycle 62 were fairly high, the move to lower flux Position I-2-SW was considered necessary. The flux in the I-3 position did not increase as anticipated and it was possible to relocate the capsule to I-3-NW for Cycle 64. The temperatures decreased during Cycles 65 and 66 and the capsule was relocated to I-3-C for Cycle 67 (beginning September 28, 1964); however, temperatures were only slightly increased over those obtained in I-3-NW during Cycle 66. The capsule was, therefore, relocated into Position I-3-SW for Cycle 68 (beginning November 16, 1964) where design temperatures were maintained through Cycle 74 (ending September 13, 1965). It was necessary to accept lower than desired temperatures in I-3-SW for Cycles 75 through 81 (September 13, 1965 to July 4, 1966) because facilities having the required thermal neutron flux (up to 2.2×10^{14} nv) were not available. Coupled with this was the uncertainty in reactor flux levels as a result of the many special reactor core loadings which were made to meet the requirements of certain other experiments. By Cycle 82, calculations showed that the samples in the capsule had accrued enough burnup to allow a relocation into Position E-4, provided a special hafnium shroud were installed around the "B" basket to depress the flux approximately 15 percent. With the shroud in place for Cycle 82, temperatures were far below desired levels and the shroud was subsequently removed during a midcycle shutdown; temperatures increased by about 15 percent, as expected. A request to relocate the capsule to F-4 was approved for Cycle 83; however, temperatures were only slightly improved over the previous cycle and the capsule was discharged at the end of the cycle (September 26, 1966).

6. BMI 43-6

Capsule BMI 43-6 was inserted into ETR Position Q-13-NW for Cycle 51 (beginning November 26, 1962), where it operated at lower than desired temperatures.

It was moved to Q-12-SW for Cycle 52 (beginning January 7, 1963) and satisfactory temperature levels were maintained through Cycle 54. Temperatures fell below desired limits during Cycle 55 (beginning May 13, 1963) but no other positions were available until Cycle 58 (beginning September 16, 1963), when it was moved into P-12-NE. The capsule experienced an overtemperature at partial reactor power during startup for Cycle 58, and the reactor was scrammed to permit relocation of the capsule into Position Q-12-NW, where it remained for the rest of Cycle 58 and all of Cycle 59. It was relocated into Position P-13-SW for Cycle 60 (beginning December 9, 1963), but once again it experienced an overtemperature condition; the reactor was scrammed and the capsule moved into Position P-13-NE, where temperatures were maintained at satisfactory levels through Cycle 63 (ending May 25, 1964). Temperatures decreased during Cycles 64 through 66, and the capsule was moved into Position P-12-SE for Cycle 67 (beginning September 28, 1964). However, temperatures were not significantly changed over the previous cycle and the capsule was relocated into Position P-12-SW for Cycle 68, where desired temperatures were maintained through Cycle 75 (ending September 13, 1965). The capsule was relocated into Position P-12-NW for Cycle 76 in a final attempt to achieve design temperatures; however, temperatures were lower by 25 percent than in P-12-SW. The capsule was discharged at the end of Cycle 76 (December 6, 1965).

After the capsules were removed from the reactor they were returned to the Battelle Columbus hot cells for postirradiation examination. Neutron radiography, a relatively new nondestructive testing technique available at the Battelle Research Reactor, was used to examine capsules BMI 43-3 and 43-5. This technique was not available prior to the discharge of BMI 43-3 from the reactor, and the other four capsules in the program could not be examined in the same manner. Neutron radiography essentially provides a one-to-one reproduction over the entire capsule, and measurements of capsule components can be obtained directly. Prints of the neutron radiographs of the two capsules taken after irradiation are shown in Figures IV-7 and IV-8. From the neutron radiographs it was found that the specimen train had moved upward about $3/8$ inch in the case of BMI 43-3 and approximately $3/4$ inch in BMI 43-5. This was substantiated during the examination of the capsules in the hot cell. It was also

FIG. IV-7 NEUTRON RADIOGRAPH OF BMI 43-3 AFTER IRRADIATION

FIG. IV-8 NEUTRON RADIOGRAPH OF BMI 43-5 AFTER IRRADIATION

found that the axial position of the thermocouple did not change appreciably with respect to the inner finned shell; however, the thermocouple position with respect to the midplane of the fuel changed by about the amount indicated above. A possible explanation for the upward movement of the specimen train lies in the fact that the density of sodium decreases appreciably in the phase change from solid to liquid. Accordingly, uneven melting of the sodium as a result of the large fuel-to-void length in the specimens could lead to a net upward force on the specimen assembly train. Any movement, however small, would probably occur during periods of reactor startup when the sodium in the capsule undergoes a phase change. A small upward displacement of the specimen train would allow more sodium to be present below the specimen train. Expansion of this sodium could produce additional upward displacements during the next reactor startup.

The movement of the specimen train in BMI 43-5 would explain the relatively low estimated burnup as calculated from the capsule temperature data. It would be expected that the thermocouples would indicate a lower than actual temperature, and the corresponding burnups calculated from these temperatures would be low. Therefore, thermal conditions of samples in capsule 43-5 were significantly greater than those indicated by thermocouple readings. A comparison of the fuel burnups in each capsule as determined from capsule heat transfer and temperature data with that obtained from isotopic analysis is given in Table IV-11. As expected, the burnup estimate for BMI 43-5 was low compared to the isotopic analysis. However, in the case of BMI 43-3, the estimated burnup as determined by temperature data was higher than that obtained by isotopic analysis. Here the discrepancy could be attributed to a higher than normal temperature drop across the finned region of the capsule. Although the assembly procedure and "fit up" was designed to be the same for the six capsules in the program, it is possible that a slight difference existed which led to different heat transfer situations at the fin-outer shell interface.

The agreement between the calculated burnup and isotopic burnup for the specimens in all capsules other than 43-5 were very good with the greatest deviation being about 10 percent.

TABLE IV-11
COMPARISON OF BURNUP ANALYSIS FOR BMI 43 SERIES

Capsule Number	Specimen Designation	Estimated Burnup As Determined From Thermocouple Data		Burnup as Determined From Isotopic Analysis	
		a/o By Fission	Fission/cc $\times 10^{21}$	a/o By Fission	Fission/cc $\times 10^{21}$
BMI 43-1	Z-10-A	40	4.4	40	4.4
BMI 43-1	C-10-A	42	6.0	46	6.6
BMI 43-2	Z-10-F	59	6.5	57	6.3
BMI 43-2	C-10-C	59	8.4	58	8.3
BMI 43-3	Z-10-J	(a)	(a)	70	7.8
BMI 43-3	C-10-E	81	11.6	74	10.6
BMI 43-4	Z-22-M	40	10.1	40	10.1
BMI 43-4	C-25-M	38	14.3	43	16.2
BMI 43-5	Z-22-X	61	15.4	74	18.7
BMI 43-5	C-25-N	67	25.4	76	28.8
BMI 43-6	Z-22-P	69	17.5	60	15.2
BMI 43-6	C-25-P	67	25.4	61	23.1

(a) Burnup as determined from temperature data for this specimen considered to be invalid. During irradiation, specimen temperatures were consistently higher than other specimens. By Cycle 74 the calculated burnup had reached 100 percent of the total U^{235} , however, no change in temperature for this specimen noted.

V. [✓] POST-IRRADIATION EXAMINATION

A. GENERAL

After irradiation, all capsules were returned to the Battelle-Columbus hot cells for both nondestructive and destructive evaluation. Post-irradiation examination consisted of visual inspection; gamma scanning; burnup analyses; dimensional and density measurements; fission gas sampling and analyses; metallographic examination; x-ray diffraction analyses; and alpha and beta autoradiography. The results are summarized in the following sections.

B. VISUAL EXAMINATION OF CAPSULES AND SPECIMENS

Examination during disassembly indicated that all capsules were in good condition. It was noted that the specimen train in Capsule BMI 43-5 had shifted upward by about 3/4 inch, confirming the results of neutron radiography.

Visual inspection of the exterior surface of the specimens at magnifications up to 30X indicated that there was no evidence of either corrosive attack on the cladding or severe distortion. The typical appearance of several specimens is shown in Figures V-1 to V-6.

C. BURNUP

Fuel burnups were determined by uranium isotopic analyses of at least one specimen of each fuel composition contained in each capsule. The burnup of the remaining specimens was determined by comparisons of gamma scan data with those of the analyzed specimen of the same composition.

All samples used for burnup analyses, with the exception of a single sample from the end of Specimen Z-10-J used to determine if an end effect existed, were removed from the axial center of the specimen fuel stack. Each sample was then dissolved and analyzed by mass spectrometry to determine uranium isotopic distribution. The resultant data were then used to calculate the burnup in atom percent by fission of the U-235 using the following

equation:

$$F_5 = \frac{1}{R_{5/8}^{\circ}} (R_{5/8}^{\circ} - R_{5/8}) - (R_{6/8} - R_{6/8}^{\circ})$$

where

F_5 = a/o of $^{235}_{92}\text{U}$ burnup due to fission.

$R_{5/8}^{\circ}$ = isotopic ratio of $^{235}_{92}\text{U} / ^{238}_{92}\text{U}$ in unirradiated fuel

$R_{5/8}$ = isotopic ratio of $^{235}_{92}\text{U} / ^{238}_{92}\text{U}$ in unirradiated fuel

$R_{6/8}$ = isotopic ratio of $^{236}_{92}\text{U} / ^{238}_{92}\text{U}$ in irradiated fuel

This equation gives a reasonable approximation of the burnup in fuels of high enrichment in which greater than 10 percent of the fissionable uranium has been consumed. The loss of $^{238}_{92}\text{U}$ and $^{236}_{92}\text{U}$ is assumed to be negligible.

An estimate of the burnup of each of the remaining specimens in each capsule was obtained by comparing the relative area under the gamma scan curve for each fuel specimen. The gamma scan curve for each fuel specimen was obtained by plotting the activity of the 0.77 Mev characteristic photo-peak of the fission products Zr-95 and Nb-95 as a function of distance along the length of the fuel specimen. The area under the curve should be proportional to the amount of these fission products contained in the fuel and it is proportional to the relative burnup of the fuel. Burnup data are tabulated in Table V-1 along with burnups estimated from thermal gradient data obtained during irradiation. The burnups as determined from the gamma scan data are believed to be more reliable than the ones obtained from thermal gradient data. As can be seen, the burnups of the axial center sample and the top sample from Specimen Z-10-J were essentially identical, suggesting

TABLE V-1

BURNUP DATA FOR SPECIMENS FROM CAPSULES
BMI 43-1, -2, -3, -4, -5, and -6

Specimen	Burnups Estimated from Thermal Gradient Data		Burnups Determined from Mass Spectrometric Data		Burnups Estimated from Gamma-Scan Data	
	a/o U-235	Fissions/cm ³ x 10 ²⁰	a/o U-235	Fissions/cm ³ x 10 ²⁰	a/o U-235	Fissions/cm ³ x 10 ²⁰
<u>Capsule BMI 43-1</u>						
Z-10-A	40	4.4	40	4.4	40	4.4
Z-10-B	45	4.9			40	4.4
Z-10-C	45	4.9			42	4.6
C-10-A	42	6.4	43	6.5	43	6.5
C-10-B	38	5.8			44	6.7
<u>Capsule BMI 43-2</u>						
Z-10-D	56	6.3			52	5.7
Z-10-E	58	6.5			56	6.2
Z-10-F	60	6.7	57	6.3	57	6.3
C-10-C	58	8.1	58	8.1	58	8.1
C-10-D	50	7.0			61	8.6
<u>Capsule BMI 43-3</u>						
Z-10-G	83	9.3			70	7.8
Z-10-H	83	9.3			69	7.7
Z-10-J (center) (a)	(a)	(a)	71	7.9	71	7.9
Z-10-J (end) (a)	(a)	(a)	71	7.9	71	7.9
C-10-E	81	11.6	74	10.6	74	10.6
C-10-F	79	11.3			77	11.0
<u>Capsule BMI 43-4</u>						
Z-22-M	40	10.5	40	10.5	40	10.5
Z-22-N	40	10.4			37	9.2
Z-22-O	41	10.7			40	10.5
C-25-M	38	14.5	44	17.0	44	17.0
C-25-O	39	15.0			41	15.7
<u>Capsule BMI 43-5</u>						
Z-22-T	64	16.0			73	18.4
Z-22-X	61	15.3	74	18.5	74	18.5
Z-22-Y	62	15.5			62	15.6
C-25-N	67	25.2	76	28.4	76	28.4
C-25-S	56	21.0			69	25.8
<u>Capsule BMI 43-6</u>						
Z-22-P	69	17.5	60	15.2	60	15.2
C-25-P	67	25.2	61	23.0	61	23.0
-22-R	63	16.0			58	14.7
-22-Z	60	15.2			58	14.6
C-25-R	54	20.4			57	21.5

(a) Burnups could not be estimated because the thermocouples failed 4 cycles before the end of the irradiation.

1X

HC14564

(a)

1X

HC14558

(b)

FIG. V-1 SPECIMENS FROM CAPSULE BMI 43-1

(a) Specimen Z-10-B, (b) Specimen C-10-A

1X

HC16632

(a)

1X

HC16625

(b)

FIG. V-2 SPECIMENS FROM CAPSULE BMI 43-2

(a) Specimen Z-10-F, (b) Specimen C-10-C

1X

HC18288

(a)

1X

HC18285

(b)

FIG. V-3 SPECIMENS FROM CAPSULE BMI 43-3

(a) Specimen Z-10-J (b) Specimen C-10-F

1X

HC14576

(a)

1X

HC14570

(b)

FIG. V-4 SPECIMENS FROM CAPSULE BMI 43-4

(a) Specimen Z-22-0 (b) Specimen C-25-0

4X

P531-534

(a)

4X

P535-538

(b)

FIG. V-5 SPECIMENS FROM CAPSULE BMI 43-5 (a) Specimen Z-22-Y (b) Specimen C-25-N.

1X

HC18281

(a)

1X

HC18283

(b)

FIG. V-6 SPECIMENS FROM CAPSULE BMI 43-6

(a) Z-22-P (b) C-25-P

that no end peaking effect existed. These measurements were made in an effort to determine the cause of large fuel volume changes which were sometimes observed (to be described later) at the upper end of some fuel columns. It was originally thought that these volume changes were a result of end peaking. However, the burnup comparison did not appear to support this assumption.

D. FISSION GAS RELEASE

Gasses from both capsules and specimens were sampled by placing the individual capsules and specimens in an evacuated chamber, drilling a hole through the side and pumping the released gasses into a collection system of known volume. The pumping efficiency from the sampling chamber to the collection system was determined by releasing a known volume of neon gas into the sampling chamber at the same time the capsule or specimen was drilled. It was assumed that the fraction of gasses pumped over was the same for both the neon and the gaseous fission products. Samples of gasses were removed from the collection system and analyzed by both mass and gamma spectrometric techniques. In most cases, the agreement between the two techniques was very good. However, the mass spectrometric data are believed to be more reliable and gas release data reported in Table V-2 are based on the mass spectrometric analysis of Kr-85. Results of gamma ray spectroscopy of gasses in the capsules indicated that less than 10^{-5} percent of the gasses contained in the specimens had diffused through the cladding. This observation confirms the integrity of the specimen cladding.

The fraction of the fission gas released from the fuels varied from 22 percent to 96 percent of the theoretical amount formed. In general, the fractional release increased with increasing burnup for each fuel composition.

E. DIMENSIONAL MEASUREMENTS AND SECTIONING PLAN

1. Dimensional Measurements

Dimensional stability of the fuel was assessed by measurement of fuel length changes. Changes in sample diameter were not expected as a result of the ratio of cladding thickness to diameter used to ensure high burnups without cladding failures. Also, end strengthening influences due to the end

TABLE V-2

FISSION GAS RELEASE DATA

Specimen	Fission Gas Release, (%)	Burnup ³ (Fissions/cm ³ x 10 ²⁰)	Average Centerline Irradiation Temperature (°C)	Average Centerline Irradiation Temperature during last 20 percent of irradiation period	Total Time in Reactor (Days)
Z-10-B	43	4.4	1875	1780	503
Z-10-C	32	4.6	1870	1710	503
Z-10-E	37	6.2	1730	1335	728
Z-10-F	46	6.3	1805	1545	728
G-10-G	58	7.8	1935	1815	1022
Z-10-J	56	7.9	2025	1815	1022
C-10-A	22	6.5	1415	1245	503
C-10-B	28	6.7	1295	1195	503
C-10-C	48	8.1	1400	1205	728
C-10-D	62	8.6	1200	1050	728
C-10-E	58	10.6	1400	1245	1022
C-10-F	59	11.0	1295	1165	1022
Z-22-M	46	10.5	1975	1775	524
Z-22-O	58	10.5	2000	1710	524
Z-22-P	62	15.2	2095	1635	1105
Z-22-R	66	14.7	1905	1580	1105
Z-22-X	69	18.5	1630	1200	1274
Z-22-Y	84	15.6	1660	1145	1274
C-25-M	74	17.0	1480	1425	524
C-25-O	79	15.7	1525	1295	524
C-25-P	88	23.0	1660	1500	1105
C-25-R	87	21.5	1315	1175	1105
C-25-N	84	28.4	1405	995	1274
C-25-S	96	25.8	1195	690	1274

caps were expected to be high due to the low length to diameter ratio used for each sample to maximize the number of samples per capsule. Because of the fragile nature of the irradiated fuel, it was not possible to remove whole fuel pellets for these measurements and somewhat indirect means had to be used to obtain the desired dimensions. Optical techniques and precise gamma scans were used to measure axial swelling. Diameters were also measured at several points along the specimen lengths.

Lengths of several longitudinally sectioned fuel pellets were measured by optical means using a filar eyepiece and a calibrated optical system. During the examination of specimens from Capsule BMI 43-2, a precise gamma scanner became available and was used for nondestructive measurement of fuel lengths. The specimen was moved axially past a collimating slit at a controlled speed and the radiation passing through the slit was measured with a solid state detector. The signal was recorded on a strip chart. Fuel lengths were then obtained by measuring the length of the gamma scans and applying the proper multiplication factor. In some cases, it was possible to distinguish individual fuel pellets, and in all cases it was possible to measure total fuel lengths. This gamma scan technique was judged to be more satisfactory for obtaining fuel lengths than the optical technique, since slight specimen misalignment or calibration errors can introduce significant errors in optical measurements. Moreover, the optical measurements were restricted to single pellets and in general it was difficult to distinguish the interface between pellets.

The results of the dimensional measurements are shown in Table V-3. As expected, the diametrical changes are almost insignificant. Two types of axial dimensional changes were observed. One was a small change of the fuel column or pellet length in the cooler operating outer fuel regions (ΔL_1 in Table V-3) and the other a much larger length change which occurred along the fuel centerline and which was manifested by localized swelling at the top center of the fuel column (ΔL_2 in Table V-3).

TABLE V-3
RESULTS OF FUEL SPECIMEN DIMENSIONAL MEASUREMENTS

Specimen Number	Capsule Number	Burnup, (fissions/cm ³ x 10 ²⁰)	Clad Diameter			Fuel Column Length			ΔL_1 (%)	Postirrad. L ₂ **	ΔL_2 (%)
			Preirrad. (in.)	Postirrad. (in.)	Change (%)	Preirrad., (in.)	Postirrad. L ₁ *				
Z-10-A	43-1	4.4	0.411	0.412	0.2	0.500	0.505 ^(a)	1.0 ^(a)	-	-	-
Z-10-B	43-1	4.4	0.411	0.412	0.2	-	-	-	-	-	-
Z-10-C	43-1	4.6	0.411	0.412	0.2	-	-	-	-	-	-
Z-10-D	43-2	5.7	0.411	0.412	0.2	1.50	1.51	0.7	-	-	-
Z-10-E	43-2	6.2	0.411	0.412	0.2	1.50	1.52	1.4	1.58	5.3 ^(b)	-
Z-10-F	43-2	6.3	0.411	0.412	0.2	1.50	1.52	1.4	1.73	15.3 ^(b)	-
Z-10-G	43-3	7.8	0.411	0.412	0.2	1.50	1.55	3.3	2.08	38.7	-
Z-10-H	43-3	7.7	0.411	0.412	0.2	1.50	1.54	2.7	2.08	38.7	-
Z-10-J	43-3	7.9	0.411	0.412	0.2	1.50	1.50	0	2.19	46.0	-
C-10-A	43-1	6.5	0.361	0.360	-0.3	-	-	-	-	-	-
C-10-B	43-1	6.7	0.361	0.360	-0.3	-	-	-	-	-	-
C-10-C	43-2	8.1	0.361	0.362	0.3	1.50	1.51	0.7	1.53	2.0 ^(b)	-
C-10-D	43-2	8.6	0.361	0.361	0	1.50	1.52	1.4	1.55	3.3 ^(b)	-
C-10-E	43-3	10.6	0.361	0.362	0.3	1.50	1.52	1.3	1.93	28.7	-
C-10-F	43-3	11.0	0.361	0.362	0.3	1.50	1.60	6.7	1.92	28.0	-
J-A	Z-22-M	43-4	0.310	0.311	0.3	-	-	-	-	-	-
	Z-22-N	43-4	0.310	0.310	0	-	-	-	-	-	-
	Z-22-O	43-4	0.310	0.311	0.3	-	-	-	-	-	-
	Z-22-P	43-6	0.310	0.311	0.3	1.50	1.57	4.7	1.82	22.0	-
	Z-22-R	43-6	0.310	0.312	0.6	1.50	1.51	0.7	1.62	8.0	-
	Z-22-Z	43-6	0.310	0.311	0.3	1.50	1.53	2.0	1.63	8.6	-
	Z-22-T	43-5	0.310	0.309	-0.3	1.50	1.54	2.7	1.74	16.0	-
	Z-22-X	43-5	0.310	0.311	0.3	1.50	1.51	0.7	1.68	12.0	-
	Z-22-Y	43-5	0.310	0.310	0.3	1.50	1.50	0	1.67	11.3	-
C-25-M	43-4	17.0	0.250	0.251	0.4	-	-	-	-	-	-
C-25-O	43-4	15.7	0.250	0.250	0	0.202	0.206 ^(a)	2.0 ^(a)	-	-	-
C-25-P	43-6	23.0	0.250	0.250	0	-	-	-	-	-	-
C-25-R	43-6	21.5	0.250	0.250	0	1.50	1.54	2.7	1.62	8.0	-
C-25-N	43-5	28.4	0.250	0.251	0.4	1.50	1.55	3.3	1.66	10.7	-
C-25-S	43-5	25.8	0.250	0.251	0.4	1.50	1.51	0.7	1.57	4.7	-

(a) Measured optically on single pellet.

* Outer, cooler region

(b) Measured from photomacrograph, all other lengths measured from gamma scans.

** Center of fuel column

2. Sectioning Plan

Specimens were sectioned for further analysis as shown in Figures V-7 to V-12. Specimens Z-10-D, Z-10-H, Z-22-N, Z-22-T, and Z-22-Z from Capsules BMI 43-2 through 6, respectively, were left intact for future corrosion tests. Some cross sectional views of typical sectioned surfaces are shown in Figure V-13. Views from above the top of the fuel pellet column are shown in Figure V-14.

F. FUEL DENSITY MEASUREMENTS

Fuel densities were determined by using two different measuring techniques, i.e., CCl_4 immersion and mercury immersion. Both techniques were hampered by the friable nature of the irradiated fuel which made it difficult to obtain specimens of adequate size for meaningful density measurements. Moreover, the fuel deteriorated further during the mercury immersion measurements.

By very careful sampling and handling, it was possible to select fragments of fuel from various radial positions of the Z-10-F and C-10-C fuels and to obtain CCl_4 immersion densities of the fragments. The density data presented in Table V-4 do not provide any clear-cut information on fuel swelling behavior. They do, however, provide the first clue that fuel segregation occurred along the thermal gradient in the fuel materials. The densities of the intermediate region (radially) in Z-10-F and of the outer regions in these two specimens; in fact, these densities are significantly larger than the unirradiated theoretical densities of the fuel materials. Since fuel densities in both stabilized zirconia base and ceria base fuels increase with increasing urania content, the observed density differences may be associated with solute (urania) migration down the thermal gradient.

G. METALLOGRAPHY

Sections of fuel assemblies were prepared for metallographic examinations by grinding through 600 grit SiC and then polishing through Linde A powder on microcloth using a vibrating polisher. Etching characteristics of the fuels varied with base material and UO_2 concentration. The following etchants were found to be most satisfactory for bringing out structural details:

TABLE V-4

VARIATION OF DENSITY WITH RADIUS IN THE Z-10 AND
C-10 FUELS AFTER IRRADIATION

Specimen	Approximate Position (Radially)	Apparent Density (g/cm ³)
Z-10-F	Center	5.14 ± 0.08
Z-10-F	Intermediate	6.01 ± 0.11
Z-10-F	Outer	5.27 ± 0.11
C-10-C	Center	7.03 ± 0.08
C-10-C	Outer	7.60 ± 0.06

Note: Theoretical density of Z-10 fuel is 5.74 g/cm³, preirradiation density was 5.18 g/cm³.

Theoretical density of C-10 fuel is 7.46 g/cm³, preirradiation density was 7.05 g/cm³.

SPECIMEN Z-10-A

SPECIMEN Z-10-B

SPECIMEN Z-10-C

SPECIMEN C-10-A

SPECIMEN C-10-B

FIG. V-7 SECTIONING OF SPECIMENS FROM CAPSULE BMI 43-I

SPECIMEN Z-10-E

SPECIMEN Z-10-F

SPECIMEN C-10-C

SPECIMEN C-10-D

FIG. V-8 SECTIONING OF SPECIMENS FROM CAPSULE BMI 43-2

SPECIMEN Z-10-G

SPECIMEN Z-10-J

SPECIMEN C-10-E

SPECIMEN C-10-F

FIG. V-9 SECTIONING OF SPECIMENS FROM CAPSULE BMI 43-3

SPECIMEN Z-22-M

SPECIMEN Z-22-0

SPECIMEN C-25-M

SPECIMEN C-25-0

FIG. V-10 SECTIONING OF SPECIMENS FROM CAPSULE BMI 43-4

SPECIMEN Z-22-X

SPECIMEN Z-22-Y

SPECIMEN C-25-N

SPECIMEN C-25-S

FIG. V-11 SECTIONING OF SPECIMENS FROM CAPSULE BMI-43-5

SPECIMEN Z-22-P

SPECIMEN Z-22-R

SPECIMEN C-25-P

SPECIMEN C-25-R

FIG. V-12 SECTIONING OF SPECIMENS FROM CAPSULE BMI 43-6

6X

HC18398

(a) Specimen Z-10-G

6X

HC18542

(b) Specimen Z-10-J

6X

HC18405

(c) Specimen C-10-E

6X

HC18394

(b) Specimen C-10-F

FIG. V-13 REPRESENTATIVE VIEWS OF FUEL CROSS SECTIONS

Z-10 Fuel

40 v/o concentrated lactic acid

40 v/o concentrated nitric acid

Swab

20 v/o concentrated hydrofluoric acid

or

30 units H_2O

40 units concentrated HNO_3

Dip

40 units concentrated HF

C-10 Fuel

20 v/o NH_4F

30 v/o H_2O_2

Dip

50 v/o concentrated H_2SO_4

Z-22 Fuel

Boiling saturated solution of NH_4F

Dip

C-25 Fuel

80 v/o H_2O_2

Dip

20 v/o concentrated H_2SO_4

Macroscopic views of several metallographically prepared specimen surfaces are shown in Figures V-15 to V-38. In the transverse sections, a gradation in coloration from the center to the surface of the fuel is of interest. Combined with data obtained in other tests, the lighter color of fuel in the center regions is believed to be caused by depletion of UO_2 in these regions by migration of UO_2 down the thermal gradient toward the fuel surface. Both ZrO_2 and CeO_2 are lighter in color than the solid solution fuels.

Longitudinal sections of the top pellets from several specimens show localized regions of swelling at the top-center portions of the top fuel pellets. Restriant of radial swelling by the cladding is believed to have forced swelling of the plastic fuel center in the axial direction. Some evidence of reaction between fuel and the ZrO_2 and CeO_2 end spacer can be

6X

HC18410

(a) Top ZrO_2 Spacer
Specimen Z-10-G

6X

HC18401

(b) Bottom ZrO_2 Spacer
Specimen Z-10-G

6X

HC18375

(a) Top ZrO_2 Spacer
Specimen Z-22-P

6X

HC18407

(b) Top ZrO_2 Spacer
Specimen C-10-E

FIG. V-14 REPRESENTATIVE VIEWS OF ZrO_2 INSULATING SPACERS

FIG. V-15 TRANSVERSE METALLOGRAPHY, SPECIMEN Z-10-B

FIG. V-16 TRANSVERSE METALLOGRAPHY, SPECIMEN Z-10-F

6X

HC17384

FIG. V-17 LONGITUDINAL METALLOGRAPHY, TOP PELLET,
SPECIMEN Z-10-F

6X

HC17669

FIG. V-18 LONGITUDINAL METALLOGRAPHY, BOTTOM PELLET,
SPECIMEN Z-10-F

FIG. V-19 TRANSVERSE METALLOGRAPHY, SPECIMEN Z-10-J

FIG. V-20 LONGITUDINAL METALLOGRAPHY, TOP PELLET,
SPECIMEN Z-10-E

FIG. V-21 LONGITUDINAL METALLOGRAPHY, TOP PELLET,
SPECIMEN Z-10-G

FIG. V-22 LONGITUDINAL METALLOGRAPHY, BOTTOM PELLET,
SPECIMEN Z-10-G

6X

HC15559

FIG. V-23 TRANSVERSE METALLOGRAPHY, SPECIMEN C-10-B

6X

HC17383

FIG. V-24 TRANSVERSE METALLOGRAPHY, SPECIMEN C-10-D

3X

TE0597

FIG. V-25 TRANSVERSE METALLOGRAPHY, SPECIMEN C-10-F

6X

HC17382

FIG. V-26 LONGITUDINAL METALLOGRAPHY, SPECIMEN C-10-C

6X

HC17377

FIG. V-27 LONGITUDINAL METALLOGRAPHY, TOP PELLET,
SPECIMEN C-10-D

6X

HC15561

FIG. V-28 TRANSVERSE METALLOGRAPHY, SPECIMEN Z-22-M

3X

TE0595

FIG. V-29 TRANSVERSE METALLOGRAPHY, SPECIMEN Z-22-P

3X

TE0604

FIG. V-30 TRANSVERSE METALLOGRAPHY, SPECIMEN Z-22-X

3X

TE0603

FIG. V-31 LONGITUDINAL METALLOGRAPHY, TOP PELLET 1,
SPECIMEN Z-22-P

3X

TE0593

FIG. V-32 LONGITUDINAL METALLOGRAPHY, TOP PELLET,
SPECIMEN Z-22-R

3X

TE0592

FIG. V-33 LONGITUDINAL METALLOGRAPHY, BOTTOM PELLET,
SPECIMEN Z-22-X

6X

HC15555

FIG. V-34 TRANSVERSE METALLOGRAPHY, SPECIMEN C-25-M

FIG. V-35 TRANSVERSE METALLOGRAPHY, SPECIMEN C-25-P

FIG. V-36 TRANSVERSE METALLOGRAPHY, SPECIMEN C-25-N

3X

TE0591

FIG. V-37 LONGITUDINAL METALLOGRAPHY, TOP PELLET,
SPECIMEN C-25-R

3X

TE0588

FIG. V-38 LONGITUDINAL METALLOGRAPHY, TOP PELLET,
SPECIMEN C-25-S

seen in Figures V-17, V-21, V-31, V-37 and V-38. Since such swelling results in a more difficult path for heat dissipation, it is conceivable that swelling could have been aggravated by temperatures in these regions which were in excess of the calculated fuel centerline temperatures. Little or no evidence of overheating or localized fuel swelling was noted at the bottom fuel ZrO_2 or CeO_2 spacer interfaces, Figures V-18 and V-33. The stainless steel bottom end cap provided restraint to axial swelling and temperatures were lower because fission heat could be more readily dissipated from this region than from the upper fuel regions.

Results of the metallographic examinations are reported below. Low magnification traverses of the specimens are shown together with higher magnification photomicrographs of selected areas.

To aid interpretation of microstructures, radial temperature profiles of Z-10 and C-10 specimens at surface temperature of 357°C (675°F) were determined with a two-dimensional, finite difference digital computer program developed at Battelle for another research program.⁽¹⁹⁾ Plots of radial position versus temperature at the specimen mid-planes are shown in Figures V-39 and V-40.

1. Z-10 Fuel

As seen in the radial traverses of Specimens Z-10-B and Z-10-F, Figures V-41 and V-42 (irradiated to nominal fission burnups of 40, 50 a/o U-235, respectively), the general microstructural features of the low and intermediate burnup Z-10 fuels are similar. Four distinctively different zones are apparent in each specimen.

a. Outer Zone

At all burnups, the outer zone consists of fuel apparently little affected by irradiation. Temperatures in this region range from fuel surface temperature to about 1030°C (1900°F). Grains are equiaxed and the pore structure is similar to that of unirradiated fuel. There are, however, two striking microstructural features in this area. There is a heavy population of a filament-like phase near the fuel surface, Figures V-43 and V-44.

FIG. V-39 DIAMETRAL TEMPERATURE PROFILE OF Z-10 FUEL SPECIMEN AT SURFACE TEMPERATURE OF 675° F. ONE DIAMETER UNIT IS EQUIVALENT TO 0.00625 INCH

FIG. V-40 DIAMETRAL TEMPERATURE PROFILE OF C-10 FUEL SPECIMEN AT SURFACE TEMPERATURE OF 675°F. ONE DIAMETER UNIT IS EQUIVALENT TO 0.00536 INCH

FIG. V-41 RADIAL TRAVERSE OF SPECIMEN Z-10-B, ETCHED

FIG. V-42 RADIAL TRAVERSE OF SPECIMEN Z-10-F, ETCHED

100X

HC20248

FIG. V-43 FUEL-CLAD INTERFACE OF SPECIMEN Z-10-G

500X

HC15108

FIG. V-44 FUEL-CLAD INTERFACE OF SPECIMEN Z-10-C

The identity of the filaments has not been established. One explanation offered is that the filaments are regions of high dislocation density which have swept down the thermal gradient. Movement slows down or stops as the cooler surface regions of the fuel are approached which would account for the pile-up of the filaments near the fuel surface. Another possibility is that the filaments started as cracks which later healed by filling with UO_2 or UO_{2+x} preferentially lost from the solid solution fuel.

b. Outer Middle Zone

This zone occupies a region between the outer unaffected zone and the region of grain growth. Fuel temperatures within the zone range from about 925 to 1420°C (1700 to 2600°F). The microstructure in this zone consists of equiaxed grains outlined by indistinct irregular grain boundaries outlined by porosity, Figure V-45. Also, a heavy population of fine porosity is present within the grains. There is an apparently small decrease in the quantity of as-fabricated porosity.

c. Inner Middle Zone

Grains in this zone are somewhat columnar in appearance and increase in size with increasing distance from the fuel surface. The temperature in this zone ranges from about 1420 to 2300°C (2600 to 4200°F). The grain boundaries are heavily outlined with porosity, with lenicular-like pores at the high temperature ends of the grains. Generally, inner porosity exists within the individual grains. A substructure outlined by finer porosity can be seen within the grains, Figure V-46. This substructure is more predominant in the high temperature portions of the zone. Also present in this zone is a filament-like structure reminiscent of the filaments in the outer zone. Some of the filaments are long and extend across grains, while others traverse only part of a grain. These may be forerunners of the outer zone filaments.

d. Central Zone

Fuel in the center region of the low and intermediate burnup fuel consists of a discontinuous highly porous structure which culminates with a

500X

HC17346

FIG. V-45 MICROSTRUCTURE OF FUEL IN OUTER MIDDLE ZONE
OF SPECIMEN Z-10-F

250X

HC17344

FIG. V-46 MICROSTRUCTURE OF FUEL IN INNER MIDDLE ZONE
OF SPECIMEN Z-10-F

large but poorly defined void in the thermal center of the specimen. The central void was more distinct and the porosity greater in the intermediate burnup specimens Z-10-E and Z-10-F. A substructure, Figure V-47, and some filaments similar to those found in the adjacent zone are present. It is believed that no melting occurred in any of the low and intermediate burnup specimens and that the central void was formed as a result of initial porosity being swept to the fuel center by lenticular pore migration. Temperatures in this zone probably exceeded 2300°C (4200°F) during irradiation.

The microstructure of the high burnup fuel (represented by Z-10-J:70% nominal burnup), differed considerably from the microstructures of the lower burnup Z-10 fuels. As seen in Figure V-48, specimen Z-10-J had a large, well defined center void. Immediately adjacent to the void was a thin band of relatively nonporous fuel surrounded by a region with large, irregularly shaped pores. Proceeding toward the fuel surface from this region, the pores became smaller, more numerous and were preferentially aligned to give the appearance of radiating from the fuel center. The lenticular porosity and heavy porosity buildup on the grain boundaries seen in the lower burnup fuel specimens was not apparent in the high burnup specimens. Near the fuel surface, the fuel microstructure was similar to that of the lower burnup fuels in that it was virtually unaffected by the irradiation except for the presence of a filament-like phase. As with the lower burnup Z-10 fuels, the zone adjacent to the outer region exhibited some evidence of grain growth but grain boundary movement was apparently sporadic as evidenced by the irregular nature of the grain boundaries.

The differences in microstructure are believed to be associated with the fact that the high-burnup Z-10 specimens in Capsule BMI 43-3 experienced higher irradiation temperatures than did the lower burnup Z-10 specimens in Capsules BMI 43-1 and 43-2. The maximum centerline temperatures of specimens Z-10-B and Z-10-F were 2345 and 2565°C (4250 and 4650°F), respectively, and no melting is believed to have occurred. Specimen Z-10-J on the other hand, had a maximum temperature of 2790°C (5050°F) and probably experienced melting.

250X

HC17285

FIG. V-47 MICROSTRUCTURE OF FUEL IN CENTRAL ZONE OF SPECIMEN Z-10-E

100X

HC20024 to 20027

FIG. V-48 RADIAL TRAVERSE, SPECIMEN Z-10-J, CAPSULE BMI 43-3, AS-POLISHED

Some evidence of a reaction between the fuel and cladding was observed, Figures V-43, V-44 and V-49. The layer between the fuel and cladding is not continuous and of a darker gray color than the fuel and is similar in appearance to the gray phase observed within the fuel. The gray phase within the fuel and the gray colored layer between the fuel and cladding is continuous, in some instances and would suggest that they are probably the same material. In any case, attack of the cladding is only minimal and no significant differences in reaction thicknesses were noted between specimens irradiated to different burnups.

Two identified phases were present in the Z-10 specimens, a white metallic appearing phase which was distributed across the fuel, and a dark gray colored phase which was predominately in the outer half of fuel and similar in appearance to the product at the fuel-clad interface.

The presence of light colored, metallic appearing particles was common in all the ZrO_2 base specimens, Figures V-50 and V-51. These particles were observed in all portions of the fuel. The ductile nature of the particle material is illustrated in Figure V-52, which shows a particle extending across a crack in the fuel. Some clue as to the identity of this phase can be gained by examination of its characteristic shapes in various regions of the fuel. In the center fuel regions, the particles are always spherical in shape, suggesting possible melting, Figure V-53. Toward the fuel surface, the particles often assume irregular configurations, Figure V-54. If it is assumed that the spherical particles form by melting, it can be seen that the particles existed as a solid at some relatively high temperature. The particles are believed to consist of mixtures of high-melting, nonoxidized fission products, i.e., palladium, ruthenium, etc. This belief is supported by results of the analysis of similar particles in an oxide fuel reported by one investigator which showed the particles to be composed of ruthenium, molybdenum, rhodium, and a minor amount of palladium. No uranium or zirconium was found.⁽¹⁹⁾ Other investigators report similar results using electron microprobe analytical techniques.⁽²⁰⁾

FIG. V-49 FUEL-CLAD INTERFACE OF SPECIMEN Z-10-E

500X

HC15069

FIG. V-50 METALLIC-LIKE PARTICLES IN SPECIMEN Z-10-A

500X

HC15106

FIG. V-51 METALLIC-LIKE PARTICLE IN SPECIMEN Z-10-C

500X

HC15105

FIG. V-52 METALLIC-LIKE PARTICLES EXTENDING ACROSS A CRACK IN SPECIMEN Z-10-C

500X

HC17308

FIG. V-53 METALLIC-LIKE PARTICLES NEAR CENTER OF SPECIMEN Z-10-E

Note spherical configuration.

FIG. V-54 METALLIC-LIKE PARTICLES NEAR FUEL SURFACE OF SPECIMEN Z-10-F

Note the irregular configuration.

FIG. V-55 STRINGERS OF GRAY-COLORED PHASE IN SPECIMEN Z-10-E

The gray phase, Figures V-55 to V-57, was found in greatest abundance in the higher burnup Z-10 specimens. The phase assumed varying configurations and in some cases appeared to have filled or partially filled voids and cracks. One puzzling aspect of the configuration of the gray phase is that in some instances the phase contained relatively large pores, or passed undisturbed through a pore without apparently affecting the pore. One possible explanation of the origin and identity of this phase is that it is constituted by oxides of fission products which are insoluble in the fuel matrix. Another possibility is that the gray phase is $(U,Zr)O_2$ or $(U,Zr)O_{2+x}$ separated from the solid solution by preferential vaporization and deposition.

2. C-10 Specimens

The general microstructural features of the C-10 specimens were somewhat similar at all levels of burnup, Figures V-58 to V-60, with the exception of a second phase noted in the center regions of the intermediate and high burnup specimens and bands of porosity in the outer regions of these specimens.

The outer portion of the C-10 fuel, which operated at temperatures up to about 1035°C (1900°F), generally exhibited little change in grain size or pore size and density. Isolated regions of heavy pore population were noted near cracks. These may be the result of loss of oxide by preferential vaporization of $(U,Ce)O_2$ or more likely $(U,Ce)O_{2+x}$. As in the Z-10 specimens, relatively small quantities of a dark gray colored phase were observed within the fuel and at the fuel-clad interface, Figure V-61 and V-62. Also observed (Figure V-63) in this region were networks of filaments similar to the filaments observed in the Z-10 fuels. However, the filaments in the C-10 fuels were not as distinct and their population not as heavy as in the Z-10 and Z-22 fuels. White, metallic appearing particles were present but in lesser quantities than in the Z-10 fuels.

Adjacent to the outer zone was a region of equiaxed grain growth. At the cooler outer portions of the zone, grain growth was barely perceptible. Grain growth progressed with increasing fuel temperatures to about 1200°C (2200°F). Pores in this region are relatively large, suggesting coalescence

FIG. V-56 GRAY-COLORED PHASE IN SPECIMEN Z-10-F

FIG. V-57 GRAY-COLORED PHASE IN SPECIMEN Z-10-B

FIG. V-58 RADIAL TRAVERSE OF SPECIMEN C-10-B

100X

HC17248 to 17251

FIG. V-59 RADIAL TRAVERSE OF SPECIMEN C-10-D, ETCHED

40X

HC19954 to 19958

FIG. V-60 DIAMETRAL TRAVERSE OF SPECIMEN C-10-F

FIG. V-61 FUEL-CLAD INTERFACE AND GRAY-COLORED PHASE
IN SPECIMEN C-10-D

FIG. V-62 FUEL-CLAD INTERFACE IN SPECIMEN C-10-F

FIG. V-63 FILAMENT-LIKE STRUCTURE IN SPECIMEN C-10-C, ETCHED

FIG. V-64 MICROSTRUCTURE SHOWING EQUIAXED GROWTH NEAR CENTER OF SPECIMEN C-10-D

by a sweeping action accompanying grain growth. It is interesting to note that the grain boundaries are not heavily decorated with porosity, Figure V-64.

In the central region of the fuel exposed to temperatures in excess of about 1420 to 1480°C (2600 to 2700°F), the grains are elongated and culminate at a small, poorly defined, central void. Fuel around the central voids is spongy in appearance with exceptionally large pores compared to the rest of the fuel.

It is in this central region that the apparent second phase is present in the intermediate and high burnup specimens, Figures V-65 and V-66. It is interesting to note the similarity in the appearance of this microstructure with that of CeO_2 sintered in hydrogen at 1700°C (3100°F)*. This similarity suggests that an acicular microstructure may be typical of CeO_2 . Thus, while the identity of the second phase remains unknown, it appears that the development of the microstructure is related to the central portion of the fuel becoming rich in CeO_2 by migration of UO_2 down the thermal gradient. This is consistent with the previously cited evidence for segregation of CeO_2 and UO_2 by thermal migration.

Two bands of fine porosity were observed at positions corresponding to about 0.7 and 0.9 of the radius in both the intermediate and high burnup C-10 specimens. The cause and significance of these porous bands is not clear. They might be fission gasses coalesced by the sweeping action of grain growth but trapped in this region because low temperatures generally restricted any gross mobility.

*Cf. Reference 10, pp. 74.

FIG. V-65 SECOND PHASE IN CENTER REGION OF SPECIMEN C-10-D,
ETCHED

FIG. V-66 SECOND PHASE IN CENTER REGION OF SPECIMEN C-10-F,
AS-POLISHED

3. Z-22 Fuel

As with the Z-10 fuel, radial traverses of Z-22 fuel specimens at low and intermediate burnup, Figures V-67 to V-69, showed four zones with distinct microstructural features.

a. Outer Zone

Except for the filament-like material, the gray phase and possibly some small fission gas bubbles, Figures V-70 and V-71, the microstructure of this zone is similar to that of the as-sintered, preirradiated structure. A very thin reaction layer at the fuel-clad interface was observed in some areas.

b. Outer Middle Zone

It is in this relatively narrow zone that the fuel first shows any gross effects of irradiation. Some sintering apparently occurred. The nature of porosity has changed, the pores are fewer in number and in a different configuration than in the preirradiation structure. Grain boundaries are not distinct and, where they are visible, are very irregular, Figure V-72. The structure appears to be two phase, but this may be due to inadequate etching procedures.

c. Inner Middle Zone

Fuel in this region exhibits definite signs of grain growth with the grains becoming columnar in nature as the fuel center is approached. Grain boundaries are heavily decorated with porosity. Finer pores are also present within the grains, Figure V-73.

d. Central Zone

Grains in the outer parts of this region are elongated, apparently as a result of lenticular pore movement toward the fuel center. In the fuel center the grains are more equiaxed. Grain boundaries throughout the zone are heavily outlined by porosity. As in some of the Z-10 fuel specimens, a sub-grain structure outlined by fine porosity is present within the grains, Figure V-74.

100X

HCl5163 to 15167

FIG. V-67 RADIAL TRAVERSE OF SPECIMEN Z-22-0, AS-POLISHED

100X

HC20125 to 20128

FIG. V-68 RADIAL TRAVERSE OF SPECIMEN Z-22-P, CAPSULE BMI 43-6,
AS-POLISHED. BURNUP 15.2×10^{20} FISSIONS/CM³

100X

HC20302 to 20304

FIG. V-69 RADIAL TRAVERSE, SPECIMEN Z-22-Y

FIG. V-70 FILAMENT-LIKE STRUCTURE IN OUTER ZONE OF SPECIMEN Z-22-M, ETCHED

FIG. V-71 FILAMENT-LIKE STRUCTURE IN OUTER ZONE OF SPECIMEN Z-22-X, ETCHED

FIG. V-72 OUTER MIDDLE ZONE OF SPECIMEN Z-22-M

FIG. V-73 INNER MIDDLE ZONE OF SPECIMEN Z-22-M

250X

HC15172

FIG. V-74 CENTER REGION OF SPECIMEN Z-22-0

500X

HC15185

FIG. V-75 FUEL-CLAD INTERFACE OF SPECIMEN Z-22-M, AS-POLISHED

The high burnup Z-22 specimen microstructures differed from the lower burnup microstructures in two respects. In the high burnup specimen a relatively large quantity of fine fission gas bubble porosity was present in the outer fuel zone next to the fuel-clad interface. See Figures V-75 and V-76. At lower burnups, little or no fission gas porosity was present in this area. Also, the center voids in the high burnup specimens were large and distinct as compared to the small, poorly defined center voids in the lower burnup specimens. The large center voids are probably associated with higher centerline temperature than were indicated by the capsule thermocouples and suggests that centerline melting occurred. As noted earlier, the thermocouples in Capsule BMI-43-5 were displaced relative to the fuel specimen midplanes and, as a consequence, probably indicated unrealistically low temperatures. The gas bubbles in the outer fuel regions may also be related to higher than indicated temperature.

As seen in Figure V-77 and the previous figures, the metallic like particles were present throughout the Z-22 fuels. The particles were, however, more prevalent in a region extending from about $1/3$ to $2/3$ of the fuel radius, Figure 78. Also, the particles became coarser closer to the fuel center.

4. C-25 Fuel

The microstructural features of the irradiated C-25 fuel were generally similar to those of the C-10 specimens with the exception of the central regions, as shown in the radial traverse, Figures V-79 to V-81.

In the low and intermediate burnup specimens, the center voids were small and sharply defined, Figures V-79 and V-80, while the high burnup specimens, Figure V-81, had a much larger center void. As in the case of the Z-22 fuels, the large void in the high burnup specimen is probably associated with very high centerline temperatures and can be considered as evidence that fuel temperatures in Capsule BMI 43-5 were much higher than indicated by the capsule thermocouples, and that melting probably occurred at the fuel center.

FIG. V-76 FUEL-CLAD INTERFACE OF SPECIMEN Z-22-X, AS-POLISHED

Note apparent fission gas porosity near fuel edge.

FIG. V-77 METALLIC-LIKE PARTICLES IN SPECIMEN Z-22-M

250X

HC20213-20215

FIG. V-78 BAND ABOUT MIDWAY BETWEEN FUEL CENTER AND FUEL SURFACE
WITH HIGH POPULATION OF WHITE METALLIC PARTICLES,
SPECIMEN Z-22-X

FIG. V-80 RADIAL TRAVERSE, SPECIMEN C-25-P, CAPSULE BMI 43-6

40X

HC20156 to 20158

FIG. V-81 DIAMETRAL TRAVERSE, SPECIMEN C-25-N, CAPSULE BMI 43-5

In all fuels, porosity around the center void was low. This low porosity may be associated with the high volatility noted for fuel of this composition in out-of-pile tests. Because of the high volatility, vapor-phase transport of fuel may occur very rapidly. The lifetime of a pore or fission gas bubble may thus be brief, with the consequence that fewer pores will be in existence at any one time.

Fuel in the outer regions had a fine-grained, equiaxed structure (Figure V-79) similar to the preirradiation structure. Thread or filament like tracks seen in this region are like those seen in the C-10 specimens. Their relationship, if any, to the filament-like structure seen in the Z-10 and Z-22 specimens is not known. An apparent two phase reaction between the fuel and clad was observed, Figures V-82 and V-83. The reaction zones were very thin and did not introduce any significant degradation in cladding performance. Small pores, which may be fission gas bubbles were present in the outer region of the high burnup specimens, Figure V-83.

Bands of high porosity were located adjacent to the outer fuel regions positions of about 0.7 to 0.8 of the radius. It is possible that grain growth may have resulted in the coalescence of gas bubbles and porosity in this zone. However, low temperatures in the zone may have restricted movement of porosity out of this region. Another possibility is that the porosity is associated with a Kirkendahl effect arising from thermal migration of fuel components.

Fuel between the porous zone and the center of the fuel consisted of relatively large, equiaxed grains, Figure V-84. Porosity in this region was concentrated at the grain boundaries and appeared to be aligned in a radial direction.

No evidence of the two phase acicular structure seen in the center regions of the intermediate and high burnup C-10 specimens was observed in any of the C-25 fuel specimens (Figure V-85).

White, metallic-like particles were noted in the C-25 fuels, Figure V-86. The particles were most numerous in a band located about half-way between the fuel centerline and the fuel--clad interface, Figure V-87.

FIG. V-82 REACTION PRODUCT AT FUEL-CLAD INTERFACE, SPECIMEN C-25-0

FIG. V-83 FUEL-CLAD INTERFACE, SPECIMEN C-25-N

500X

HC15142

FIG. V-84 MICROSTRUCTURE OF SPECIMEN C-25-M IN REGION
ADJACENT TO CENTER

FIG. V-85 MICROSTRUCTURE OF SPECIMEN C-25-M IN CENTER REGION

FIG. V-86 WHITE, METALLIC-LIKE PARTICLES NEAR CENTER OF SPECIMEN C-25-M

FIG. V-87 BAND WITH HEAVY POPULATION OF WHITE, METALLIC-LIKE PARTICLES LOCATED ABOUT MIDWAY BETWEEN FUEL CENTER AND SURFACE, SPECIMEN C-25-N

Cladding

With the exception of the previously described minor reaction at the fuel--clad interfaces, the cladding structures did not appear to have been affected by the irradiation as indicated in Figures V-88 to V-93.

H. AUTORADIOGRAPHY

Alpha and beta autoradiography of selected fuel samples from Capsules BMI 43-3, 43-4, 43-5 and 43-6 were used to detect evidence of fission product migration and uranium migration. Alpha autoradiographs were obtained by placing cellulose nitrate sheet in intimate contact with the fuel for several seconds. The image produced by the alpha activity was developed by etching the cellulose nitrate in a NaOH solution. Enlargement of the image using standard photographic techniques facilitated detailed examination of the autoradiographs.

Beta autoradiographs were obtained in a similar manner except that photographic film with an emulsion relatively insensitive to gamma radiation was employed.

Representative samples of the resultant autoradiographs along with reference macrophotographs of the test samples are shown in Figures V-94 to V-98. In both alpha and beta-gamma autoradiographs, lighter toning is indicative of greater activity. Voids and cracks often show up lighter in toning in beta autoradiographs because of the greater fuel surface area exposed to the film.

Beta activity in the Z-10 specimens followed the general pattern illustrated in Figure V-48 for Specimen Z-10-J. The fuel regions around the center void were relatively devoid of fission product activity. Adjacent to this in the columnar grain growth region was an area of high beta activity. Beyond this region, toward the fuel surface, the beta activity was relatively uniform.

A similar pattern of beta activity was noted in some of the Z-22 specimens (Z-22-X and Z-22-Y), Figure V-97. On the other hand, Specimen Z-22-P exhibited relatively uniform beta activity across its radius (Figure V-96).

FIG. V-88 TYPE 347 STAINLESS STEEL CLAD, SPECIMEN Z-10-F

FIG. V-89 TYPE 347 STAINLESS STEEL CLAD, SPECIMEN C-10-C

250X

HC15174

FIG. V-90 TYPE 347 STAINLESS STEEL CLAD, SPECIMEN Z-22-O

250X

HC15162

FIG. V-91 TYPE 347 STAINLESS STEEL CLAD, SPECIMEN C-25-O

FIG. V-92 CLADDING FROM SPECIMEN Z-10-J

FIG. V-93 CLADDING FROM SPECIMEN C-25-N

(a)

(b)

(c)

FIG. V-94 SPECIMEN Z-10-J

- (a) Photomacrograph
- (b) Beta autoradiograph
- (c) Alpha autoradiograph

(a)

(b)

(c)

FIG. V-95 SPECIMEN C-10-F

- (a) Photomicrograph
- (b) Beta autoradiograph
- (c) Alpha autoradiograph

(a)

(b)

(c)

FIG. V-96 SPECIMEN Z-22-P

- (a) Photomicrograph
- (b) Beta autoradiograph
- (c) Alpha autoradiograph

(a)

(b)

(c)

FIG. V-97 SPECIMEN Z-22-Y

- (a) Photomicrograph
- (b) Beta autoradiograph
- (c) Alpha autoradiograph

(a)

(b)

(c)

FIG. V-98 SPECIMEN C-25-N

- (a) Photomicrograph
- (b) Beta autoradiograph
- (c) Alpha autoradiograph

Beta activity in the ceria base fuels exhibited variable patterns. In Specimen C-10-F, Figure V-95, beta activity was highest in the outer 1/3 of the fuel. Thin bands of high activity bordering this outer region correspond to the locations of the metallographically observed porous bands. It is believed that the high activity in the bands merely reflects the greater surface area associated with porosity. Other ceria base specimens, such as Specimen C-25-N, Figure V-98, exhibited low beta activity in the region immediately around the center void, followed by a relatively wide band of higher activity and then constant activity to the fuel surface.

In general, it appears that the largest degree of fission product segregation occurred in specimens which operated at the highest center temperatures. It appears that under properly high thermal gradient conditions, fission products migrate out of the fuel center and build up in or near the region of columnar grain growth.

Alpha autoradiographs of the fuel specimens presented highly variable results. In some specimens, such as Specimens Z-10-J and Z-22-Y, Figures V-94 and V-97, alpha activity in the center regions appeared to be lower than in the outer regions. Other specimens, e.g., C-10-F, Z-22-P, and C-25-N, Figures V-95, V-96 and V-98 had relatively constant levels of alpha activity across the fuel radius. The low levels of alpha activity observed in the center regions of some specimens suggest that the center fuel regions were depleted in uranium. However, it is possible that there was a buildup of highly alpha-active trans-uranium transmutation products which may have masked these results.

I. X-RAY DIFFRACTION DATA

One specimen of every fuel type from each capsule together with unirradiated control specimens of each fuel type, were subjected to x-ray diffraction analysis.

The x-ray samples from Capsule BMI 43-1 and 43-4 consisted of cross sections of fuel removed from the center pellet.

Sampling of fuel specimens from other capsules was more selective, as separate samples were taken from the central and the surface regions of the

fuel either by drilling or by picking out fuel chips with tweezers. These samples were then analyzed individually.

Results of the analyses are tabulated in Table V-5. All samples exhibited single phase face centered cubic structures. However, a variation in lattice parameter between the center and surface regions of the fuel was found in most of the selectively sampled fuel specimens. In almost all cases, the lattice parameters of fuel in the center regions were smaller than the lattice parameters of surface fuel. Since the lattice parameters of both $\text{ZrO}_2\text{-UO}_2$ and $\text{CeO}_2\text{-UO}_2$ solid solutions contract with decreasing UO_2 , these variations might be the result of thermal migration causing fuel in the outer regions to become UO_2 rich and fuel in the center to become rich in ZrO_2 or CeO_2 .

Another possible explanation is oxygen migration up the thermal gradient which made the center fuel oxygen rich. Excess oxygen is known to contract the lattice of UO_2 and $\text{ZrO}_2\text{-UO}_2$. However, the postulated oxygen migration up the thermal gradient is contrary to experimentally observed oxygen migration down the thermal gradient.⁽²¹⁾

In the bulk samples, a decrease in lattice parameter occurred as a result of the irradiation.

J. CORROSION TESTS

Post-irradiation corrosion tests were conducted on each of the four fuel compositions studied in this program.

Comparisons were made with unirradiated depleted and enriched pellets. Defects were introduced by drilling a 5/64 inch hole through the cladding at the approximate center plane of the fuel and also at the gas plenum at the top of the fuel column. The latter hole facilitated sample drying before and after corrosion testing. Some ceria-base samples utilized for post-irradiation corrosion testing were cross sections of samples which had been previously examined in the hot cells. A listing of all test samples is provided in Table V-6, together with results of post-irradiation evaluations. Figure V-99 shows typical views of specimens prior to corrosion testing.

TABLE V-5
RESULTS OF X-RAY DIFFRACTION ANALYSIS

Specimen	Sample Location	Lattice Parameter (A)	Burnup ³ (Fissions/cm ³ x 10 ²⁰)
Z-10	Control	5.149	---
Z-10-B	Bulk	5.128	4.4
Z-10-F	Center	5.109	6.3
Z-10-F	Outer	5.134	6.3
Z-10-J	Center	5.136	7.9
Z-10-J	Outer	5.150	7.9
C-10	Control	5.415	---
C-10-A	Bulk	5.399	6.5
C-10-C	Center	5.391	8.1
C-10-C	Outer	5.498	8.1
C-10-F	Center	5.410	11.0
C-10-F	Outer	5.416	11.0
Z-22	Control	5.173	---
Z-22-M	Bulk	5.158	10.5
Z-22-R	Center	5.166	14.7
Z-22-R	Outer	5.165	14.7
Z-22-X	Center	5.159	18.5
Z-22-X	Outer	5.163	18.5
C-25	Control	5.421	---
C-25-M	Bulk	5.380	17.0
C-25-R	Center	5.396	21.5
C-25-R	Outer	5.419	21.5
C-25-N	Center	5.413	28.4
C-25-N	Outer	5.417	28.4

TABLE V-6
RESULTS OF CORROSION TESTS

Specimen Identification	Specimen Description	Burnup (Fissions/cc x 10 ²⁰)	Percent Change in Weight
Z-10-D	Clad (defected)	5.7	-0.35
Z-10-H	" "	7.7	0.16
Z-10-M	" "	unirradiated	0.40
Z-10 pellet 1	Bare pellet (depleted)	"	0.16
Z-10 pellet 2	" " "	"	0.36
C-10-D	Clad (sectioned through fuel)	8.6	0.04
C-10-E	" " " "	10.6	0.51
C-10-H	Clad (defected)	unirradiated	0.17
C-10-K	Bare pellet (enriched)	"	0.33
C-10	" " "	"	0.07
C-10 pellet 8	" " "	"	-0.39
C-10 pellet 19	" " "	"	0.25
C-10 pellet 2	" " (depleted)	"	0.85
C-10 pellet 3	" " "	"	0.16
Z-22-N	Clad (defected)	9.2	-1.47
Z-22-Z	" "	14.6	0.06
Z-22-T	" "	18.4	-1.95
Z-22-W	" "	unirradiated	-0.33
Z-22-O	Bare pellet (enriched)	"	0.88
Z-22	" " "	"	0.51
Z-25-2-1	" " (depleted)	"	0.96
Z-25-2-3	" " "	"	1.04
C-25-M	Clad (defected)	17.0	-4.48
C-25-R	" "	21.5	0.17
C-25-S	" "	25.8	-0.08
C-25-T	" "	unirradiated	-0.14
C-25-W	Bare pellet (enriched)	"	-0.07
C-25 pellet 32	" " "	"	0.13
C-25 pellet 2	" " (depleted)	"	-3.33
C-25 pellet 3	" " "	"	0.43

P982

6X

(a) Defect in fuel area
of Specimen Z-22-T
from Capsule BMI-43-5.

P987

6X

(b) Defect in void area of
Specimen C-10-D from
Capsule 43-2.

P990

6X

(c) Specimen C-25-R from
Capsule BMI-43-6

P1012

6X

(d) Unirradiated Specimen
Z-10 Pellet 2

FIG. V-99 REPRESENTATIVE VIEWS OF CORROSION SPECIMENS
BEFORE TESTING

All specimens were placed in an evacuated furnace and dried at 210°C (410°F) overnight. The specimens were removed from the furnace and their weights determined to the nearest tenth of a milligram. The specimens were then placed in the autoclave and the pH was adjusted to 10 by adding NH_4OH . The autoclave was sealed, evacuated, allowed to set for five minutes, and evacuated again to ensure that no excess oxygen was present in the water.

The original intent was to corrosion test at 345°C (650°F) for 90 days (2160 hours). However, due to a failure of the autoclave heater, the tests were terminated after slightly over 48 days (1160 hours) of operation at temperature. The specimens were removed from the autoclave, cleaned, dried in a vacuum furnace at 110°C (230°F) overnight, and then photographed and weighed as before. Representative photographs of the specimens after corrosion testing are presented in Figure V-100; for weight changes, see Table V-6. None of the specimens showed any visible evidence of corrosion and all weight changes were minimal. There was little, if any, difference between weight changes in the irradiated and unirradiated samples. Weight losses experienced by a few specimens are believed to be due to loss of fuel and are not a result of corrosion. The fuel was friable. Some of it was badly cracked during the specimen defecting operation and small pieces may have fallen out during post-corrosion handling even though care was taken to avoid this. In the case of bare pellets, small pieces may have chipped off of the sharp corners of the pellets.

One of each irradiated fuel composition was metallographically examined for evidence of corrosion. Figures V-101 to V-104 show representative views of the four different fuel compositions at the defected area and 90 degrees from the defected area. The microstructures are similar to those of untested and unirradiated fuel and did not show any evidence of corrosive attack on the fuel or the cladding.

It is concluded that irradiation to burnups between 5 and 25×10^{20} fissions/cm³ did not adversely affect the excellent corrosion resistance to 650°F water noted previously for unirradiated material.

P1093

6X

(a) Defect in fuel area
of Specimen Z-22-T
from Capsule BMI-43-5.

P1096

6X

(b) Defect in void area of
Specimen C-10-D from
Capsule BMI-43-2.

P1091

6X

(c) Specimen C-25-R from
Capsule BMI-43-6.

P1066

6X

(d) Unirradiated Specimen
Z-10 Pellet 2.

FIG. V-100 REPRESENTATIVE VIEWS OF CORROSION SPECIMENS
AFTER TESTING

HC20931

40X

(a) Area of Defect.

HC20946

250X

(b) Area of Defect.

HC20940

250X

(c) Area 90 degrees from
Defect.

FIG. V-101

REPRESENTATIVE VIEWS OF THE MICROSTRUCTURE AT AND
AWAY FROM THE DEFECTED AREA OF SPECIMEN Z-10-H FROM
CAPSULE BMI 43-3

HC20962

40X

(a) Area of Defect.

HC20963

250X

(b) Area of Defect.

HC20971

250X

(c) Area 90 degrees from Defect.

FIG. 102

REPRESENTATIVE VIEWS OF THE MICROSTRUCTURE AT AND AWAY FROM THE DEFECTED AREA OF SPECIMEN C-10-E FROM CAPSULE BMI 43-3

HC20922-20923

40X

(a) Traverse from Center to Edge of Specimen (Typical).

HC20928

250X

(b) Clad Fuel Interface (Typical).

FIG. V-103

TYPICAL VIEWS OF MICROSTRUCTURE OF SPECIMEN Z-22-T FROM CAPSULE BMI 43-5. THE DEFECT AREA WAS POLISHED AWAY ON THIS SPECIMEN

HC20953

250X

(a) Area Near Defect.

HC20956

250X

(b) Area 90 Degrees from Defect.

FIG. V-104

REPRESENTATIVE VIEWS OF MICROSTRUCTURE AT AND AWAY
FROM THE DEFECTED AREA OF SPECIMEN C-25-S FROM
CAPSULE BMI 43-5

VI. ✓ ANALYSES OF POST-IRRADIATION DATA

Primary emphasis in this section will be placed upon discussions of thermal conductance, fission gas release, grain growth, and swelling. A number of interesting relationships are plotted. These relationships will be used as a basis for discussions with respect to the performance of these fuels.

Table VI-1 contains a summary of important thermal conditions, gas release, grain growth volumes, and fuel length changes.

A. THERMAL CONDUCTANCE

Although measurements of in-reactor thermal conductance were not part of this program, certain trends in the post-irradiation data provide subtle indicators of the possible influence of burnup on thermal conductance. Figures VI-1 and VI-2 contain relationships between percent grain growth and burnup for zirconia-base and ceria-base fuels. All data points, with one exception on each plot, fall within the indicated trend bands. These data points represent samples which operated substantially hotter during the last cycle than other samples plotted in Figures VI-1 and VI-2. In both instances, the deviations are toward larger percent grain growth than the trend band. The slope and width of these trend bands for zirconia-base and ceria-base fuels are almost identical.

Although the unirradiated conductivity values for Z-22 and C-25 fuels are somewhat lower than those for Z-10 and C-10 fuels, these initial differences may not be controlling at the high burnups encountered in this program. In fact, there is some question as to whether these variations in UO_2 content play any role in the ceria-base system at temperatures exceeding $800^\circ C$.^{*} Examination of Figure VI-2 indicates that the trend band provides significant differences in grain growth for the C-25 composition (constant UO_2) as a function of burnup. Similar, but less startling trends are noted within the Z-22 compositions plotted in Figure VI-1. We believe that the trends shown in Figures VI-1 and VI-2 are associated with a burnup dependency.

^{*}KAPL-1918

Table VI-1
SUMMARY OF IRRADIATION CONDITIONS AND
POSTIRRADIATION EXAMINATION RESULTS

Specimen No.	Position in Capsule	Burnup		Centerline Irradiation Temperature, °C						Fission Gas Remaining in Fuel, atoms/cm ³ x 10 ²⁰	Portion of Fuel Undergoing Grain Growth, %	Fuel Column *		Clad Diameter Change, %	Fuel Lattice Parameter			
		Fission/cm ³ a/o	x 10 ²⁰	Avg. Last		Max Last		Fission Gas Release, %	Length Change, %			Unirrad.	Fuel Center		Fuel Edge			
				Irrad.	20% of Irrad.	20% of Irrad.	20% of Irrad.									ΔL ₁	ΔL ₂	
Z-10-A	1	40	4.4	1675	2150	1670	1790	1620	1790	-	-	-	1.0 ^(a)	-	0.2	5.149	5.128	(Bulk)
Z-10-B	3	40	4.4	1875	2345	1780	1955	1760	1955	43	-	44	-	-	0.2	-	-	-
Z-10-C	4	42	4.6	1870	2455	1710	1900	1650	1790	32	-	48	-	-	0.2	-	-	-
Z-10-D	1	52	5.7	1655	2345	1250	1425	1260	1345	-	-	-	0.7	-	0.2	-	-	-
Z-10-E	2	56	6.2	1730	2510	1335	1510	1345	1510	37	1.0	44	1.4	5.3 ^(b)	0.2	-	5.109	5.134
Z-10-F	3	57	6.3	1805	2565	1545	1790	1705	1790	46	0.8	52	1.4	15.3 ^(b)	0.2	-	-	-
Z-10-G	1	70	7.8	1935	2955	1815	2955	2480	2955	58	0.8	-	3.3	38.7	0.5	-	-	-
Z-10-H	2	69	7.7	1890	2925	1730	2925	2400	2925	-	-	-	2.7	38.7	0.4	-	-	-
Z-10-J	3	71	7.9	2025	3040	1815	3040	2345	3040	56	0.9	71	0	46.0	0.8	-	5.136	5.150
C-10-A	2	43	6.5	1415	1760	1245	1510	1010	1510	22	-	46	-	-	-0.3	5.415	5.399	(Bulk)
C-10-B	5	44	6.7	1295	1595	1195	1315	1150	1260	28	-	33	-	-	-0.3	-	-	-
C-10-C	4	58	8.1	1400	1955	1205	1400	1315	1400	48	1.0	48	0.7	2.0 ^(b)	0.3	-	5.391	5.418
C-10-D	5	61	8.6	1200	1650	1050	1175	1120	1175	62	0.7	44	1.4	3.3 ^(b)	0	-	-	-
C-10-E	4	74	10.6	1400	2120	1245	2120	1730	2120	58	1.1	-	1.3	29.0	0.3	-	-	-
C-10-F	5	77	11.0	1295	1955	1165	1955	1730	1955	59	1.0	74	6.7	28.0	0.3	-	5.410	5.416
Z-22-M	1	40	10.5	1975	2455	1775	2095	1815	1870	46	-	58	-	-	0.3	5.173	5.138	(Bulk)
Z-22-N	3	37	9.2	1955	2650	1710	2290	1980	2065	-	-	-	-	-	0	-	-	-
Z-22-O	4	40	10.5	2000	2730	1635	2150	1870	1925	58	-	65	-	-	0.3	-	-	-
Z-22-P	1	60	15.2	2095	2480	1580	2175	1510	1705	62	1.7	61	4.7	22.0	0.3	-	-	-
Z-22-R	3	58	14.7	1905	2260	1200	2095	1120	1620	66	1.3	-	2.0	8.6	0.6	-	5.166	5.165
Z-22-Z	4	58	14.6	1760	2095	1145	1980	1345	1455	-	-	-	0	0	0.3	-	-	-
Z-22-T	1	73	18.4	1700	2425	1355	1650	1425	1480	-	-	-	2.7	16.0	-0.3	-	-	-
Z-22-X	2	74	18.5	1630	2425	1200	1540	1290	1375	69	1.4	72	0.7	12.0	0.3	-	5.159	5.163
Z-22-Y	3	62	15.6	1660	2510	1145	1425	1205	1260	84	0.6	77	0	11.3	0.3	-	-	-
C-25-M	2	44	17.0	1480	1870	1425	1730	1565	1595	74	-	58	-	-	0.4	5.421	5.38	(Bulk)
C-25-O	5	41	15.7	1525	1955	1295	1595	1425	1480	79	-	63	2.0	-	0	-	-	-
C-25-P	2	61	23.0	1660	1900	1500	1815	1260	1400	88	0.7	79	0.7	8.0	0	-	-	-
C-25-R	5	57	21.5	1315	1595	1175	1455	925	1290	87	0.7	-	2.7	8.0	0	-	5.396	5.419
C-25-N	4	76	28.4	1405	2040	925	1205	1040	1095	84	1.1	97	3.3	10.7	0.4	-	5.413	5.417
C-25-S	5	64	25.8	1195	1815	690	870	650	705	96	0.3	-	0.7	4.7	0.4	-	-	-

(a) Measured optically.

(b) Measured from photomicrographs, all other lengths measured from gamma scans.

* ΔL_1 is the fuel length change adjacent to the fuel-clad interface;

ΔL_2 is the fuel length change at the center of the fuel column.

Figure VI-1
GRAIN GROWTH VERSUS BURNUP FOR ZIRCONIA-BASE FUELS

Figure VI-2
GRAIN GROWTH VERSUS BURNUP FOR CERIA-BASE FUELS

The change in the grain growth percent with burnup is probably associated with a decrease in thermal conductance of the element with higher burnups. It is possible that the minimum temperature for grain growth may be influenced by burnup; however, this prospect, if it occurs, is less likely to be the cause of the large changes in grain growth regions which were observed. It is likely that the large volumes of fission gas generated at these high burnups contribute to a degradation of fuel thermal conductivity by accumulation of some of these gases in the grain boundaries in regions of the fuel which are at temperatures just below the minimum grain growth temperature. A network of fission gas bubbles was observed at high magnification. Another possible reason for lower conductance may be associated with oxygen stoichiometry in the fuel. Results of experiments with stoichiometric UO_2 suggest the possibility that the fuel becomes hyperstoichiometric with respect to oxygen as burnup increases. With the high burnups in the zirconia base and ceria base fuels, any tendency toward higher oxygen contents would have been encountered, possibly resulting in lower thermal conductivity. Thus, this mechanism may also be a cause for the inferred lower thermal conductance of these fuel samples with increasing burnup. A degradation of thermal conductivity at very high burnups may also be associated with the large volume of fission fragments in the fuel lattice. This latter factor has not been of significant influence in $\text{UO}_2\text{-PuO}_2$ and may not be a contributing factor here. However, observed agglomeration of fragments at lower temperature regions of the fuel may be a factor. Another possible cause of these observed relationships may be associated with the formation of a thermal barrier in the form of a second phase resulting from an apparent fuel-cladding reaction reported in earlier sections.

It is interesting to note that the influence of burnup appears to be more significant than calculated variations in temperature during irradiation for any of the samples comprising the trend bands shown in Figures VI-1 and VI-2. This is apparent when any of the temperatures in Table VI-1 are evaluated as a function of grain growth. Therefore, it may be concluded that, if the above observations concerning the influence of burnup on thermal conductance are real,

the factors contributing to this degradation in fuel element thermal conductance exert significantly stronger influences on observed end-of-life grain growth than do any of the temperatures which were considered. However, there is one notable exception on each plot and this exception represents the one sample which, during the last irradiation cycle, operated considerably hotter than the other samples plotted in Figures VI-1 and VI-2.

B. FISSION GAS RELEASE

A summary of fission gas release data for both zirconia base and ceria base samples is shown in Table VI-1. It was originally believed that correlations between fission gas release and centerline temperatures would be evident in the data. Figures VI-3 through VI-8 contain relationships between fission gas release and average centerline temperature, maximum centerline temperature, average and maximum centerline temperatures during the last 20 percent of the irradiation, and average and maximum centerline temperature during the last irradiation cycle.

In Figures VI-3 through VI-8 there is no apparent correlation between fission gas release and any of the centerline temperatures which are plotted. However, these data are calculations of fuel centerline temperatures based upon in-reactor measurements of cladding surface temperatures and assuming beginning of life fuel element thermal conductances. It was suggested in Section VI-A, above, that reductions in fuel element thermal conductance with burnup might occur and that these reductions in thermal conductance were consistent with the observed changes in grain growth areas. Thus, the poor correlation between gas release and the centerline temperatures plotted in Figures VI-3 through VI-8 is not surprising since these temperatures may not be realistic indicators of actual fuel conditions.

FIGURE VI-3 FISSION GAS RELEASE VERSUS AVERAGE CENTERLINE TEMPERATURE

FIGURE VI-4 FISSION GAS RELEASE VERSUS MAXIMUM CENTERLINE TEMPERATURE

FIGURE VI-5 FISSION GAS RELEASE VERSUS AVERAGE CENTERLINE TEMPERATURE IN THE LAST 20% OF THE IRRADIATION

FIGURE VI-6 FISSION GAS RELEASE VERSUS MAXIMUM CENTERLINE TEMPERATURE IN LAST 20% OF THE IRRADIATION

FIGURE VI-7 FISSION GAS RELEASE VERSUS AVERAGE CENTERLINE TEMPERATURE IN THE LAST IRRADIATION CYCLE

FIGURE VI-8 FISSION GAS RELEASE VERSUS MAXIMUM CENTERLINE TEMPERATURE IN THE LAST IRRADIATION CYCLE

If one considers the percent grain growth as a reasonable bench mark for thermal conditions influencing fuel performance*, a plot of fission gas release versus percent grain growth might provide an interesting relationship. Figures VI-9 and VI-10 contain these relationships for zirconia- and ceria-base fuels. Although the data for zirconia-base fuels fall within a fairly narrow scatter-band, those for the ceria-base fuels do not, and only general trends can be implied from the very broad scatter-band indicated. Nevertheless, these data trends tend to support earlier implications that the fuel element thermal conductance may be decreasing with increasing burnup.

Figures VI-11 and VI-12 contain relationships between fission gas release and burnup. The narrow scatter-bands observed for both the zirconia- and ceria-base systems are almost identical with respect to width and slope. For burnups above approximately 8×10^{20} f/cm³, fission gas release appears to increase linearly with burnup, for both the zirconia-base and ceria-base systems.

The following relationships appear to represent the bulk** of the plotted data for these two systems for burnups in excess of 8×10^{20} f/cm³:

$$R_{(z)} = \frac{B + 14.4 (\pm 2.5)}{0.44}$$

$$R_{(c)} = \frac{B + 15.5 (\pm 1.8)}{0.42}$$

$R_{(z)}$ = Percent gas release from zirconia-base fuels

$R_{(c)}$ = Percent gas release from ceria-base fuels

B = Burnup (f/cm³ x 10^{20})

The correlations between burnup and fission gas release are probably associated with the increase in grain growth volume as a function of burnup. Examination of data for the zirconia-base system (Figures VI-9 and VI-11) would tend to add support to this observation. Thus, the increase in gas release with

* Without any concern for the relative times at which grain growth occurred.

**The major exceptions are one data point for the ceria base fuel which exhibited an abnormally low gas release after a burnup of about 28×10^{20} f/cm³ and a data point for the zirconia-base which exhibited a slightly greater gas release after a burnup of about 16×10^{20} f/cm³.

Figure VI-9

FISSION GAS RELEASE AS A FUNCTION OF
GRAIN GROWTH FOR ZIRCONIA-BASE FUELS

Figure VI-10

FISSION GAS RELEASE AS A FUNCTION OF
GRAIN GROWTH FOR CERIA-BASE FUELS

Figure VI-11

FISSION GAS RELEASE AS A FUNCTION OF
BURNUP FOR ZIRCONIA-BASE FUELS

Figure VI-12
FISSION GAS RELEASE AS A FUNCTION OF BURNUP FOR CERIA-BASE FUELS

increasing burnup in this system may have, as its prime driving force, a lower thermal conductance with a resultant increase in grain growth volume. However, the differences noted for the ceria base system between Figures VI-10 and VI-12 suggest that a similar mechanism may not be the controlling factor in this system. Grain growth volume may be a driving force but its dominance may not be as great, as evidenced by the data in Figure VI-10. Changes in gas release mechanisms, or gross changes in effective fission gas diffusion rates with increasing burnup are probably explanations for the differences in scatter between data in Figures VI-10 and VI-12.

C. SWELLING

Most of the swelling observed in the fuels was characterized by small increases in the fuel column length in the outer region of the fuel and, in some cases, by more severe swelling at the top center of the fuel column. Table VI-1 contains results of measurements of these fuel column lengths.

Originally, it was believed that the more severe swelling noted in some samples at the top center of the fuel column was a result of end peaking effects resulting in higher burnups and higher temperatures. This postulate was tested by means of burnup analysis from sample Z-10-J in the localized swelling region as well as in the axial center but away from the swelling region. The burnup measured for each sample was 7.9×10^{20} f/cm³. On this basis, it was concluded that this localized swelling was not related to end peaking factors and that it was a result of gross swelling of the hot plastic central fuel region into the gas plenum primarily as a result of the large radial restraints on the fuel. One possible reason for the "overheated" appearance of the extruded fuel may be the poor radial thermal conductivity associated with this bulge after it had formed. Attempts to establish a relationship between this localized swelling and a number of experimental variables were unsuccessful primarily because the geometric shape assumed by these bulges was not consistent. Therefore, gross volume changes cannot be predicted on the bases of ΔL_2 measurements in Table VI-1 since the proportionality factor between the linear extent of the uppermost central bulge (ΔL_2) and the volume associated with this bulge is not known, nor is it predictable. Therefore, the ΔL_2 values in Table VI-1 are not indicative of volume changes in the fuel. Even in view of this, it is interesting to note that ΔL_2 values, expressed as ΔL_2 per 10^{20} f/cm³, are quite small for

both zirconia- and ceria-base samples with fission gas release values in excess of 60%. Since these central bulges contain large diameter gas bubbles, these data are not surprising since fission gas which is released cannot be effective in contributing to end-of-life swelling.

The fuel length changes in the annular sector near the surface (ΔL_1) are small. As a result of the cladding restraint, these ΔL_1 values can be considered as indications of fuel volume changes in this annular region. All values fall well below the value of 0.7% ΔL per 10^{20} f/cm³ found for UO₂. Actual values are determined by fuel plasticity, fuel density and the ability of voids to accommodate volume changes due to solid and gaseous fission products. With only a few exceptions, values for ΔL_1 (ΔV) per 10^{20} f/cm³ fall below 0.2 which is indicative of good swelling accommodation within the hot plastic center of the fuel column. The swelling behavior of these fuels is quite similar to that of UO₂.

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