**STOICHIOMETRY EFFECTS IN OXIDE
NUCLEAR FUELS**

**I. POWER RATING REQUIRED
FOR MELTING AND OXYGEN
REDISTRIBUTION IN MOLTEN
CENTER UO_{2+x} FUELS**

J. A. CHRISTENSEN

DECEMBER 1967

**AEC RESEARCH &
DEVELOPMENT REPORT**

ROUTE TO	P.O. NO.	EX. NO.	FILE NO.	DATE

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

PACIFIC NORTHWEST LABORATORY

RICHLAND, WASHINGTON

operated by

BATTELLE MEMORIAL INSTITUTE

for the

UNITED STATES ATOMIC ENERGY COMMISSION UNDER CONTRACT AT(45-1)-1830

3 3679 00060 6675

BNWL-536

UC-25, Metals
Ceramics, and Materials

STOICHIOMETRY EFFECTS IN OXIDE NUCLEAR FUELS
I. POWER RATING REQUIRED FOR MELTING AND OXYGEN
REDISTRIBUTION IN MOLTEN CENTER $\text{UO}_{2\pm x}$ FUELS

By

J. A. Christensen

Ceramics and Graphite Research Section
Materials Department

December 1967

PACIFIC NORTHWEST LABORATORY
RICHLAND, WASHINGTON

Printed in the United States of America
Available from
Clearinghouse for Federal Scientific and Technical Information
National Bureau of Standards, U.S. Department of Commerce
Springfield, Virginia 22151
Price: Printed Copy \$3.00; Microfiche \$0.65

STOICHIOMETRY EFFECTS IN OXIDE NUCLEAR FUELS
I. POWER RATING REQUIRED FOR MELTING AND OXYGEN
REDISTRIBUTION IN MOLTEN CENTER $\text{UO}_{2\pm x}$ FUELS

J. A. Christensen

ABSTRACT

Effects of departures from stoichiometry on heat transfer in $\text{UO}_{2\pm x}$ ($-0.10 \leq x \leq 0.15$) were measured by irradiation experiments employing partially molten fuel specimens. Redistribution of excess oxygen or uranium was measured following irradiation.

TABLE OF CONTENTS

ABSTRACT	iii
LIST OF FIGURES	vii
LIST OF TABLES	xi
INTRODUCTION	1
SUMMARY	2
PROCEDURE	4
Materials Preparation and Characterization	4
Irradiation Procedures	17
Postirradiation Examination	17
RESULTS	18
Metallography	19
Identification of the Fuel Melt Radius	36
Integrated Conductivity Versus O/U	39
Thermal Conductivity Versus Composition and Temperature	41
Variation in Composition Across the Fuel Radius	47
ANALYSIS OF ERROR	62
ADDITIONAL WORK	67
ACKNOWLEDGEMENTS	70
APPENDICES	
A: Raw Data	A.1
B: Calculation of Heat Transfer Parameters	B.1
C: Fuel Surface Temperature Calculations	C.1
D: Calculation of Integrated Conductivity Values	D.1
E: Summary of Heat Transfer Results	E.1
F: Variation in Oxygen and Temperature Distributions with Fractions of Fuel Molten	F.1
G: References	G.1
DISTRIBUTION	Distr.1

LIST OF FIGURES

1	Irradiation Capsule	7
2	Components Used in Fabricating Pneumatically Impacted UO_{2+x} Irradiation Specimens	8
3	$\text{UO}_{2.00}$ After Pneumatic Impaction at 1200 °C	9
4	$\text{UO}_{2.02}$ After Pneumatic Impaction at 1200 °C	10
5	$\text{UO}_{2.05}$ After Pneumatic Impaction at 1200 °C	11
6	$\text{UO}_{2.15}$ After Pneumatic Impaction at 1200 °C	12
7	$\text{UO}_{1.99}$ After Pneumatic Impaction at 1200 °C	13
8	$\text{UO}_{1.90}$ After Pneumatic Impaction at 1200 °C	14
9	Stoichiometry Effect on UO_2 Hardness	16
10	$\text{UO}_{1.90}$ Postirradiation Macrostructure and Fission Fragment Distribution	20
11	$\text{UO}_{1.90}$ Postirradiation Microstructure	21
12	$\text{UO}_{1.99}$ Postirradiation Macrostructure and Fission Fragment Distribution	22
13	$\text{UO}_{1.99}$ Postirradiation Microstructure	23
14	$\text{UO}_{2.02}$ Postirradiation Macrostructure and Fission Fragment Distribution	24
15	$\text{UO}_{2.02}$ Postirradiation Microstructure	25
16	$\text{UO}_{2.05}$ Postirradiation Macrostructure and Fission Fragment Distribution	26
17	$\text{UO}_{2.05}$ Postirradiation Microstructure	27
18	$\text{UO}_{2.15}$ Postirradiation Macrostructure and Fission Fragment Distribution	28
19	$\text{UO}_{2.15}$ Postirradiation Microstructure	29
20	$\text{UO}_{2.05}$ Fuel Core After Sampling with Diamond Core Drills	30
21	Power Rating Required for Center Melting of UO_{2+x} Fuels	31
22	Thermal Conductivity Integrated over the Interval 500 °C - Columnar-Grain-Growth Temperature for UO_{2+x}	32

23	Thermal Conductivity Integrated Between the Columnar-Grain-Growth Temperature and the Melting Temperature for UO_{2+x}	33
24	Integrated Thermal Conductivity for Conventional UO_2 Fuels	34
25	Uranium-Oxygen Phase Diagram	35
26	Annealing Effects on the Microstructures of UO_{2+x}	38
27	Maximum Upward Segregation of Shrinkage Porosity; $\text{UO}_{2.00}$ Specimen	40
28	Mean Thermal Conductivity Between 500 °C and the Melting Temperature for UO_{2+x}	42
29	Mean Thermal Conductivity Between 500 °C and the Columnar-Grain-Growth Temperature for UO_{2+x}	43
30	Mean Thermal Conductivity Between the Columnar-Grain-Growth Temperature and Melting Temperature for UO_{2+x}	44
31	Radial Oxygen Distribution in Irradiated $\text{UO}_{2.00}$; Sampling Plan	49
32	Radial Oxygen Distribution in Irradiated $\text{UO}_{2.00}$	50
33	Radial Oxygen Distribution in Irradiated $\text{UO}_{2.02}$; Sampling Plan	51
34	Radial Oxygen Distribution in Irradiated $\text{UO}_{2.02}$	52
35	Radial Oxygen Distribution in Irradiated $\text{UO}_{2.05}$; Sampling Plan	53
36	Radial Oxygen Distribution in Irradiated $\text{UO}_{2.05}$	54
37	Radial Oxygen Distribution in Irradiated $\text{UO}_{2.15}$; Sampling Plan	55
38	Radial Oxygen Distribution in Irradiated $\text{UO}_{2.15}$	56
39	Oxygen Distribution in UO_{2+x} Following Irradiation; Summary	57
40	Redistribution of Uranium and Oxygen in Irradiated UO_{2+x} Showing Composition Discontinuity at the Solid-Liquid Interface	60
41	Uranium-Oxygen Phase Diagram Showing Both Solidus and Liquidus	61
42	Variation in Melt Radius with Power Rating for a Typical Oxide Fuel	64

43	Error Analysis of Melting Power Rating Results . . .	69
F-1	Hypothetical Phase Diagram	F.2
F-2	Functional Relationship Between Liquidus and Solidus Compositions for UO_{2+x}	F.4
F-3	Variation in Liquid and Solid Compositions as a Function of Melt Radius in $UO_{2.02}$	F.5
F-4	Variation in Liquid and Solid Compositions as a Function of Melt Radius in $UO_{2.05}$	F.6
F-5	Variation in Liquid and Solid Compositions as a Function of Melt Radius in $UO_{2.15}$	F.7
F-6	Decrease in Melting Power Rating with Increase in O/U Showing Both Melting Point and Thermal Conductivity Effects	F.9
F-7	Melt Radius and Stoichiometry Effects on the Melting Power Rating for UO_{2+x}	F.10

LIST OF TABLES

I	Mean Fuel Compositions Studied	5
II	Variation in UO_2 Microhardness with O/U	15
III	Oxygen Migration Effects on Fuel Melting Temperature	47
IV	Precision of Measuring Melt Radii	65
V	Error Associated with Melting Power Rating Measurements	68
A-I	Postirradiation Fuel Dimensions	A.1
B-I	Relative Integrated Thermal Conductivities for Columnar-Grain-Growth and Melting	B.3
C-I	Fuel Surface Temperature Normalization	C.1
E-I	Summary of Computed Integrated and Mean Thermal Conductivities	E.1
F-I	Comparison of Irradiation Test Results with Calculated Effects of Melting Extent on Power Rating Required for Melting in UO_{2+x}	F.8

STOICHIOMETRY EFFECTS IN OXIDE NUCLEAR FUELS
I. POWER RATING REQUIRED FOR MELTING AND OXYGEN
REDISTRIBUTION IN MOLTEN CENTER $\text{UO}_{2\pm x}$ FUELS

J. A. Christensen

INTRODUCTION

Physical, thermal, and electrical properties of pure oxide ceramics are significantly altered by departures from the stoichiometric compositions. Variations which occur can be exploited to improve critical materials properties; or, if not understood, unexpected composition changes may seriously limit the usefulness of ceramic components. For oxides used as nuclear fuels, the most important stoichiometry effects are those reflected as changes in thermal properties. A strong thermal conductivity dependence on stoichiometry has been observed for UO_2 and probably exists for other fissile oxides as well. Thus, fabrication processes must be controlled to yield oxide fuels with optimum compositions.

Experiments were performed at the Pacific Northwest Laboratory to measure the extent of oxygen or uranium redistribution in $\text{UO}_{2\pm x}$ fuels during irradiation with center melting, and to determine redistribution and mean composition effects on fuel structure and thermal profile. Of particular concern were the influences of controlled composition variations on the power rating required to initiate central melting. This area of study has received attention from several investigators. Their efforts as well as comprehensive reviews of other relevant heat transfer studies are documented in References 1 through 8. The need for the present work is two fold:

1. A wide range of compositions was investigated and results quantitatively expressed in terms of heat-transfer parameters used in design of fuel elements. Other existing

studies are either too limited in scope, or were performed in environments too different from those existing in operating fuel elements to be of quantitative technological benefit.

2. Because of the large temperature extremes and gradients experienced by oxide fuels over long periods of time, compound disproportionation and redistribution of components are thermodynamically and kinetically possible. Resulting concentration gradients will affect thermal profiles and, both directly and indirectly, will affect a variety of other characteristics which determine the utility of a material as a fuel (e.g., fission-gas retention, fission-product relocation, specific volume, bulk fuel movements, etc.). Measurements of the equilibrium composition profiles which exist during irradiation are basic to understanding these effects.

SUMMARY

Temperature distributions in 100% dense UO_{2+x} fuels during molten-center irradiation were determined as functions of composition for $-0.10 \leq x \leq 0.15$. Postirradiation radial oxygen redistribution was measured in $\text{UO}_{2.00}$, $\text{UO}_{2.02}$, $\text{UO}_{2.05}$, and $\text{UO}_{2.15}$, using remotely performed coulometric analyses of samples removed with diamond core drills. Results include:

1. The power rating required to initiate center melting decreased continuously with O/U between 1.90 and 2.15. The variation is adequately defined for design purposes by the linear function

$$\int_{500}^{T_m} k dT = -75.8(\overline{\text{O/U}}) + 221 \quad \text{W/cm}$$

where,

T_m = melting point, °C

k = thermal conductivity, W/cm °C

$\overline{O/U}$ = mean atomic ratio in the interval

$$1.90 \leq O/U \leq 2.15.$$

2. This decrease in melting power rating reflects mainly the decrease in melting point as O/U increases above 2.00. Other contributing influences include
 - (a) A decrease in low-temperature (<1700 °C) thermal conductivity for $O/U > 2.00$, while for $O/U < 2.00$ little effect was observed.
 - (b) An apparent increase in high-temperature (>1700 °C) thermal conductivity for both $O/U < 2.00$ and $O/U > 2.00$.
3. Migration of oxygen to the molten center occurred for O/U 's > 2.00 , presumably because of higher oxygen solubility in the melt in equilibrium with the solid. Central compositions of $UO_{2.43}$, $UO_{2.18}$, and $UO_{2.09}$ were measured in fuels with preirradiation uniform compositions of $UO_{2.15}$, $UO_{2.05}$, and $UO_{2.02}$, respectively. Slight oxygen movement both to the center and to the cooler fuel regions was observed in $UO_{2.00}$. The microstructure of UO_{2-x} specimens showed displacement of uranium metal precipitates from the columnar grains to the molten center.

In general, center melting appears to reduce the effects of departures from stoichiometry on fuel properties, since the excess component segregates to the melt.

Microhardness increased continuously from 530 KHN to 880 KHN over the interval $1.90 \leq O/U \leq 2.15$.

PROCEDURE

Oxygen migration and its effect on fuel-temperature distribution during irradiation may be influenced by several variables. These include average O/M, irradiation time, power rating, fuel surface temperature, thermal gradient, oxide purity, oxide grain size, sheath material and temperature, the presence of reactive foreign materials in the system (e.g., temperature sensors), and probably others. The most important variables, assuming ample time for equilibration, are stoichiometry and power rating. Specimens with the compositions listed in Table I were irradiated at a nominal

$$\int_{T_s}^{T_m} k dt^* \text{ of } 80 \text{ W/cm}^2,$$

which yields appreciable center melting of the fuel. Specimens were right circular cylinders and were irradiated with the axis in a horizontal position. Surface temperature of the fuel was $500^\circ\text{C} \pm 50^\circ\text{C}$ which is near the fuel surface temperatures of interest in contemporary thermal fuels.

MATERIALS PREPARATION AND CHARACTERIZATION

The oxide contained <300 ppm of cation impurities, was fine grained, and was encapsulated in AISI 310 stainless steel which is inert to the system environment. No foreign materials were included in the system.

The irradiation assembly was designed to hold a UO_{2+x} ($x \neq 0$) specimen and a $\text{UO}_{2.00}$ specimen of identical geometry which served as an internal standard (Figure 1). Each

* See Appendix B for definition of temperature integrated thermal conductivity.

TABLE I. Mean Fuel Compositions Studied

<u>Capsule</u>	<u>Specimen O/U (As Fabricated)</u>	
	<u>Position A</u>	<u>Position B</u>
SNC-1	2.02	2.00
SNC-2	1.90	2.00
SNC-3	2.05	2.00
SNC-4	1.99	2.00
SNC-5	2.15	2.00

specimen was 5 in. long and had a nominal fuel diameter of 1.375 in. Specimens were fabricated by pneumatically impacting micron size oxide powders of the desired stoichiometry at 250,000 psi and 1200 °C. During impaction, the oxide was contained in AISI 310 stainless steel cans which, after surface machining, served as integral fuel sheaths (Figure 2). This fabrication method was chosen because the temperatures and times employed (1200 °C maximum for 1 hr) permitted retention of initial oxide stoichiometries. Also, oxide porosity and fuel-sheath gap, both of which appreciably affect fuel thermal profile, are minimized and standardized. Oxide powders of the required stoichiometry were produced by blending $\text{UO}_{2.00}$ with $\text{UO}_{2.25}$ or uranium powder. For hyperstoichiometric powders, an O/U reduction of 0.02 which occurred during fabrication was compensated in fabricating specimens. Stoichiometric and hypostoichiometric specimens did not change appreciably in composition during fabrication. Duplicate specimens for each oxide composition were prepared for pre-characterization. Metallographic examination at magnifications to 500X (Figures 3 through 8) showed each specimen to have zero porosity and no fuel-sheath gap. The $\text{UO}_{2.00}$ (Figure 3) consisted of a dense, forged matrix with no intragranular structural changes.

Recrystallization and grain growth occurred in the $\text{UO}_{2\pm x}$, but not in the $\text{UO}_{2.00}$ in which the only apparent boundaries were those of the powder feed particles. Specimens with compositions of $\text{UO}_{2.02}$, $\text{UO}_{2.05}$, and $\text{UO}_{2.15}$ (Figures 4, 5, and 6) had an as-fabricated average grain size of 10 to 15 μ . This consistency in grain size suggests that cation self-diffusion rates are not significantly affected by composition variations. Anion diffusivity increases rapidly with increase in O/U; thus, if cation diffusion also increases with oxygen additions, grain growth rates should be directly proportional to O/U. Structure of the $\text{UO}_{1.99}$ (Figure 7) is not directly comparable with that of the other compositions because the powder used in preparing this material was vacuum annealed at 2000 °C, and thus had a much larger initial grain size. The annealing procedure was undertaken to reduce the O/U from 2.00 to 1.99. Recrystallization and grain growth to an average diameter of 5 to 10 μ occurred in the $\text{UO}_{1.90}$; the uranium, which was added as 100 μ shot, was uniformly dispersed in irregular, 10 to 20 μ diameter inclusions following impaction (Figure 8).

Grain-growth kinetics at various temperatures were studied in an attempt to correlate grain structure with temperature in irradiated fuel cores. Specimens of each composition were double-clad in platinum and an evacuated quartz envelope to prevent compositional changes during heating. They were then annealed at 1200 °C and 1500 °C for 1, 10, and 25 hr and metallographically examined for grain size. Original intentions were to span the temperature interval from 1200 to 1700 °C, since below 1200 °C no grain growth should occur in reasonable times, and above 1700 °C, a thermal-gradient-dependent mechanism, which gives rise to a columnar grain structure, becomes rate controlling in oxide fuels. However, the postannealing condition of specimens exposed to 1500 °C indicated this to be near

FIGURE 1. *Irradiation Capsule*

FIGURE 2. Components Used in Fabricating Pneumatically Impacted UO_{2+x} Irradiation Specimens

500X

75X

FIGURE 3. $UO_{2.00}$ After Pneumatic Impaction at 1200 °C. No Recrystallization Has Occurred [Etchant: 90% H_2O_2 (30%), 10% H_2SO_4].

500X

75X

FIGURE 4. $UO_{2.02}$ After Pneumatic Impactation at 1200 °C. Recrystallization, Grain Growth, and some U_4O_9 Precipitation Is Evident. [Etchant: 90% H_2O_2 (30%), 10% H_2SO_4]

500X

75X

FIGURE 5. $UO_{2.05}$ After Pneumatic Impactation at 1200 °C. Recrystallization and Grain Growth Equivalent to $UO_{2.02}$ and Appreciable U_4O_9 Precipitation Has Occurred. [Etchant: 90% H_2O_2 (30%), 10% H_2SO_4].

500X

75X

FIGURE 6. $UO_{2.15}$ After Pneumatic Impaction at 1200 °C. Recrystallization is Complete but Substantially Less Grain Growth than Was Observed in $UO_{2.02}$ and $UO_{2.05}$ Is Evident. Note the Extensive U_4O_9 Precipitate. [Etchant: 90% H_2O_2 (30%), 10% H_2SO_4].

Unetched

75X

Unetched

500X

75X

FIGURE 7. *UO_{1.99} After Pneumatic Impactation at 1200 °C. Note Localized Recrystallization, Grain Growth, and Uranium Precipitates. [Etchant: 90% H₂O₂ (30%), 10% H₂SO₄]. (Magnifications Reduced 25% During Reproduction.)*

500X

75X

FIGURE 8. $UO_{1.90}$ After Pneumatic Impactation at 1200 °C. Recrystallization and Extensive Grain Growth Has Occurred. Not High Concentration of Uranium Precipitates [Etchant: 90% H_2O_2 (30%), 10% H_2SO_4].

the maximum use temperature for the quartz, and no higher temperature anneals were attempted. No consistent changes in grain size occurred during annealing. Apparently other processes, such as recrystallization and second-phase precipitation which interfere with grain growth, were activated by the anneal.

Microhardness as a function of oxide stoichiometry was also measured as an adjunct to the main experiment. Results of ten different observations for each of the six compositions are given in Table II and Figure 9. Above O/U = 2.00, hardness increased rapidly with increasing O/U in good agreement with other measurements.⁽⁹⁾ The addition of excess uranium reduced the hardness, possibly because the uranium was present as soft inclusions which could not be completely avoided in placing the indenter.

TABLE II. Variation in UO_2 Microhardness with O/U

<u>O/U</u>	<u>Knoop Hardness Number</u>	<u>Range</u>	<u>Mean Deviation</u>
1.90	529	361 - 755	±34.9
1.99	657	516 - 728	±22.3
2.00	662	454 - 770	±28.5
2.02	802	715 - 912	±23.7
2.05	797	696 - 885	±19.6
2.15	881	762 - 1028	±22.2

$$\text{Mean Deviation} = \sqrt{\frac{\sum (\Delta N^2)}{n(n-1)}}$$

ΔN = Difference of average Knoop hardness and hardness reading.

n = Number of samples.

FIGURE 9. *Stoichiometry Effect on UO_2 Hardness; for Corresponding Microstructures see Figures 3 Through 8.*

IRRADIATION PROCEDURES

Specimens were shrink fitted into 2.7 in. diameter, 12.5 in. long aluminum sleeves (Figure 2) which could be inserted into or withdrawn from the reactor at any time during a cycle by means of an attached 3/4 in. diameter guide tube and a system of locks and lead casks. Each sleeve held a UO_{2+x} specimen and a $\text{UO}_{2.00}$ standard, the latter being located at the inner end of the assembly so that it was exposed to the maximum flux experienced by the assembly. With this physical arrangement, deduced heat transfer parameters for the UO_{2+x} specimen relative to the $\text{UO}_{2.00}$ standard (as determined from subsequent postirradiation examination) are minimum values. The irradiation cycle employed for each assembly was as follows.

1. Insertion into the flat flux region over a period of 4 hr. This slow insertion rate insured phase equilibration of the initially two phase UO_{2+x} specimens, thereby preventing formation of structures not representative of equilibrium operating conditions.
2. Irradiation in a constant, flat flux for several hours, i.e., ample time to achieve the equilibrium stoichiometry distribution.
3. Removal from the flux zone as rapidly as possible (several seconds). This rapid quench was intended to inhibit rehomogenization of redistributed oxygen which could be expected if slow cooling were permitted.

POSTIRRADIATION EXAMINATION

Following irradiation, the aluminum sleeves were removed and each specimen and standard was sectioned at the midplane and at a point 1 1/2 in. outward from the midplane. The 1 1/2 in. long segments were impregnated with epoxy resin and metallographically examined on both faces. Both faces were

studied to determine the longitudinal structural uniformity of the fuel cores. Figures 10 through 19 show macrographs, micrographs, and γ - β autoradiographs of the midplane sections of specimens with O/U's of 1.90, 1.99, 2.02, 2.05, and 2.15 and their associated $\text{UO}_{2.00}$ standards. These photographs were used to calculate heat transfer parameters. The use of melt and grain growth radii, which are small relative to the fuel radius, to calculate these parameters is inherently a precise technique because the parabolic temperature distribution existing in a fuel rod results in low gradients near the center. The radial positions of the higher temperature isotherms are, thus, very sensitive to small changes in fuel heat rating or thermal conductivity. Disadvantages associated with this technique include the large ΔT 's involved, and the fact that fuel structure is representative only of peak or terminal operating conditions.

Radial sampling of fuel sections to determine oxygen distribution was accomplished using 1/4 in. OD x 0.190 in. ID diamond core drills. Full length cores were removed from the fuel section at various radial positions (Figure 20) and analyzed for O/U by controlled potential coulometry. Since this method is usable only for O/U > 2 and no suitable technique was available for measuring O/U in hypostoichiometric oxides, only the stoichiometric and hyperstoichiometric specimens were sampled.

RESULTS

Integrated thermal conductivity values from 500 °C to the temperature required to initiate columnar grain growth (T_{gg}), 500 °C to melting (T_m), and 1700 °C to melting, were calculated from measurements of the melt and columnar grain growth radii from Figures 10 through 19 (see Appendix A for mensuration data).

Results presented in Figures 21 through 23 are all based on the most reasonable $\int k dT$ versus T curve which can be constructed for conventional stoichiometric UO_2 fuels,⁽¹⁰⁾ (Figure 24). Methods employed in computing relative integrated thermal conductivities are detailed in Appendix B.

Melting temperatures as a function of composition (Figure 25), were obtained from recent phase equilibrium studies,^(11,12) and T_{gg} has been measured, for compositions close to $O/U = 2$, as $1700^\circ C$.⁽¹³⁾ Grain-growth temperatures, however, may vary with large departures from oxide stoichiometry; thus, results are expressed in terms of T_{gg} rather than a specific temperature. Phenomena which pertain to fuel utility (gas release, fuel redistribution, fission-product relocation, etc.) seem to be associated with the same mechanisms which give rise to columnar grain growth; thus, the use of the arbitrary quantity, T_{gg} , may indeed be more meaningful than quoting specific temperatures.

METALLOGRAPHY

Postirradiation metallography consisting of macro-examination, γ - β autoradiography, and micro-examination at magnifications to 500X, was performed on sections from each specimen and standard. Results were generally as anticipated (Figures 10 through 19). In agreement with Bain's observations on high density, restrained UO_2 ,⁽¹⁴⁾ the recrystallized fuel regions consisted principally of large pie-shaped, columnar grains. No lenticular voids and few small columnar grains were present. A few radially elongated pores were observed in hyperstoichiometric specimens (Figure 17). Specimens with mean O/M 's < 2.00 were enriched in metallic uranium in the once molten center at the expense of the surrounding columnar grains (Figures 11 and 13). At $\overline{O/M} = 2.05$, the columnar grain region contained

FIGURE 10. $UO_{1.90}$ Postirradiation Structure Compared with that of $UO_{2.00}$ Internal Standard. Areas Outlined in White are Shown at Higher Magnification in Figure 11.

0.104 cm

SNC-2A $\text{UO}_{1.90}$
Unetched

0.004 cm

Near Outer Edge; Small Irregular U Precipitates
 $\text{O/U} = 1.90$

0.004 cm

Mid-Radius; Mostly Small Oriented U Precipitates
 $\text{O/U} = 1.90 - 1.95$

0.004 cm

Near Center; Large Oriented U Precipitate
 $\text{O/U} \approx 1.80$

Note "Coring" Effect in Once-Molten Central Region

SNC-2A $\text{UO}_{1.90}$
Unetched

FIGURE 11. Microstructure of Irradiated $\text{UO}_{1.90}$ and Associated $\text{UO}_{2.00}$ Standard. See Preceding Figure for Macrographs and Autoradiographs.

FIGURE 12. $UO_{1.99}$ Postirradiation Structure Compared with that of $UO_{2.00}$ Internal Standard. Areas Outlined in White are Shown at Higher Magnification in Figure 13.

FIGURE 13. Microstructure Associated UO_2 . Figure for Macr

SNC-4B, $\text{UO}_{2.00}$ 0.102 cm SNC-4A, $\text{UO}_{1.99}$, Etched 0.101 cm
Note Coring as in $\text{UO}_{1.90}$

0.101 cm

0.004 cm

0.004 cm

SNC-4A, $\text{UO}_{1.99}$
Unetched

FIGURE 13. Microstructure of Irradiated $\text{UO}_{1.99}$ and Associated $\text{UO}_{2.00}$ Standard. See Preceding Figure for Macrographs and Autoradiographs.

radius; Mostly Small Oriented U Precipitates

Near Center; Oriented U Precipitates

FIGURE 14. $UO_{2.02}$ Postirradiation Structure Compared with that of $UO_{2.00}$ Internal Standard. Areas Outlined in White are Shown at Higher Magnification in Figure 15.

SNC-1A, $\text{UO}_{2.02}$ 0.10 cm

Note: Increased Equiaxed Grain Size Relative to $\text{UO}_{2.00}$;
Apparent Fine Precipitate Near Center and High
Contrast of Central Grains.

FIGURE 15. Microstructure of
Associated $\text{UO}_{2.0}$
Figure for Macro

SNC-1B, $\text{UO}_{2.00}$

0.10 cm

SNC-1A, $\text{UO}_{2.02}$ 0.10 cm

Note: Increased Equiaxed Grain Size Relative to $\text{UO}_{2.00}$;
Apparent Fine Precipitate Near Center and High
Contrast of Central Grains.

FIGURE 15. Microstructure of Irradiated $\text{UO}_{2.02}$ and
Associated $\text{UO}_{2.00}$ Standard. See Preceding
Figure for Macrographs and Autoradiographs.

FIGURE 16. $UO_{2.05}$ Postirradiation Structure Compared with that of $UO_{2.00}$ Internal Standard. Areas Outlined in White are Shown at Higher Magnification in Figure 17.

- Notes: 1. Orange-Peel and Feathery Precipitate from Edge of Columnar Grains Inward, X-ray
(UO_2 , 05) Diffraction Shows Only Fluoride Phase.
2. Greatly Enhanced Equiaxed Grain Growth Relative to UO_2 , 00.
3. Radially Elongated Pores Near Outer Edge of Columnar Grains.
4. Large "Bubble" at top (Left) of Molten Zone
5. Exceptional Contrast of Large Grains; This is Thought to Be
Caused by Preferred Orientation of U_4O_9 Precipitates.

FIGURE 17. Micro
Asso
Figu

- Notes: 1. Orange-Peel and Feathery Precipitate from Edge of Columnar Grains Inward, X-ray
(UO_{2.05}) Diffraction Shows Only Fluoride Phase.
2. Greatly Enhanced Equiaxed Grain Growth Relative to UO_{2.00}.
3. Radially Elongated Pores Near Outer Edge of Columnar Grains.
4. Large "Bubble" at top (Left) of Molten Zone
5. Exceptional Contrast of Large Grains; This is Thought to Be
Caused by Preferred Orientation of U₄O₉ Precipitates.

FIGURE 17. Microstructure of Irradiated UO_{2.05} and Associated UO_{2.00} Standard. See Preceding Figure for Macrographs and Autoradiographs.

FIGURE 18. $UO_{2.15}$ Postirradiation Structure Compared with that of $UO_{2.00}$ Internal Standard. Areas Outlined in White are Shown at Higher Magnification in Figure 19.

- Notes:
1. Massive Precipitates Near Center; These were Identified by X-ray Diffraction as U_3O_8 .
 2. Orange-Red and Feathery Precipitate in Columnar and Large Equiaxed Grains, X-ray Diffraction Showed only Fluorite Phase.
 3. Greatly Enhanced Equiaxed Grain Growth Relative to $UO_2.00$.
 4. Large "Bubble" at Top (Left) or Molten Zone.
 5. Exceptional Contrast of Large Grains, Thought to Reflect Preferred Orientation of U_4O_9 Precipitates.

FIGURE 19.

Micronstruc
Associate
for Macro

- Notes: 1. Massive Precipitates Near Center; These were Identified by X-ray Diffraction as U_3O_8 . ($UO_{2.15}$) 2. Orange-Peel and Feathery Precipitate in Columnar and Large Equiaxed Grains, X-ray Diffraction Showed only Fluorite Phase. 3. Greatly Enhanced Equiaxed Grain Growth Relative to $UO_{2.00}$. 4. Large "Bubble" at Top (Left) or Molten Zone. 5. Exceptional Contrast of Large Grains; Thought to Reflect Preferred Orientation of U_4O_9 Precipitates.

FIGURE 19. Microstructure of Irradiated $UO_{2.15}$ and Associated $UO_{2.00}$. See Preceding Figure for Macrographs and Autoradiographs.

FIGURE 20. *UO_{2.05} Fuel Core After Sampling
with Diamond Core Drills*

FIGURE 21. Power Rating Required for Center Melting of UO_{2+x} Fuels

FIGURE 22. Thermal Conductivity Integrated over the Interval 500 °C; Columnar-Grain-Growth Temperature (T_{gg}) for UO_{2+x} .

FIGURE 23. Thermal Conductivity Integrated over the Interval Columnar-Grain-Growth Temperature (T_{gg}) and the Melting Temperature (T_m) for UO_{2+x} .

FIGURE 24. Integrated Thermal Conductivity for Conventional UO_2 Fuels.

FIGURE 25. Uranium-Oxygen Phase Diagram

a second phase thought to be U_4O_9 (Figure 17). Much more of this precipitate developed at $\overline{O}/M = 2.15$, and massive inclusions, subsequently identified by X-ray diffraction as U_3O_8 , appeared in the once molten region (Figure 19). Specimens containing excess oxygen exhibited regions of large equiaxed grain growth surrounding the columnar grains. This is consistent with MacEwan's observations of increased grain-growth rates in UO_{2+x} relative to stoichiometric UO_2 .⁽¹⁵⁾ The large shrinkage or gas voids found in most sections were useful in analyzing the extent of fuel melting as discussed below. A consistent upward displacement of the thermal center was exploited in characterizing convection heat transfer in the molten oxide.⁽¹⁶⁾

IDENTIFICATION OF THE FUEL MELT RADIUS

Structural features corresponding to the melt radius are somewhat in question. Lyons et al.⁽¹⁷⁾ report that melting occurred to the edge of the high-density region of the columnar grains, while Horn and Christensen⁽¹⁸⁾ and Robertson⁽³⁾ favor the outer edge of the porous central, columnar-grain region. On a γ - β autoradiograph, these correspond, respectively, to the outer and inner edges of the fission-fragment depleted zone. Since the measurements reported here are all relative to $UO_{2.00}$ internal standards, the choice of melt radius is relatively immaterial if consistency is maintained. Only for the $UO_{1.90}$ and $UO_{2.00}$ pair did the choice of melt radius significantly influence calculated conductivity integrals. This effect is noted on Figures 21 and 23.

Large "central" voids were observed in the fuel specimens during postirradiation metallography. These voids (or portions thereof) were displaced upward relative to the geometric and thermal centers of the fuel (Figures 10, 14, 16, 18). Two types of displaced voids were apparent: those which

created a perturbation in the fission fragment distribution and those which did not. Occurrence of the former type was restricted to hyperstoichiometric specimens (Figure 14, top); the latter were observed only in the stoichiometric standards (Figure 14, bottom). These observations suggest that voids of the former type (perturbing voids) existed during irradiation, while the latter (nonperturbing voids) are probably shrinkage cavities derived from the decrease in volume which occurs during solidification of the molten center.⁽¹⁹⁾ Since all specimens contained no initial porosity and had zero fuel-sheath gap,* creation of a central void during operation implies substantial gas desorption or dissociation from the fuel. For fuels containing excess oxygen the volatile species presumably is $\text{UO}_3(\text{g})$. This hypothesis is supported by results of the annealing studies. Heating UO_{2+x} specimens to 1500 °C caused the formation of small spherical voids which appear to be gas bubbles (Figure 26).

Both types of void segregated upward. Voids existing during irradiation should behave much like the bubble in a spirit level with the upper surface of the void coinciding with the solid - liquid interface. In general, this upper surface tended to coincide with the melt radius postulated by Lyons. Voids of this type bear an interesting resemblance to those associated with the phenomenon known as "upward drilling" in glass tank refractories.⁽²⁰⁾ The mechanism by which upward drilling occurs may, in fact, provide an explanation for displacement of gas filled voids in ceramic fuels. Convection currents should forestall solidification in the upper reaches

* An irreversible increase of approximately 1.3 mm in fuel pin diameter was required to accommodate the differential expansion and volume change on melting of the fuel. No systematic variation was observed. Each pin contained an end plenum which could accommodate axially displaced fuel.

500X

Before

100X

After

FIGURE 26. Annealing Effects on the Microstructures of UO_{2+x} . Specimen is Pneumatically Impacted $UO_{2.05}$ Before and After Annealing 25 hr at 1500 °C (Specimen was Platinum-Encapsulated to Prevent Oxygen Loss). Note Disappearance of U_4O_9 Precipitates and Appearance of Many Grain Boundary Gas Bubbles During the Annealing Cycle.

of the molten zone, thus causing upward segregation of the shrinkage porosity. Given this situation, melting must have occurred to at least the outer surface of the shrinkage porosity. Figure 27, which shows the maximum observed upward segregation of shrinkage porosity, clearly illustrates the exact coincidence of the outer surface of the displaced void with the solid - liquid interface postulated by Lyons et al.

INTEGRATED CONDUCTIVITY VERSUS O/U

The conductivity integral from 500 °C to melting for 100% TD polycrystalline UO_2 , is inversely related to O/U via an apparently smooth, continuous function which decreases at a rate proportional to O/U (Figure 21; for computations and numerical tabulations see Appendices C, D, and E). For fuel design purposes, the relationship between the melting power rating and oxide composition is adequately expressed by

$$\int_{500\text{ }^{\circ}\text{C}}^{T_m} k dT = -75.8 (\overline{\text{O/U}}) + 221 \text{ W/cm}$$

for $1.90 \leq \text{O/U} \leq 2.15$ ($\overline{\text{O/U}}$ is the average fuel composition). This is the principal technological result of these studies inasmuch as it relates the basic fuel thermal parameter, i.e., the power rating required for center melting, to average oxide composition. The above equation has no specific theoretical implications since it represents the sum of several mechanisms which contribute to the thermal conductivity.

Determinations of integrated conductivities over smaller temperature intervals are also useful in that they provide semiquantitative understanding of the variables which contribute to the integral-to-melting. Figure 22 shows the

Macrograph

↑
Up During
Irradiation

Autoradiograph

FIGURE 27. *Maximum Upward Segregation of Shrinkage Porosity; $UO_{2.00}$ Specimen*

integrated conductivity across the unrecrystallized oxide (500 °C - T_{gg}); the integrated conductivity between the columnar-grain-growth terminus and the melt radius (T_{gg} - T_m) is given in Figure 23. The former was measured directly from Figures 10 through 19 and the latter was computed as the difference:

$$\int_{500\text{ }^{\circ}\text{C}}^{T_m} k dT - \int_{500\text{ }^{\circ}\text{C}}^{T_{gg}} k dT = \int_{T_{gg}}^{T_m} k dT .$$

The integral to T_{gg} was insensitive to composition changes for O/U < 2.00 and O/U > 2.05; while, between UO_{2.00} and UO_{2.05}, a decrease in integrated conductivity with increasing O/U occurred. This trend is also evident in the thermal conductivity versus O/U curve (500 °C - T_{gg}, Figure 29).

Although these variations may reflect as yet unmeasured stoichiometry effects on columnar grain growth, they are also tenable in terms of anticipated effects on heat-transfer mechanisms as discussed in the following section.

The integral from T_{gg} to melting (Figure 23) reaches a minimum near O/U = 2, and rises more rapidly as a function of stoichiometry for O/U > 2 than for O/U < 2.

THERMAL CONDUCTIVITY VERSUS COMPOSITION AND TEMPERATURE

Average thermal conductivities were computed from measured integrated conductivities by dividing the value of the integral by the temperature interval which it spans. Results are no more precise than assigned specific grain growth and melting temperatures which, in general, are not well known. Conductivity - composition curves (Figures 28, 29, and 30) show trends similar to the integrated conductivity curves from which they are derived.

FIGURE 28. Mean Thermal Conductivity Between 500 $^{\circ}\text{C}$ and Melting Temperature for UO_{2+x} .

FIGURE 29. Mean Thermal Conductivity Between 500 °C and the Columnar-Grain-Growth Temperature for UO_{2+x} (T_{gg} Assumed Constant at 1700 °C).

FIGURE 30. Mean Thermal Conductivity Between the Columnar-Grain-Growth Temperature (T_{gg}) and the Melting Temperature (T_m) for $UO_{2\pm x}$ (T_{gg} Assumed Constant at 1700 °C)

The low temperature results (500 °C - T_{gg} , Figure 29) are most interesting because a basis for anticipating stoichiometry effects exists for this temperature regime. In the absence of data to the contrary, the temperature required for columnar-grain-growth was assumed independent of oxide composition. Data in Figure 29 are consistent with theoretical expectations in that:

1. For $O/U < 2.00$, much of the excess uranium existed as second phase inclusions which contribute little toward altering thermal conductivity.
2. For $O/U > 2.00$, the excess oxygen was in solution and represented phonon scattering centers which should be very effective in reducing the lattice conductivity. At $UO_{2.05}$, conductivity is reduced to approximately that corresponding to a phonon mean-free path on the order of the lattice spacing. No additional decrease in conductivity with further increase in O/U should occur.⁽²¹⁾
3. For very high O/U (i.e., 2.15) it is reasonable to expect precipitation of U_4O_9 or some other, higher oxide phase so that as composition varies, the matrix changes only in the proportion of the two phases present without significant change in composition within a particular phase. As with UO_{2-x} , then, the thermal conductivity should be relatively unaffected by small compositional changes within the two-phase region.

If, as suspected, the addition of excess oxygen to $UO_{2.00}$ decreases the temperature at which columnar grains form,⁽¹⁵⁾ the extent to which the conductivity changes in the interval $2.00 \leq O/U \leq 2.05$ should be reduced from that shown in Figure 29. Conceivably, most of this change reflects a composition effect on grain growth.

The high temperature results ($T_{gg} - T_m$, Figure 30) are even less precise because they represent a temperature interval in which both boundaries are uncertain. Thus, a discussion of the "data" is at best academic, but is included, with appropriate reservations, in the interest of completeness.

Two measurements of excess oxygen effects on UO_2 melting point exist.^(12,22) Although individually subject to large errors, the two independent studies yielded nearly identical results (Table III, Figure 25). These results were employed in calculating mean conductivities. In intervals bounded on one side by the melting temperature, the question of what melting temperature to assign was further complicated by the uncertainty with which the composition of the solid at the solid - liquid interface was known. Results (Figure 30) were calculated for two different cases:

1. Assuming no composition discontinuity at the molten interface; and
2. Assuming the most likely discontinuity which can be deduced from radial samples.

Both curves show an increase in conductivity as a function of composition on both sides of the stoichiometric composition. This effect is probably real, since the expected decrease in columnar-grain-growth temperature for $O/U > 2.00$ would be reflected as an even greater increase in thermal conductivity. The results are relevant to observed increases in UO_2 thermal conductivity above about 1500 °C.⁽¹⁰⁾ If, as believed, the high temperature thermal conductivity increase in UO_2 represents an electronic excitation component, an increase in carrier (n or p) density may cause an increase in thermal conductivity.^(4,23) The apparently more pronounced effect of adding p-type carriers (holes) may reflect a higher electron mobility relative to holes, or may indicate incomplete dissolution of the metal in UO_{2-x} . A qualitatively

similar argument develops from a consideration of the excess concentration of uranium or oxygen ions introduced by departures from stoichiometry. For very high O/U's (2.15) the integral from T_{gg} - T_m decreases greatly, mainly because of the rapid decrease in T_m as O/U increases above 2.00 (Table III and Figure 25).

TABLE III. Oxygen Migration Effects on Fuel Melting Temperature

Solid Fuel Composition (O/U)			Melting Temperature	
Average	At Molten Boundary		No	
	Discontinuity	Discontinuity	Discontinuity	Discontinuity
2.000	2.000	2.002	2790	2800
2.02	2.005	2.04	2800	2745
2.05	2.02	2.13	2780	2520
2.15	2.06	2.25	2710	?
1.90	1.95*	1.80	2760	2560

* Estimated from metallography (Figure 11).

VARIATION IN COMPOSITION ACROSS THE FUEL RADIUS

Integrated conductivities can be discussed in terms of average oxide compositions; however, in differentiating these quantities to yield thermal conductivity values, the temperatures corresponding to salient structural features (i.e., T_{gg} and T_m) must be known. Since these quantities, and in particular T_m , vary with oxide composition, redistribution of oxygen during irradiation will affect their calculated values. Significant radial oxygen redistribution has been observed in irradiated, nearly stoichiometric fuels;⁽²⁴⁾ and some possible causes and consequences have been discussed.^(25,26) In fuels differing from the stoichiometric composition as much as the specimens used in this study, severe radial oxygen

redistribution was expected. It was thus necessary to develop methods for measuring oxygen concentration gradients within a fuel body. This was accomplished by diamond core drilling 4 cm long, 0.43 cm diameter longitudinal samples from various radial positions in a segment cut from a specimen, and subsequently analyzing the drillings for O/U by controlled potential coulometry.⁽²⁷⁾ No suitable analytical technique for measuring O/U's below 2.00 was available; however, estimates based on metallography were possible.

A typical specimen after drilling is shown in Figure 20. Results of measurements for specimens with mean compositions of $\text{UO}_{2.00}$, $\text{UO}_{2.02}$, $\text{UO}_{2.05}$, and $\text{UO}_{2.15}$ are given in Figures 31 through 38. Slight, but significant, migration of oxygen from the columnar grains outward, and to some extent to the fuel center, occurred in the pneumatically impacted $\text{UO}_{2.00}$. A maximum O/U of 2.013 was measured near the sheath and an O/U minimum in the nonmolten columnar grains was also apparent (Figures 31 and 32). Specimens with O/U's > 2.00 experienced much more oxygen redistribution during irradiation than did the stoichiometric standards. The $\text{UO}_{2.02}$ (average) varied in postirradiation O/U from 2.007 near the sheath, to a minimum of 2.000 near the outer edge of the columnar grains, to 2.095 in the molten center (Figures 33 and 34). For the $\text{UO}_{2.05}$ (average) specimen, O/U's as high as 2.18 in the molten center and a decrease with no minimum to 2.01 near the sheath were measured (Figures 35 and 36). The specimen with an initial uniform composition of $\text{UO}_{2.15}$ had O/U's as high as 2.43 in the once molten region (Figures 37 and 38). Oxygen relocation results are summarized in Figure 39. In addition to the coulometric analyses, a portion of each drilled sample was studied by X-ray diffraction. Only fluorite phases were detected except for drillings from the once molten region of the nominal $\text{UO}_{2.15}$ fuel which

Position	O/U (± 0.001)
A	2.0045
B	2.0013
C	2.0042
D	2.0093, 2.0131*
E	2.0036
F	2.0042

*Duplication Sample Confirmed High O/U

FIGURE 31. *Radial Oxygen Distribution in Integrally Clad, Pneumatically Impacted $UO_{2.00}$ Following Irradiation. Circles Show Locations of 0.190 in. diam, 1.3 in. Long Samples Removed with Diamond Core Drill and Coulometrically Analysed for O/U.*

FIGURE 32. Radial Oxygen Distribution in Integrally Clad, Pneumatically Impacted $UO_{2.00}$ Following Irradiation. (Specimen SNC-2B) Specimen Rapidly Withdrawn from Flux

Specimen SNC-1A

Position	O/U (± 0.001)
A	2.097
B	2.014
C	2.003
D	2.002
E	2.007

FIGURE 33. *Radial Oxygen Distribution in $UO_{2.02}$ Following Irradiation. Circles Show Locations of 0.190 in. diam, 1.3 in. Long Samples Removed with Diamond Core Drill and Coulometrically Analysed for O/U.*

FIGURE 34. Radial Oxygen Distribution in Integrally Clad, Pneumatically Impacted $UO_{2.02}$ Following Irradiation. (Specimen SNC-1A) Specimen Rapidly Withdrawn from Flux

Specimen SNC-3A

Position	O/U (± 0.001)
A	2.180
B	2.164
C	2.086
D	2.021
E	2.013
F	2.006

FIGURE 35. Radial Oxygen Distribution in $UO_{2.05}$ Following Irradiation. Circles Show Locations of 0.190 in. diam, 1.3 in. Long Samples Removed with Diamond Cure Drill and Coulometrically Analysed for O/U

FIGURE 36. Radial Oxygen Distribution in Integrally Clad, Pneumatically Impacted $UO_{2.05}$ Following Irradiation. (Specimen XNC-3A) Specimen Rapidly Withdrawn from Flux

Specimen SNC-5A

Position	O/U (± 0.001)
A	2.378
B	2.438
C	2.207
D	2.168
E	2.079
F	2.043

FIGURE 37. Radial Oxygen Distribution in $UO_{2.15}$ Following Irradiation. Circles Show Locations of 0.170 in. diam, 1.3 in. Long Samples Removed with Diamond Core Drill and Coulometrically Analysed for O/U.

FIGURE 38. Radial Oxygen Distribution in Integrally Clad, Pneumatically Impacted $UO_{2.15}$ Following Irradiation. (Specimen SCN-5A) Specimen Rapidly Withdrawn from Flux

FIGURE 39. Oxygen Distribution in UO_{2+x} Following Irradiation; Summary.

contained large quantities of U_3O_8 . This is consistent with the occurrence of massive second phase precipitates (evidently U_3O_8) in the central regions of this specimen (Figure 19).

Although methods for measuring radial composition variations in specimens with average O/U's < 2.00 were not available, examination of the microstructure (Figures 11 and 13) showed a nonuniform distribution of uranium precipitates. For the $UO_{1.90}$, much of the free uranium had moved from the nonmolten columnar grains to the molten region where it precipitated as massive equiaxed inclusions. Most inclusions contained a spherical void which appeared to be a shrinkage cavity. The O/M's of the solid and liquid at the molten boundary were estimated as 1.95 and 1.80 from Figure 11.

The observed movement of oxygen to the fuel center was not anticipated; just the inverse had been predicted from extrapolations of low temperature composition-oxygen pressure-temperature equilibrium data.⁽²⁵⁾ In retrospect, it seems likely that the model which predicts oxygen movement to the cooler portions of the fuel does not apply to the present experimental situation because it fails to consider the presence in the system of a reactive second phase, i.e., the molten oxide. Experimental results which purport to show oxygen migration down the thermal gradient in UO_{2+x} fuels have been published.⁽⁷⁾ These conclusions were based on metallography which is strikingly similar to that shown in Figures 17 and 19. The confusion stems from misidentification of the oxygen rich phase; i.e., the UO_2 was identified as U_4O_9 and vice versa in Reference 7. Were it not for the analytical results, a similar conclusion might have been drawn from the present experiments. The analyses show unequivocally, however, that oxygen migrates toward the center of partially molten UO_{2+x} fuels.

The migration of the excess component to the molten region may be explained by a higher oxygen or uranium solubility in the melt than in the solid; i.e., the composition of the solid in equilibrium with the liquid differs from that of the liquid. This difference is represented by the composition increment separating the solidus and the liquidus on typical temperature-composition phase diagrams. This is illustrated in Figure 40 which is similar to the summarized oxygen migration data shown in Figure 39, except that samples which straddled the liquid-solid interface have been discarded. This permits drawing crude concentration distribution curves for the solid and for the liquid. The increment by which these curves fail to coincide at the solid-liquid boundary, represents the difference in solid-liquid equilibrium composition. These data are most conveniently expressed as a conventional temperature-composition equilibrium phase diagram. Figure 41 shows such a diagram that was constructed from the composition discontinuities derived in Figure 40, and from the solidus points shown in Figure 25. The data place the melting point maximum very near the stoichiometric composition. Uranium segregated to the melt in the $\text{UO}_{1.99}$ specimen, and slight oxygen segregation to the melt occurred in the $\text{UO}_{2.002}$. The liquidus maximum, thus, must exist at a composition in the interval $1.99 < (\text{O/M})_{\text{LM}} < 2.002$. For the composition $(\text{O/M})_{\text{LM}}$, no discontinuity should occur at the solid-liquid interface.

In summary, center melting appears to provide a sink for excess components, thus reducing their effect on solid fuel properties. Distribution of the excess component and associated thermal properties may be markedly different in nonstoichiometric fuels with no center melting, and might also be sensitive to the volume fraction of fuel which is molten during irradiation.

FIGURE 40. Redistribution of Uranium and Oxygen in UO_{2+x} Fuels During Irradiation with Partial Fuel Melting. Note Composition Discontinuity at the Solid-Liquid Interface

FIGURE 41. Uranium-Oxygen Phase Diagram Derived from Oxygen Redistribution Measurements in Irradiated UO_{2+x}

ANALYSIS OF ERROR

Errors inherent in some of the data have been briefly discussed. Uncertainty in melting and grain growth temperatures detract appreciably from the precision of the thermal conductivity results as pointed out. The radial O/U surveys are very precise in terms of the analytical procedures involved; however, the results would be more informative if finer sampling techniques could be employed.

The correlation between integrated conductivity to melting and mean fuel composition (Figure 21) is suggested as useful for fuel element design. Thus, it is important to be aware of the quantitative error associated with the data. Sources of imprecision in the correlation include:

1. Measurement of the postirradiation melt radius.
2. Effects of variations in the fraction of fuel molten on the composition of the solid and, thus, on the temperature distribution in the solid.
3. Actual detection or definition of the melt radius.
4. Variation in fuel-sheath gap ΔT between specimen and standard.
5. Uncertainties in analyzing the composition or stoichiometry.
6. Structural differences between specimen and standard, i.e., differences in pore shape, orientation, or distribution.
7. Varying impurity content.
8. Random variations in irradiation condition of the specimens, e.g., crack distribution.
9. Flux gradients along the capsule length.

These error sources are considered as follows:

1. Measurement of the Postirradiation Melt Radius can introduce direct and significant errors into the results. In these measurements, made from the photomicrographs, high precision is thwarted not only by the physical limitations of measurement, but also by the fact that a molten zone is never an exactly defined, perfectly round cylinder. Molten zone diameters typical of these tests can be measured to ± 0.25 mm or better. Effects of this variation on heat-rating measurements were estimated using Figure 42 which plots the molten zone diameter as a function of heat rating for a typical oxide fuel. At the nominal heat rating at which these tests operated, the molten zone diameter is changing at a rate of approximately 5% per kW/ft. Assuming that the melt diameter can be measured to ± 0.25 mm, precisions which should be applied to individual specimens are tabulated in Table IV. Since the heat rating enters directly into the computation of relative integrated conductivities required for melting in both the numerator and the denominator (Appendix C), the cumulative error in integrated conductivity (last column, Table IV) is the sum of the individual errors of A and B specimens.
2. Variations in the Molten Fraction may cause large variations in the integrated conductivity to melting. These variations are not, however, random errors since they can be computed. Appendix F develops computational procedures for compensating variations in the extent of melting.
3. Detection of the Melt Radius is a problem because, as previously discussed, two interpretations of what features signify melting exist. For these relative tests, probably little error was introduced if

FIGURE 42. Variation in Melt Radius with Power Rating for a Typical Oxide Fuel; Data Courtesy of G.R. Horn.

TABLE IV. Precision of Measuring Melt Radii

Capsule SNC	$\overline{O/U}$	Fuel Radius r_o , mm	Melt Diameter $D_m \pm 0.5$ mm	D_m/D_o	$\frac{\Delta}{q/L}$ (Power Rating) $fkdT$		Uncertainty $\pm W/cm$	$\pm \% \int_{500}^{T_m} kdT$ $^{\circ}C$
2 A	1.90	33.2	7.9	0.74/0.23	0.2	0.4	1.05	1.4%
B	2.00	33.6	11.1	0.34/0.33	0.2	0.4	1.05	1.4%
4 A	1.99	38.6	20.0	0.52/0.51	0.25	0.55	1.45	2.0%
B	2.00	36.7	16.7	0.41/0.45	0.3	0.55	1.45	2.0%
1 A	2.02	36.3	16.6	0.46/0.45	0.3	0.6	1.60	2.3%
B	2.00	35.6	14.7	0.42/0.41	0.3	0.6	1.60	2.3%
3 A	2.05	34.5	14.0	0.41/0.40	0.3	0.45	1.20	1.9%
B	2.00	34.5	11.1	0.32/0.31	0.15	0.45	1.20	1.9%
5 A	2.15	33.8	17.6	0.53/0.52	0.35	0.65	1.70	3.0%
B	2.00	35.6	15.9	0.45/0.44	0.3	0.65	1.70	3.0%

consistency was maintained. However, in converting relative data to absolute data, the uncertainty in melt radius location must be recognized as a potential bias of approximately 7 W/cm in the integrated conductivity to melting for the standard.

4. Fuel-Sheath Gap Variations could not influence temperature distribution appreciably because of the low fuel surface-heat flux (280,000 Btu/hr-ft²). Also, specimens were made with no cold fuel-sheath gap; thus, sufficient interaction between fuel and sheath existed to cause yield in the sheath in all cases. A high, constant interfacial pressure was thus maintained. These high pressures result in high gap conductances* for which the magnitude of the ΔT associated with a given fractional conductance variation is low. Because of these considerations, no concern over gap ΔT variations seems justified.
5. Composition and Stoichiometry are accurately known. Duplicate specimens of each composition were fabricated simultaneously with the irradiation specimens and were used for metallographic and compositional characterization. The method used for O/U analyses (controlled potential coulometry) is routinely performed in these laboratories. This is a very precise technique capable of determining O/U to ± 0.0005 for $2.000 < O/U < 2.020$.⁽²⁷⁾ For higher O/U, the precision is somewhat less but is still at least as good as any other method. Coulometry has the single disadvantage of being useful only for oxides with O/M's > 2 .
6. Structural Differences, (e.g., porosity fraction, shape, size and distribution) do significantly influence ceramic thermal properties. The materials studied were

* A conductance of 2500 Btu/hr-ft²-°F was assumed in calculating temperature profiles.

- deliberately fabricated with nominally zero porosity and a uniform, small grain size to avoid these differences.
7. Cation Impurity Content of all oxide materials was less than approximately 300 ppm which is too low to significantly affect thermal conductivity in the temperature interval considered in these studies.
 8. Variations in Irradiation Conditions are indeterminant, but are not specifically suspected of introducing error into the results. For these highly restrained specimens in particular, fuel cracking has no effect on temperature distribution.⁽¹⁴⁾
 9. Flux Gradients often account for anomalous irradiation test results. These tests were performed in a facility having a uniform flux region greater than 10 ft in length. Peak-to-peak flux variation during a given cycle over the facility length has been measured using foil activation techniques as about 5%. To check this, one assembly containing two, presumably identical, $\text{UO}_{2.00}$ fuel specimens was subjected to the standard irradiation cycle. The conductivity integral to melting for the two standards (computed from the metallography using techniques developed in Appendix B) differed by 5%. This is equivalent to approximately ± 1.6 W/cm in the integral from 500 °C to melting.

Cumulative errors are tabulated in Table V and are plotted in Figure 43.

ADDITIONAL WORK

In addition to a long list of desirable peripheral studies, mostly of a laboratory nature, a particularly vital experiment suggests itself. This is to reproduce the measurements of oxygen redistribution in these same fuel materials operating just below center melting. Results of

TABLE V. Error Associated with Melting Power Rating Measurements

Error Source	Uncertainty % of $\left[\begin{array}{c} T_m \\ k \, dT \\ 500 \, ^\circ\text{C} \end{array} \right]$				
	SNC-2 UO _{1.90}	SNC-4 UO _{1.99}	SNC-1 UO _{2.02}	SNC-3 UO _{2.05}	SNC-5 UO _{2.15}
(1) Measurement of Melt Radius	±1.4	±2.0	±2.3	±1.9	±3.0
(2) Variable Extent of Melting	See Appendix E				
(3) Melt Radius Uncertainty*	-9.1	-9.9	-10.4	-10.7	-12.2
(4) Fuel-Sheath Gap ΔT	0	0	0	0	0
(5) Analytical Uncertainties	0	0	0	0	0
(6) Structural Differences	0	0	0	0	0
(7) Impurity Variations	0	0	0	0	0
(8) Irradiation Condition	0	0	0	0	0
(9) Flux Gradients	±2.5	±2.5	±2.5	±2.5	±2.5
TOTAL	+3.9/-13.0	+4.5/-14.4	+4.8/-15.2	+4.4/-15.4	+5.5/-17.7
Cumulative Error in W/cm	+3.0/-10.0	+3.2/-10.2	+3.3/-10.4	+2.9/-10.2	+3.2/-10.2

* This is not an error, but is a consistent bias which serves to shift the entire power rating versus composition curve by a maximum of the stated amount.

FIGURE 43. Error Analysis of Melting Power Rating Results

this study, which is in progress at Battelle-Northwest, should show whether or not the observed large compositional discontinuity at the melt radius is reasonable, and if operation with center melting substantially altered the solid fuel composition and the corresponding temperature distribution. Similar studies on mixed uranium-plutonium oxides are also being done.

ACKNOWLEDGEMENTS

The author is indebted to R. R. Lewis for coordinating the fabrication and irradiation of experimental assemblies; to D. W. Brite for the development of pneumatic impaction techniques employed in fabricating specimens; to the staff of the Radiometallurgy Laboratory, Battelle-Northwest, for their assistance in devising the novel postirradiation examination techniques employed in these studies, and to Douglas United Nuclear personnel for performing the irradiations.

Appreciation is extended to A. S. Bain, J. R. MacEwan, M. J. F. Notley, and J. A. L. Robertson of AECL for reviewing an early draft of this paper.

APPENDIX A
RAW DATA

APPENDIX A

RAW DATA

TABLE A-I. *Postirradiation Fuel Dimensions*

Capsule SNC	O/U	Sheath OD, cm		Fuel Diameter, cm	Column Grain Diameter, cm	Melt Diameter, cm*	
		Preirradiated	Postirradiated			Macrograph	Autoradiograph
2 A	1.90	4.210	4.225	3.32	1.95	0.80	0.79/0.84
B	2.00	4.210	4.210	3.36	2.07	1.10	1.11/1.34
4 A	1.99	4.210	4.335	3.86	2.56	1.91	2.00
B	2.00	4.210	4.290	3.67	2.41	1.58	1.67
1 A	2.02	4.210	4.300	3.63	2.60	1.55	1.66
B	2.00	4.210	4.310	3.56	2.34	1.28	1.47
3 A	2.05	4.210	4.275	3.45	2.57	1.32	1.40
B	2.00	4.210	4.275	3.45	2.13	1.05	1.11
5 A	2.15	4.210	4.325	3.38	2.53	1.70	1.76
B	2.00	4.210	4.305	3.56	2.41	1.54	1.59

* The melt diameter is more distinct on an autoradiograph, thus these measurements are employed in the calculations. Two melt diameters are listed for SNC-2 since, as explained in the text, for this capsule consideration of the two possible melt radius indications on the autoradiographs yielded significantly different results. For the other four capsules, choice of melt radius does not affect the calculations.

A.1

BNWL-536

APPENDIX B
CALCULATION OF HEAT TRANSFER PARAMETERS

APPENDIX B CALCULATION OF HEAT TRANSFER PARAMETERS

Temperature integrated thermal conductivities were employed in comparing thermal histories as functions of stoichiometry. Basic relationships, derived by Robertson,⁽²⁹⁾ show that (neglecting radial flux depression which cancels when subsequent ratios are taken) for a cylindrical fuel rod

$$\int_{T_1}^{T_2} k dT = \frac{q}{4\pi L} \left(\frac{r_1^2 - r_2^2}{r_1^2} \right), \quad (B-1)$$

where:

k = Thermal conductivity as a function of temperature.

T_2 = Temperature at r_2 .

T_1 = Temperature at r_1 .

q/L = Linear heat generation rate.

r_1 = Outer radial boundary of radius interval considered.

r_2 = Inner radial boundary of radius interval considered.

If q/L does not vary from Specimen A to Specimen B,

$$\frac{\left(\int_{T_1}^{T_2} k dT \right)_A \left(\frac{r_1^2 - r_2^2}{r_1^2} \right)_A}{\left(\int_{T_1}^{T_2} k dT \right)_B \left(\frac{r_1^2 - r_2^2}{r_1^2} \right)_B} = 1. \quad (B-2)$$

However, some variation in fuel radius, r_o , exists, and

$$q/L \sim r_o^2. \quad (B-2a)$$

Therefore,

$$\frac{\left(\int_{T_1}^{T_2} k dT \right)_A}{\left(\int_{T_1}^{T_2} k dT \right)_B} = \frac{r_{A_o}^2 \left(\frac{r_1^2 - r_2^2}{r_1^2} \right)_A}{r_{B_o}^2 \left(\frac{r_1^2 - r_2^2}{r_1^2} \right)_B} \quad (B-3)$$

If, however, all dimensions are referred to the fuel radius, then $r_1 = r_o$ and

$$\frac{\left(\int_{T_s}^T k dT \right)_A}{\left(\int_{T_s}^T k dT \right)_B} = \frac{\left(D_o^2 - D^2 \right)_A}{\left(D_o^2 - D^2 \right)_B} \quad (B-4)$$

or

$$\frac{\int_{T_s}^T k_A dT}{\int_{T_s}^T k_B dT} = \frac{\left(D_o^2 - D^2 \right)_A}{\left(D_o^2 - D^2 \right)_B} \quad (B-5)$$

where:

T_s = Fuel surface temperature.

D_o = Fuel diameter.

T = Fuel temperature at diameter "D".

Equation (B-5) together with the data in Table I was used to calculate the results in Table B-I.

TABLE B-I. *Relative Integrated Thermal Conductivities
for Columnar-Grain-Growth and Melting*

Capsule SNC	D_o^2	D_m^2	$D_o^2 - D_m^2$	$\frac{(D_o^2 - D_g^2)A}{(D_o^2 - D_g^2)B}$	D_m^2	$D_o^2 - D_m^2$	$\frac{(D_o^2 - D_m^2)A}{(D_o^2 - D_m^2)B}$
2 A	11.06	3.80	7.26	1.037	0.629/0.710	10.43/10.35	1.037/1.090
B	11.29	4.29	7.00		1.23/1.79	10.06/9.50	
4 A	14.90	6.55	8.35	1.090	4.00	10.90	1.023
B	13.47	5.81	7.66		2.80	10.67	
1 A	13.18	6.76	6.42	0.893	2.77	10.41	0.990
B	12.67	5.48	7.19		2.16	10.51	
3 A	11.90	6.61	5.29	0.718	1.97	9.97	0.935
B	11.90	4.54	7.36		1.24	10.66	
5 A	11.41	6.40	5.01	0.730	3.08	8.33	0.820
B	12.67	5.81	6.86		2.52	10.15	0.820

D_g = Columnar-grain-growth diameter;

D_m = Melt diameter (all dimensions in cm).

APPENDIX C
FUEL SURFACE TEMPERATURE CALCULATIONS

APPENDIX C FUEL SURFACE TEMPERATURE CALCULATIONS

Because of small differences in sheath thicknesses and fuel diameters, some variation in fuel surface temperature and linear heat rating was unavoidable. To permit normalization to a common base, each fuel surface temperature was calculated using standard thermal-hydraulic relationships. Results of these calculations, plus the quantity

$$\int_{T_s}^{500 \text{ } ^\circ\text{C}} k dT$$

(see Figure 14) required to normalize all integrated conductivities to a common fuel surface temperature, are listed in Table V.

TABLE C-I. Fuel Surface Temperature Normalization

Capsule SNC	O/U	Mean T_s $^\circ\text{C}$	$\int_{T_s}^{500 \text{ } ^\circ\text{C}} k dT$ W/cm
4 A	1.90	536	+1.5
B	2.00	521	+1.0
2 A	1.99	457	-2.0
B	2.00	485	-0.7
1 A	2.02	494	--
B	2.00	510	+0.5
3 A	2.05	521	+1.0
B	2.00	521	+1.0
5 A	2.15	542	+1.8
B	2.00	510	+0.5

APPENDIX D
CALCULATION OF INTEGRATED CONDUCTIVITY VALUES

APPENDIX D CALCULATION OF INTEGRATED CONDUCTIVITY VALUES

Integrated thermal conductivities and mean conductivities were calculated from the relative values listed in Table IV and the standard curve shown in Figure 14 as follows:

- (1) SNC-2, UO_{1.90} ($T_s = 536^\circ\text{C}$)

Melting

$$\int_{536}^{T_m} k dT = (1.037/1.09)(69.0) = 71.5/75.2$$

$$\bar{K}(T_m = 2800^\circ\text{C}) = 0.0315/0.0332 \text{ W/cm-}^\circ\text{C}$$

$$\bar{K}(T_m = 2750^\circ\text{C}) = 0.0323/0.0339 \text{ W/cm-}^\circ\text{C}$$

Columnar-Grain-Growth

$$\int_{536}^{T_{gg}} k dT = (1.037)(34.5) = 35.8$$

$$\bar{K}(T_{gg} = 1700^\circ\text{C}) = 0.0308 \text{ W/cm-}^\circ\text{C}$$

- (2) SNC-4, UO_{1.99} ($T_s = 457^\circ\text{C}$)

Melting

$$\int_{457}^{T_m} k dT = (1.023)(70.8) = 72.6$$

$$\bar{K}(T_m = 2800^\circ\text{C}) = 0.0309 \text{ W/cm-}^\circ\text{C}$$

Columnar-Grain-Growth

$$\int_{457}^{T_{gg}} k dT = (1.09)(36.3) = 39.6$$

$$\bar{K}(T_{gg} = 1700^\circ\text{C}) = 0.0318 \text{ W/cm-}^\circ\text{C}$$

(3) SNC-1, UO_{2.02} ($T_s = 494^\circ\text{C}$)

Melting

$$\int_{494}^{T_m} k dT = (0.99)(69.5) = 68.8$$

$$\bar{k}(T_m = 2800^\circ\text{C}) = 0.0298 \text{ W/cm-}^\circ\text{C}$$

$$\bar{k}(T_m = 2750^\circ\text{C}) = 0.0305 \text{ W/cm-}^\circ\text{C}$$

$$\bar{k}(T_m = 2560^\circ\text{C}) = 0.0334 \text{ W/cm-}^\circ\text{C}$$

Columnar-Grain-Growth

$$\int_{494}^{T_{gg}} k dT = (0.893)(35.0) = 31.3$$

$$\bar{k}(T_{gg} = 1700^\circ\text{C}) = 0.0260$$

(4) SNC-3, UO_{2.05} ($T_s = 521^\circ\text{C}$)

Melting

$$\int_{521}^{T_m} k dT = (0.935)(69.1) = 64.6$$

$$\bar{k}(T_m = 2800^\circ\text{C}) = 0.0283 \text{ W/cm-}^\circ\text{C}$$

$$\bar{k}(T_m = 2680^\circ\text{C}) = 0.0299 \text{ W/cm-}^\circ\text{C}$$

$$\bar{k}(T_m = 2360^\circ\text{C}) = 0.0353 \text{ W/cm-}^\circ\text{C}$$

Columnar-Grain-Growth

$$\int_{521}^{T_{gg}} k dT = (0.718)(34.6) = 24.8$$

$$\bar{k}(T_{gg} = 1700^\circ\text{C}) = 0.021 \text{ W/cm-}^\circ\text{C}$$

(5) SNC-5, UO_{2.15} ($T_s = 542^\circ\text{C}$)

Melting

$$\int_{542}^{T_m} k dT = (0.82)(68.3) = 56.0$$

$$\bar{k}(T_m = 2800^\circ\text{C}) = 0.0248 \text{ W/cm-}^\circ\text{C}$$

$$\bar{k}(T_m = 2400^\circ\text{C}) = 0.0302 \text{ W/cm-}^\circ\text{C}$$

Columnar-Grain-Growth

$$\int_{542}^{T_{gg}} k dT = (0.730)(33.8) = 24.6$$

$$\bar{k}(T_{gg} = 1700^\circ\text{C}) = 0.0212 \text{ W/cm-}^\circ\text{C}$$

APPENDIX E
SUMMARY OF HEAT TRANSFER RESULTS

APPENDIX E SUMMARY OF HEAT TRANSFER RESULTS

TABLE E-I. Summary of Computed Integrated and Mean Thermal Conductivities

O/U Mean	$\int k dT$, W/cm			O/U of Solid at Melt Radius	T _m °C	k, W/cm-°C		
	500 °C - T _m	500 °C - T _{gg}	T _{gg} - T _m			500 °C - T _m	500 °C - T _{gg}	T _{gg} - T _m
1.90	73.0/76.7	37.3	35.7/39.4	2.00	2800	0.0317/0.0334	0.0311	0.0324/0.0368
				1.95*	2760	0.0327/0.0340		0.0337/0.0372
				1.90	2750	0.0324/0.0341		0.0340/0.0375
				1.80**	2560	0.0354/0.0373		0.0415/0.0458
1.99	70.6	37.6	33.0	1.99	2800	0.0307	0.0313	0.0300
2.00	70.1	35.6	34.5	2.00†	2800	0.0304	0.0297	0.0314
2.02	68.8	31.3	37.5	2.00	2800	0.0295	0.0261	0.0341
				2.005†	2800	0.0295		0.0341
				2.02	2780	0.0302		0.0347
				2.04††	2745	0.0306		0.0359
2.05	65.6	25.8	39.8	2.00	2800	0.0285	0.0215	0.0362
				2.02†	2780	0.0288		0.0368
				2.05	2680	0.0301		0.0406
				2.13††	2520	0.0325		0.0485
2.15	57.8	26.4	31.4	2.00	2800	0.0251	0.0220	0.0285
				2.06†	2710	0.0261		0.0310
				2.15	2400	0.0304		0.0449
				2.25††	?			

* Estimated from metallography (Figure 11); assumes discontinuity at solid-liquid interface.

** Estimated from metallography (Figure 11); assumes no discontinuity at solid-liquid interface.

† Measured by radial sampling; assumes discontinuity at solid-liquid interface.

†† Measured by radial sampling; assumes no discontinuity at solid-liquid interface.

APPENDIX F
VARIATION IN OXYGEN AND TEMPERATURE
DISTRIBUTIONS WITH FRACTION OF FUEL MOLTEN

APPENDIX F
VARIATION IN OXYGEN AND TEMPERATURE
DISTRIBUTIONS WITH FRACTION OF FUEL MOLTEN

Assuming Figure 41 to be valid, it is obvious that the composition of the solid and of the liquid in a partially molten UO_{2+x} fuel depends upon the volume fraction of the oxide which is molten. Figure 41 permits a quantitative computation of this effect. The analysis is simplified by assuming that the system consists of solid oxide with a unique composition in equilibrium with liquid oxide with another unique composition. In actual fact, steady-state composition gradients exist in both the solid and liquid; but reference to Figure 40 suggests these to be second order effects.

From Figure F-1,

$$N_{BS} V_s + N_{BL} V_l = N_{BO} (V_s + V_l) \quad (\text{F-1})$$

where,

N_{BS} = Mole fraction "B" in the solid

V_s = Volume of solid

N_{BL} = Mole fraction "B" in the liquid

V_l = Volume of liquid

N_{BO} = Mean mole fraction "B" in the system

or

$$N_{BS} \left(\frac{V_s}{V_s + V_l} \right) + N_{BL} \left(\frac{V_l}{V_s + V_l} \right) = N_{BO} \quad (\text{F-2})$$

Now,

$$\left(\frac{V_l}{V_s + V_l} \right) = \left(\frac{D_L^2}{D_O^2} \right) \text{ and } \left(\frac{V_s}{V_s + V_l} \right) = \left(\frac{D_O^2 - D_L^2}{D_O^2} \right) , \quad (\text{F-3})$$

FIGURE F-1. *Hypothetical Phase Diagram*

where

D_L = Diameter of liquid zone

D_O = Overall fuel diameter

Inserting (F-3) in (F-2):

$$N_{BS} \frac{D_O^2 - D_L^2}{D_O^2} + N_{BL} \frac{D_L^2}{D_O^2} = N_{BO} \quad (F-4)$$

To solve (F-4) for N_{BS} and N_{BL} requires another equation interrelating them. This is empirically provided by Figure 41, from which N_{BS} versus N_{BL} is plotted in Figure F-2. This yields a nearly linear relationship which may be represented by

$$N_{BL} = 1.05 N_{BS} \quad (F-5)$$

Inserting (F-5) into (F-4) and normalizing to a unit diameter, i.e., $D_O \equiv 1$:

$$N_{BS}(1 - D_L^2) + 1.05 N_{BS} D_L^2 = N_{BO}$$

or

$$N_{BS} = N_{BO} / (1 + 0.05 D_L^2) \quad (F-6)$$

$$N_{BL} = 1.05 N_{BO} / (1 + 0.05 D_L^2)$$

Solving (F-6) for various D_L 's and for N_{BO} 's equivalent to O/U's of 2.02, 2.05, and 2.15 yield the composition versus melt radius results shown in Figures F-3, F-4, and F-5. These show that the compositions of the solid and liquid are very importantly affected by the extent of melting. This variation in solid composition causes large variations in the temperature distribution in the solid, and in the power rating required for fuel

FIGURE F-2. Functional Relationship Between Liquidus and Solidus Compositions for UO_{2+x}

FIGURE F-3. Variation in Liquid and Solid Compositions as a Function of Melt Radius in $UO_{2.02}$

FIGURE F-4. Variation in Solid and Liquid Compositions as a Function of Melt Radius in $UO_{2.05}$

FIGURE F-5. Variation in Liquid and Solid Compositions as a Function of Melt Radius in $UO_{2.15}$

melting. These variations derive from two sources: 1) composition effects on thermal conductivity, and 2) composition effects on melting point. These were evaluated using 1) Ross's composition versus conductivity data⁽¹⁾ and 2) Christensen's melting point results⁽¹²⁾ together with Figure 24. The results (Figure F-6) show individual and cumulative decreases in the power rating required for melting as O/U increases above 2.00. An equivalent analysis for UO_{2-x} was not pursued because no thermal conductivity data are available and because the microstructures of the irradiated UO_{2-x} (Figures 11 and 13) show the assumption of uniform solid composition to be unjustified. From Figure F-6 and Figures F-3, F-4, and F-5, the chief result of the foregoing analysis (Figure F-7) was constructed. This gives power rating required for melting as a function of fractional melt radius for fuels of various mean compositions. Figure F-7 shows that extent of melting is important and must be considered in computing the integrated conductivity in the solid fuel. Data determined from these irradiation tests (Figures 21 and 43) provide an independent check of Figure F-7. Results are tabulated in Table F-I.

TABLE F-I. Comparison of Irradiation Test Results with Calculated Effects of Melting Extent on Power Rating Required for Melting in UO_{2+x}

Specimen	O/U	$\frac{r_m}{r_o}$	$\int_{500}^{T_m} k dT, \text{ W/cm}$		Comparison
			Irradiation Tests (Figure 43)	Calculated (Figure F-7)	
SNC-1	2.02	0.46	68.4 ± 3.3	70	Fair
SNC-3	2.05	0.40	66.0 ± 3.3	70	Poor
SNC-5	2.15	0.52	58.0 ± 3.3	59.5	Good

The comparisons are acceptable in view of the assumptions employed and the many uncertainties involved in computing Figure F-7.

FIGURE F-6. Decrease in Melting Power Rating with Increase in O/U Showing Both Melting Point and Thermal Conductivity Effects

FIGURE F-7. Melt Radius and Stoichiometry Effects on the Melting Power Rating for UO_{2+x}

APPENDIX G
REFERENCES

APPENDIX G
REFERENCES

1. Thermal Conductivity of Uranium Oxide, IAEA Panel Report, Technical Report Series No. 59, Vienna, Austria, 1966.
2. Thermodynamic and Transport Properties of Uranium Dioxide and Related Phases, IAEA Panel Report, Technical Report Series No. 39, Vienna, Austria, pp. 55-59, 1965.
3. J. A. L. Robertson, A. M. Ross, M. J. F. Notley, and J. R. MacEwan. "Temperature Distribution in UO₂ Fuel Elements," J. Nuc. Mat., vol. 7, no. 3, pp. 225-262. 1962.
4. J. A. Christensen. "Thermal Conductivity of Nearly Stoichiometric UO₂-Temperature and Composition Effects," WCAP-2531. Westinghouse, Pittsburg, Pennsylvania, November 1963.
5. J. F. May, M. J. F. Notley, R. L. Stoute, and J. A. L. Robertson. "Observations on the Thermal Conductivity of Uranium Dioxide," AECL-1641. Chalk River, Ontario, November 1962.
6. A. M. Ross. "The Dependence of the Thermal Conductivity of Uranium Dioxide on Density, Microstructure, Stoichiometry, and Thermal Neutron Irradiation," AECL-1096. Chalk River, Ontario, September 1960.
7. A. S. Bain. ASTM Symposium on Radiation Effects in Refractory Fuel Compounds, ASTM STP-306, Washington, D.C., pp. 30-45. June 1961.
8. J. A. Robertson. ASTM Symposium on Radiation Effects on Refractory Fuel Compounds, ASTM STP-306, Washington, D.C., pp. 3-15. June 1961.
9. B. E. Schaner. "Metallographic Determination of the UO₂-U₄O₉ Phase Diagram," J. Nuc. Mat., vol. 2, pp. 110-120. 1960.
10. J. A. Christensen. Unpublished Data. Pacific Northwest Laboratory, Richland, Washington, 1966. (Report)
11. J. L. Bates. "Melting Points of Hypostoichiometric Uranium Dioxide," BNWL-224. Pacific Northwest Laboratory, Richland, Washington, June, 1966.

12. J. A. Christensen. "Irradiation Effects on Uranium Dioxide Melting," HW-69234. General Electric Company, Richland, Washington, March 1962.
13. J. A. Christensen and R. J. Allio. "In-Pile Measurement of Uranium Dioxide Fuel Temperature Distribution," ANS Trans., vol. 8, no. 1, p. 40. June 1965.
14. A. S. Bain. "Cracking and Buck Movement in Uranium Oxide Fuel Elements," AECL-1827. Chalk River, Ontario, September 1963.
15. M. R. MacEwan and J. Hayashi. "Grain Growth in UO_2 III- Some Factor Influencing Equiaxed Grain Growth," British Ceramic Society Basic Science Section Meeting on Nuclear and Engineering Ceramics, Harwell Berks, October 1966.
16. J. A. Christensen. "Connection Heat Transfer in Molten Center Oxide Fuels," BNWL-418. Pacific Northwest Laboratory, Richland, Washington, May 1967.
17. M. R. Lyons, B. Weidenbaum, H. Hausner, and T. J. Pashos. "New Evidence to Delineate the UO_2 Molten Boundary," ANS Trans., vol. 8, no. 2. November 1965.
18. G. R. Horn and J. A. Christensen. "Identification of the Molten Zone in Irradiated UO_2 ," ANS Trans., vol. 6, no. 2. November 1963.
19. J. A. Christensen. "Thermal Expansion and Change in Volume on Melting for UO_2 ," J. Am. Cer. Soc., vol. 46, no. 12, p. 607. December 1963.
20. T. S. Busby and J. Barker. "Simulative Studies of Upward Drilling," J. Am. Cer. Soc., vol. 49, no. 8. August 1966.
21. W. D. Kingery. "The Thermal Conductivity of Ceramic Dielectrics," Progress in Ceramic Science, vol. 2, p. 181. Pergamon Press, The MacMillan Company, New York. 1962.
22. R. E. Latta. Unpublished Data, (GE-NMPO), October 1966. (Personal Communication)
23. D. R. de Halas. "Understanding UO_2 Thermal Conductivity," Nucleonics, vol. 21, no. 10, p. 92. October 1963.

24. J. L. Bates. "Metallic Uranium in Irradiated UO_2 ," HW-82263. General Electric Company, Richland, Washington. May 1964.
25. J. A. Christensen. "Temperature and Stoichiometry Effects on UO_2 Fuel Heat Ratings," ANS Trans. vol. 7, no. 2, p. 392. November 1964.
26. M. D. Freshley, R. G. Wheeler, J. M. Batch, and G. N. Hesson. "Investigation of the Combined Failure of a Pressure Tube and Defected Fuel Rod in PRTR, BNWL-272. Pacific Northwest Laboratory, Richland, Washington, June 1966.
27. R. W. Stromatt, and R. E. Connally. "Determination of the Stoichiometry of Uranium Dioxide by Controlled Potential Coulometry," Analytical Chemistry, vol. 33, no. 3, pp. 345-346. March 1961.
28. R. E. Latta and R. E. Fryxell. "Determination of the Melting Point of UO_{2+x} ($-0.25 < x < 0$)," GE TM-65-11-8, November 1965.

DISTRIBUTIONNo. of
Copies

1	<u>AEC Chicago Patent Section</u> R. K. Sharp
7	<u>AEC Library, Washington</u> Division of Reactor Development and Technology G. W. Cunningham R. Grube D. K. Magnus J. M. Morrissey DeWitt Moss J. M. Simmons M. J. Whitman
2	<u>AEC RDT Site Rep.-PNL</u> P. G. Holsted
2	<u>AEC Richland Operations Office</u> C. L. Robinson Technical Information Library
58	<u>AEC Division of Technical Information</u> UK/U.S. Fast Reactor Exchange (12) EURATOM/U.S. Fast Reactor Exchange (35) Pierre Kruys A. de Stordeus (10)
270	<u>AEC Division of Technical Information</u>
1	<u>Aerojet-General</u> G. W. Titus
1	<u>Alkem</u> 7501 Leopoldshafen Karlsruhe, Germany W. Stoll
1	<u>Allgemeine Elektrizitäts Gesellschaft</u> Frankfurt AEG Hochhaus Federal Republic of Germany J. Hochel

No. of
Copies

- 5 Argonne National Laboratory
 R. J. Beals
 R. K. Edwards
 J. H. Kittel
 L. A. Neimark
 R. J. Thorn
- 4 Associazione EURATOM
 CNEN Per I Reattori Veloci
 Via Mazzini 2
 Bologna, Italy
 F. Pierantoni
- 2 Atlantic Richfield Hanford Company
 H. H. Hopkins, Jr.
 R. Y. Lyon
- 6 Atomic Energy Research Establishment
 Chemistry and Metallurgy Branch
 Fuels Development Branch
 Chalk River, Ontario, Canada
 A. S. Bain
 R. D. MacDonald
 J. R. MacEwan
 M. J. F. Notley
 J. A. L. Robertson
 A. M. Ross
- 7 Atomic Energy Research Establishment
 United Kingdom Atomic Energy Authority
 Harwell, Didcot, Berks, England
 B. T. Bradbury
 P. Murray (3)
 L. E. Russel
 J. B. Sayers
 J. Williams
- 1 Atomic Energy Commission, Brussels, Belgium
 AEC Representative

No. of
Copies

- 3 Atomic Power Development Associates
 W. H. Jens
 W. McHugh
 A. A. Shoudy
- 1 Atomics International
 H. Pearlman
- 1 Australian Atomic Energy Research Establishment
 Lucas Heights
 N.S.W., Australia
 R. Smith
- 2 Babcock and Wilcox
 C. J. Baroch
 E. Lynch
- 5 Battelle Memorial Institute
 W. F. Heenan
 D. L. Keller
 S. W. Porembka (2)
 V. W. Storhok
- 1 Battelle Memorial Institute, Frankfurt
 N. Hinsel
- 1 Brookhaven National Laboratory
 D. H. Gurinsky
- 1 Centre d'Etudes Nucleaires de Cadarache
 Poite Postale No. 1
 Saint-Paul-Lez-Durance, France
 B. Defreyn
- 1 CEN Belgonucleaire
 Mol, Belgium
 J. M. Leblanc

No. of
Copies

- 12 CEN Saclay
Boite Postale 2
Gif-Sur-Yvette (S et O), France
R. Lallement
B. Lavaud
G. Vendryes (10)
- 2 Combustion Engineering, Inc.
W. P. Chernock
S. S. Christopher
- 8 Douglas United Nuclear, Inc.
T. W. Ambrose
E. C. Bennett
L. Bussey
A. E. DeMers
T. L. Deobold
L. E. Kusler
J. T. Stringer
DUN File Copy
- 1 du Pont Company, Aiken
W. R. McDonnell
- 4 General Atomics
San Diego, California
J. C. Bokros
R. G. Rose
J. W. Siltamen
L. Yang
- 1 General Electric Company, APD
Special Purpose Nuclear Systems Operation
P. O. Box 846
Pleasanton, California
J. E. Van Hoomissen
- 6 General Electric Company, Cincinnati
C. Brassfield
W. Briskin
J. Conway
A. D. Feith
R. E. Fryxell
J. McGurty

No. of
Copies

- 5 General Electric Company, Pleasanton
 E. A. Aitken
 L. P. Bupp
 L. N. Grossman
 A. I. Kaznoff
 R. E. Sharp
- 6 General Electric Company, San Jose
 K. Cohen
 R. N. Duncan
 H. H. Klepfer
 M. F. Lyons
 T. J. Pashos
 B. Weidenbaum
- 3 General Electric Company, Sunnyvale
 W. E. Bailey
 C. N. Craig
 E. Zebroski
- 10 Kernforschungszentrum Karlsruhe
 7500 Karlsruhe, Germany
 W. Haefele
- 1 Kerr-McGee Industries, Inc.
 Oklahoma City, Oklahoma
 H. Lambertus
- 1 Knolls Atomic Power Laboratory
 W. K. Barney
- 1 Lawrence Radiation Laboratory, Livermore
 A. J. Rothman
- 8 Los Alamos Scientific Laboratory
 R. Baker
 M. Bowman
 H. Messing
 J. A. Leary
 D. MacMillan
 R. H. Perkins
 R. Spence
 M. C. Smith

No. of
Copies

- 2 NASA Lewis Research Center
 A. F. Lietzke
 N. T. Saunders
- 1 Naval Air Systems Command
 C. Bersch
- 2 Nuclear Materials and Equipment Corporation
 C. S. Caldwell
 T. D. Thomas
- 2 Oak Ridge National Laboratory
 Research Material Information Center
 P. O. Box X
 Oak Ridge, Tennessee 37831
 T. F. Connally
 J. L. Scott
- 1 Office of Naval Research
 A. M. Dinness
- 1 Rensselaer Polytechnic Institute
 Department of Materials Engineering
 Troy, New York
 C. B. Willingham, Jr.
- 1 Siemens-Schuckertwerks AO
 Abt. R. E.
 352 Erlangen
 Federal Republic of Germany
 R. Holtzer
- 1 Tokyo Shibaura Electric Company, Ltd.
 Central Research Laboratory
 Komukai, Kawasaki, Japan
 T. Nishijima

No. of
Copies

2	<u>Transuranium Institute (EURATOM)</u> Karlsstrasse 42-44 Karlsruhe, Germany H. M. Mattys H. E. Schmidt
4	<u>Union Carbide Corporation (ORNL)</u> R. M. Carroll D. McElroy J. L. Scott W. C. Thurber
1	<u>United Aircraft Corporation</u> Research Laboratory East Hartford, Connecticut G. H. McLafferty
1	<u>United Nuclear Corporation</u> A. A. Strasser
1	<u>University of Arizona</u> Nuclear Engineering Department Tucson, Arizona M. V. Davis
1	<u>University of Michigan</u> Ann Arbor, Michigan W. Kerr, College of Engineering
3	<u>USAEC Scientific Advisor</u> Avenue des Arts Brussels, Belgium G. E. Helfrich
1	<u>Westinghouse Electric Corporation, McKenna (AEC)</u> J. M. Tobin

No. of
Copies9 Westinghouse Electric Corporation

Robert Allio
M. G. Balfour
A. Biancheria
M. L. Bleiberg
A. Boltax
H. M. Ferrary
D. R. McClintock
R. E. Olson

4 Westinghouse Bettis Atomic Power Laboratory

J. Belle
R. C. Daniel
B. Lustman
J. E. McCauley

70 Battelle-Northwest

E. A. Astley
W. J. Bailey
D. E. Baker
R. J. Baker
J. L. Bates
R. E. Bardsley
J. A. Basmajian
M. P. Bauleke
D. W. Brite
C. A. Burgess
T. B. Burley
M. P. Burns
D. C. Carlson
T. D. Chikalla
J. A. Christensen (10)
P. D. Cohn
R. G. Curran
R. E. Dahl
G. M. Dalen
J. L. Daniel
D. R. de Lialas
K. Drumheller
E. A. Evans
P. L. Farnsworth
G. L. Fox
M. D. Freshley
R. L. Gibby

Battelle-Northwest (contd)

W. J. Gruber
W. L. Hampson
J. E. Hanson
B. R. Hayward
R. J. Hennig
G. R. Horn
R. R. Lewis
R. J. Lobsinger
S. J. Mayhan
C. E. McNeilly
J. O. McPartland
M. K. Millhollen
R. P. Nelson
R. E. Nightingale
L. A. Pember
A. L. Pitner
W. E. Roake
R. K. Robinson
O. D. Slagle
F. M. Smith
H. A. Taylor
R. Teats
G. L. Tingey
E. T. Weber
W. J. Woods
H. H. Yoshikawa
F. R. Zaloudek
Technical Information Files (5)
Technical Publications (2)