ARGONNE NATIONAL LABORATORY
9700 South Cass Avenue
Argonne, Illinois 60439

ACTINIDE REDISTRIBUTION IN
MIXED-OXIDE FUELS
IRRADIATED IN A FAST FLUX*

by

R. O. Meyer, E. M. Butler,
and D. R. O'Boyle

Materials Science Division

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*Including an appendix by W. T. Sha and P. R. Huebotter

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ABSTRACT

Measurements of uranium and plutonium concentrations obtained with an electron-microprobe analyzer are presented for 11 mixed-oxide fuel elements irradiated in EBR-II. The results are consistent with a vapor-transport mechanism in which uranium is preferentially evaporated from the hotter fuel region and transported, by means of porosity, down the temperature gradient. Actinide segregation is closely related to central-void formation, which depends on linear power rating, but for burnups of 1-11 at. % no effect of burnup on redistribution was observed. Fuels operated at moderate power ratings show an enhanced plutonium concentration near the central void that is typically 35-50% greater than the initial concentration, whereas unstructured fuels show no actinide segregation. Fuel elements that operated with fuel melting sometimes exhibit greater than 100% plutonium enhancement. Various transport mechanisms are discussed, and a quantitative model to predict actinide concentrations is outlined. The effect of actinide redistribution on allowable power rating and Doppler broadening is discussed in the appendix.

I. INTRODUCTION

The radial and longitudinal distribution of fissile atoms in a mixed-oxide fuel element is important in the design and operation of fuels for the Liquid Metal Fast Breeder Reactor (LMFBR). As is known, the actinides uranium and plutonium, which are originally distributed homogeneously (on a macroscopic scale) in the mixed-oxide (U,Pu)O₂ fuel element, become redistributed during irradiation. Because this redistribution affects numerous fuel properties, such as fuel plasticity and melting temperature, it is important to the understanding of fuel-element behavior and to fuel-element modeling.^{1,2}

Actinide redistribution also influences two aspects of reactor operation that directly affect reactor safety. Increases in plutonium concentration

that are commonly observed near the central void of a fuel element raise the fuel centerline temperature for a given power rating. Thus, in establishing maximum safe operating conditions, actinide redistribution must be taken into account. Segregation of uranium and plutonium can also affect the promptness of negative-reactivity feedback from the Doppler effect during power transients. These two effects are discussed in detail in the appendix, and it is shown that, for moderate amounts of actinide redistribution, the allowable linear power rating must be reduced by about 0.5-0.8 kW/ft. When a large amount of actinide redistribution occurs, the allowable linear power rating may be reduced as much as 3 kW/ft, but Doppler broadening is not significantly affected in either case.

Early attempts to determine radial plutonium concentration distribution in oxide fuels^{3,4} by means of alpha autoradiography and radiochemical analysis did not detect any extensive plutonium redistribution. The first investigation to show significant plutonium redistribution was reported by Lauritzen *et al.*,⁵ who examined several mixed-oxide ceramic fuels irradiated in a thermal flux using both radiographic and core-drilling techniques. Their results showed a general increase in plutonium concentration near the fuel centerline, but the accuracy of their experimental methods was limited. One of the first studies that used electron-microprobe techniques to determine the radial plutonium distribution in mixed-oxide fuel irradiated in a fast-neutron flux was reported by O'Boyle *et al.*⁶ Again, an increase in the plutonium concentration near the central void was found.

Several recent reports have discussed actinide redistribution in mixed-oxide fuel elements.⁷⁻¹⁰ Considering the large number of variables in fuel-element fabrication and operation, the available data on actinide distribution were not adequate to formulate an analytical model for actinide migration. The current report presents the results of a series of systematic measurements on a number of mixed-oxide fuel elements irradiated in a fast-neutron flux in EBR-II. The experimental results are discussed in terms of several mechanisms for actinide migration, and a theoretical model based on vapor transport is briefly outlined.

II. EXPERIMENTAL METHOD

Transverse cross sections of irradiated mixed-oxide fuel were cut from the full-length elements and mounted in electrically conducting metallographic mounts. These mounts were backfilled with epoxy and polished on diamond abrasive through a 1- μ particle size, and the surface was photographed with a shielded metallographic microscope. No further coating or surface treatment was performed before the microprobe analysis.

The fuel specimen within the metallographic mount was typically 1/4 in. long and had a gamma activity of about 50 R/hr at 9 in. The specimen

was handled remotely and transferred from the hot cell to the electron-microprobe analyzer by means of a pneumatic transfer system without leaving the protective dry nitrogen atmosphere of the facility. The transfer system and the shielded MAC-450 microprobe have been described in detail.^{11,12} The specimen-transfer process requires only a few minutes to change specimens, permitting more efficient operation than can be attained at other shielded microprobe installations.

Chemical concentrations in the specimen were determined by measuring the intensity of characteristic X rays, produced by a 1- μ -dia electron beam, and comparing them with the intensities measured from pure UO_2 and PuO_2 standards. Two spectrometers were used simultaneously to measure the intensities of the uranium M_α and plutonium M_β X-ray lines. The geometry of the MAC-450 spectrometers required the use of two diffracting crystals for these X-ray lines: an organic PET* crystal for the uranium line, and a LiF crystal for the plutonium line.

A number of corrections are applied to the X-ray intensity values to obtain weight-percent compositions of uranium and plutonium. Gamma-induced background, beam-current drift, and system dead time are measured at the time of the analysis. These effects, along with the atomic number, X-ray absorption, and fluorescence effects, are taken into account by the MAGRAM computer code,¹³ which yields the corrected weight-percent concentrations of each element.

Data are collected along radii of transverse fuel cross sections, as shown in Fig. 1. The X-ray intensity ratios are measured at 15-20 evenly spaced locations from the central-void edge to the fuel-cladding interface. Inclusions and pores are avoided so that the results are representative of the uranium and plutonium concentrations in solid solution in the fuel matrix. For each specimen, data were obtained along three radii spaced about 120°

Fig. 1. Typical Transverse Cross Section through Mixed-oxide Fuel Showing Radial Locations Where Microprobe Data Were Obtained. (Fuel element NUMEC C-11, top section.) Neg. No. MSD-56335.

*Pentaerythritol, $\text{C}_5\text{H}_{12}\text{O}_4$.

apart, and, as an example, all the data for one fuel-element cross section are shown in Fig. 2. The uranium and plutonium concentrations are complementary with their sum ~ 88 wt %, the total weight percent of metal ions in $(\text{U,Pu})\text{O}_2$. Because they are complementary, it is adequate to present only one type of data; therefore, subsequent figures will show only plutonium data. The accuracy of the concentration measurements is estimated at $\pm 3\%$ of the value measured; i.e., the uncertainty is approximately ± 2 wt % for uranium and $\pm 1/2$ wt % for plutonium. Therefore, scatter of the measured values around the line segments shown in Fig. 2 is real and represents variability in the specimen being examined.

Fig. 2. Plutonium and Uranium Concentration Data for Typical Examination of Irradiated Mixed-oxide Fuel. (Fuel element NUMEC C-11, top section.) Three separate traces were taken on each fuel cross section, and the data near the central void were averaged by a least-squares method, as shown by the line segment. Neg. Nos. MSD-56336 and -56337.

Several considerations affect the accuracy of the measured concentrations. The PET diffracting crystal, used for the uranium analysis, has a strongly peaked response relative to the LiF crystal. It is therefore subject to accidental detuning with a corresponding decrease in counting rate, which introduces an error in the uranium data. An additional experimental difficulty arises that occasionally causes erroneously low concentration values to be measured. If the electron beam is placed near the edge of an oxide specimen--e.g., within 1 mil of the central void--the deposited electrons cannot leak away rapidly because of the low electrical conductivity of $(\text{U,Pu})\text{O}_2$. The charge buildup that results deflects the beam and produces low counting rates. This problem is not encountered frequently, but the occasional indication of low apparent concentrations near the central void is assumed to be due to this effect.

III. RESULTS

Seven pellet-type fuel elements irradiated in EBR-II at moderate power ratings were analyzed for actinide redistribution, and the results are summarized in Table I. The fuel elements covered a range of calculated burnups from 1 to 11 at. % and were operated at power levels of 8-16 kW/ft. Fifteen cross sections from these fuels were examined with the electron microprobe, and Fig. 3 shows one of the three data sets from each specimen. The straight-line segments in the figure are least-squares averages of the first six to eight data points from the three data sets for that specimen. In the top section of element NUMEC C-15 shown in Fig. 3(g), six data sets were obtained and averaged.

Table I lists characteristic values that describe the fuel elements, calculated centerline temperatures, and measured results. For fuel elements PNL 17-10, NUMEC C-6, C-11, and C-15, microprobe data were obtained from near the top, middle, and bottom of each fuel element. The location of each specimen relative to the interface between the reactor core and blanket is listed in the table. Except for Elements ANL 007 and 012, which were shorter than the $13\frac{1}{2}$ -in. length of the core, the bottom of the fuel column in each case was aligned with the bottom of the core.

Local values of burnup and linear power, corresponding to each fuel section examined, were calculated from the average values for each fuel element. These calculations were made using the fission-rate profile for the first six rows of EBR-II.¹⁸ Figure 4 shows this profile and the values calculated for the top, middle, and bottom sections of fuel element NUMEC C-11, which is used as a typical example.

TABLE I. Summary of Pellet-type Mixed-oxide Fuel Specimens Examined for Uranium and Plutonium Redistribution

Fuel-element Identification	Distance from Bottom of Core, in.	Local Burnup at %	Local Linear Power, kW/ft	Initial Fuel O/M Ratio	Fuel Type ^a	Initial Fuel Pellet Density, % TD	Initial Pu/U + Pu, Pu/U + Pu	Measured Maximum Pu/U + Pu	Pu/U + Pu Increase, %	Void Radius, mils	Calculated Centerline Temperature, °C
PNL 17-10 ^b Middle	6.0	0.85	10.3	1.974	AMB E	92.5	0.25	0.250	0	0.0	1620
PNL 17-10 ^b C Top	13.0	2.7	8.3	1.965	AMB U	93.3	0.25	0.249	0	0.0	1680
Middle	6.9	3.5	10.9	1.965	AMB U	93.3	0.25	0.247	-1	0.5	1790
Bottom	0.0	2.9	9.0	1.965	AMB U	93.3	0.25	0.246	-2	0.0	1620
ANL 007 ^d Middle	6.6	4.7	15.6	1.98	CP U	79.0	0.20	0.295	48	46.0	2210
ANL 012 ^d Middle	6.5	2.9	16.0	1.98	CP U	81.1	0.20	0.230	35	40.0	2280
NUMEC C-6 ^e Top	13.6	7.9	10.3	1.984	AMB E	91.2	0.20	0.248	24	16.4	1710
Middle	6.8	10.5	13.6	1.988	AMB E	91.3	0.20	0.247	24	36.6	1810
Bottom	0.5	6.4	11.0	1.980	AMB E	91.3	0.20	0.242	21	17.1	1750
NUMEC C-11 ^f Top	12.0	8.7	11.1	2.000	AMB E	90.6	0.20	0.292	46	23.0	1800
Middle	7.0	10.0	13.9	2.000	AMB E	89.8	0.20	0.293	47	34.0	1970
Bottom	0.4	8.7	11.2	2.008	AMB E	89.9	0.20	0.292	46	20.0	1830
NUMEC C-15 ^g Top	13.6	8.5	10.4	1.998	AMB E	85.0	0.20	0.330	65	28.3	1760
Middle	6.8	10.5	12.8	1.993	CP E	83.9	0.20	0.297	48	37.8	1910
Bottom	0.5	8.5	10.4	1.993	CP E	83.9	0.20	0.292	46	27.0	1830

^aCP = Cryoprecipitated; MM = Master Alloy; MB = Mechanically Blended; E = Encapsulated; and U = Unencapsulated.

^bSee Ref. 14.

^cSee Ref. 19.

^dSee Ref. 15.

^eSee Ref. 17.

(a) Fuel Element PNL 1-14

(b) Fuel Element PNL 17-10

(c) Fuel Element ANL 007

(d) Fuel Element ANL 012

(e) Fuel Element NUMEC C-6

(f) Fuel Element NUMEC C-11

(g) Fuel Element NUMEC C-15

Fig. 3. Radial Distribution of Plutonium in Seven Pellet-type Fuel Elements Irradiated in EBR-II. The fuel type, irradiation conditions, and maximum plutonium concentrations for these elements are listed in Table I. Neg. Nos. MSD-56338 through -56344.

void. The middle section of Element PNL 17-10 that was irradiated at 10.9 kW/ft developed an irregular opening ~1 mil across, which is probably the embryo of a central void. The other fuel elements formed large central voids, even though some of the fuel sections operated at linear power ratings as low as 10.3 kW/ft. Variations in initial O/M ratio and fuel density as well as uncertainties in determining linear power values are probably responsible for these differences in behavior at linear power ratings close to 11 kW/ft.

Fig. 5. Calculated Radial Temperature Distribution before and after Restructuring for the Top and Middle Sections of a Typical Mixed-oxide Fuel Element. Neg. No. MSD-56346.

calculated from the tabulated values of linear power and central-void radius and, therefore, represent the temperatures after restructuring early in the life of the fuel element.

Early in the ANL fuels-irradiation program, several elements that were designed to test the performance limits of vibratorily compacted mixed-oxide fuel at high power ratings were examined for actinide distribution. Results of these examinations are summarized in Table II. Because

TABLE II. Summary of Vibratorily Compacted Mixed-oxide Fuel Specimens Examined for Uranium and Plutonium Redistribution

Fuel-element Identification	Local Burnup, at. %	Local Linear Power, kW/ft	Initial Fuel O/M Ratio	Initial Fuel Smeared Density, % TD	(Initial Pu/(U + Pu))	Measured Maximum Pu/(U + Pu)	Pu/(U + Pu) Increase, %
SOV-1							
Middle	5.0	20.8	2.00	79.9	0.20	0.28	40
Middle	5.0	20.8	2.00	79.9	0.20	0.27	35
Bottom	4.3	17.9	2.00	79.9	0.20	0.37	85
SOV-3							
Middle	3.7	21.3	2.00	83.1	0.20	0.24	20
SOV-7							
Top	2.9	17.3	2.00	85.1	0.20	0.28	40
HOV-15							
Middle	3.5	21.3	2.00	79.8	0.20	0.43	115
Bottom	3.0	18.3	2.00	79.8	0.20	0.43	115

of the high power ratings--peak values in excess of 20 kW/ft--all the elements are believed to have operated with molten fuel during some portion of their life. Therefore, centerline temperatures were not calculated. Fuel operation and fabrication characteristics were similar for all four elements, but the measured results varied from a small increase in plutonium content near the central void (+20%) to several cases where large increases (+115%) occurred. Each entry in Table II represents one data set, as compared with three data sets per entry in Table I, so the information content and accuracy are lower. Some of the measurements listed in Table II have been reported previously.²⁰⁻²²

IV. DISCUSSION

The major fuel constituents (uranium, plutonium, and oxygen) and the volatile fission products may be redistributed both radially and axially in a fuel element during irradiation. The extent of the redistribution is

Fig. 6 Typical Plutonium-concentration Profile in a Mixed-oxide Fuel Element Irradiated at a Linear Power Rating > 11 kW/ft. Neg. No MSD-56408.

strongly dependent on the fuel temperature, the temperature gradients, and the O/M ratio. Steep radial temperature gradients within the fuel provide a driving force for radial redistribution, however, and evidence also indicates that some redistribution of fuel constituents occurs axially. Figure 6 shows the qualitative general features of radial plutonium redistribution presented in Sec. III. In each case, the maximum plutonium concentration observed near the central void was accompanied by a minimum plutonium concentration near the cool end of the columnar-grain zone. This redistribution of the acti-

nides implies that either plutonium migrates from the cooler to the hotter region of the fuel or that uranium migrates in the opposite direction. The flat portion of the curve shown in Fig. 6 indicates that the temperatures were too low ($< 1400^{\circ}\text{C}$) to permit any significant migration of the actinides. This conclusion is supported by the large inhomogeneity observed in the Master Mix* portion of Elements NUMEC C-6 and C-11, even after 11 at. % burn-up.

The typical plutonium distribution that follows irradiation, as illustrated in Fig. 6, does not indicate whether the process is exclusively radial or includes some axial contribution, nor is it possible to decide from this figure whether the process is controlled by a solid-state diffusion or by a

*Master Mix²³ is a mechanically blended mixture of coprecipitated UO_2 -50 wt % PuO_2 and UO_2 .

vapor-transport mechanism. The distribution as shown would result from a changing concentration due to a divergent mass flux, regardless of which transport mechanism was responsible for the flux.

A. Vapor Transport

Under conditions of low total gas pressure, the rate of vapor transport may be limited by vaporization kinetics,²⁴ but the vapor-transport mechanism is usually assumed to be diffusion limited²⁵ as the vapor species migrate within the fission-gas (or cover-gas) atmosphere of the fuel voidage. For the diffusion-limited case, the flux equation for uranium and plutonium can be obtained from Fick's law

$$J_i = -D_i \frac{dc_i}{dx}, \quad (1)$$

where J_i is the flux, D_i is the diffusion coefficient for the gas phase, and dc_i/dx is the concentration gradient of species i in the vapor (either uranium or plutonium). Assuming ideal gas behavior,

$$c_i = \frac{p_i}{kT} = \frac{p_{0i}}{kT} \exp\left(-\frac{\Delta H_i}{kT}\right), \quad (2)$$

where p_i is the equilibrium vapor pressure, p_0 is a constant, ΔH_i is the heat of vaporization, k is the Boltzmann constant, and T is the absolute temperature. In the presence of a concentration gradient in the solid and a temperature gradient dT/dx , Eqs. 1 and 2 can be combined to yield

$$J_i = -\frac{D_i}{kT} \frac{\partial p_i}{\partial x} - \frac{D_i \Delta H_i p_i}{k^2 T^3} \frac{dT}{dx}. \quad (3)$$

The first term in Eq. 3 yields the flux due to a concentration gradient in the vapor that would result from a concentration gradient in the solid. The second term is the temperature-gradient flux term and is the same as Eq. 1 of Nichols.²⁵ The diffusion coefficient can be obtained from kinetic theory²⁶ and is given by

$$D_i = \frac{2}{3(c_i + c_f)\sigma} \sqrt{\frac{2RT}{\pi} \left(\frac{1}{M_i} + \frac{1}{M_f} \right)}, \quad (4)$$

where σ is the collision cross section, R is the gas constant, and c_f and M_f are, respectively, the concentration and molecular weight of the fission gas (or cover gas) within the vapor phase.

Equation 3 gives the flux of actinide atoms within a moving pore; therefore, the expression must be modified by a porosity function to obtain an average flux expression. The average flux must vanish for fully dense

fuel where vapor transport is no longer possible, and multiplying Eq. 3 by the porosity fraction is a simple porosity modification that is suitable. Placing the flux expression in cylindrical coordinates and using the divergence theorem, the divergence of the average flux equals the time rate of change of the actinide concentration. Thus the changes in uranium and plutonium concentration can be followed as a function of time. This method is the basis of a quantitative model being developed to describe actinide redistribution; a simplified flow diagram for the model is shown in Fig. 7.

Fig. 7. Simplified Flow Diagram for Actinide Redistribution Model. Neg. No. MSD-56054.

Segregation of uranium and plutonium by a vapor-transport process should be possible if the vapor pressures, and hence transport rates, of the two actinide oxides are significantly different. Such a vapor-transport mechanism was first discussed by Rand and Markin,²⁷ who calculated the partial pressures of the various vapor species over $(U,Pu)O_{2+x}$. These calculations showed that, near the stoichiometric composition, the composition of the vapor was enriched in uranium relative to the solid, with UO_3 the predominant vapor species. Therefore, uranium would preferentially evaporate from the hotter region of the fuel leaving a plutonium-rich solid behind, and the excess uranium vapor would condense in the cooler region of the fuel.

This behavior agrees with the measured results for nearly stoichiometric fuels, as illustrated in Fig. 6. Additionally, as can be seen in Table I, actinide redistribution is closely related to fuel restructuring, in particular to central-void formation. Since central-void formation is caused by a vapor-transport process, such a relationship is expected. As the central void is being formed, a large quantity of material is transported, during which time substantial segregation can occur. When the maximum fuel temperature drops because of geometry and densification effects (see Fig. 5), the vapor-transport process ceases to be active, which makes the final actinide distribution relatively insensitive to burnup. A 300°C temperature decrease, for example, reduces the total vapor pressure and hence the diffusion flux by two orders of magnitude.²⁸

Several other effects could occur that would eventually slow a vapor-transport process. Oxygen is believed to redistribute from the high- to the low-temperature region in hypostoichiometric mixed-oxide fuels,²⁹ lowering the fuel-centerline O/M ratio. Lowering the O/M ratio reduces the segregation process in two ways. First, a fuel composition exists between the O/M ratios of 1.93 and 1.98, where vaporization of

uranium and plutonium species is congruent^{10,27,28,30} and segregation would not occur. As this congruent composition is approached, the vapor-phase segregation process will diminish. Secondly, as the O/M ratio of the fuel near the central void is reduced, the total vapor pressure is lowered sharply. For example, if the O/M ratio decreased from 2.00 to 1.95, the total vapor pressure would be lowered by an order of magnitude,²⁸ slowing all vapor-transport processes, whether congruent or noncongruent.

Establishment of a concentration gradient also tends to slow the segregation process. As fuel near the central void becomes enriched in plutonium, the vapor species also becomes enriched in plutonium with the result that less uranium vapor is transported down the temperature gradient. This behavior of diffusion currents is an example of le Chatelier's principle and is of basic importance in the Soret effect. In the Soret effect, a steady-state concentration distribution is achieved when the fluxes due to the temperature gradient and the concentration gradient cancel at every point. With back diffusion through either the vapor or solid phase, it is possible to postulate an equilibrium concentration distribution, and such steady-state conditions have been proposed by Adamson and Aitken.⁷

However, a distinction should be made between a time-independent steady-state distribution and one that is essentially frozen as a result of the temperature history of the specimen. As is obvious from Fig. 6, steady state has not been achieved at radii greater than 0.5 (temperatures below ~1600°C). Concentration changes that occur in this region, however slowly, will necessarily cause concentration changes in the higher temperature regions, which prevent the use of equilibrium conditions to predict the concentration distribution. Therefore, even though temperature gradient and back diffusion are in opposition in the high-temperature region of the fuel, the actinide concentration distributions observed in fuel elements are not steady-state distributions. Rather, they are distributions formed during the early high-temperature portion of fuel life and have been quenched-in as restructuring lowered the fuel-centerline temperature.

The initial fuel O/M ratio will affect the segregation process substantially. In the same manner as described above, a low O/M ratio will result in low vapor pressures and less segregation than would occur in stoichiometric fuel. Although a large range of O/M ratios was not included in the present work, a significant O/M variation existed between the three companion NUMEC elements. The most hypostoichiometric fuel, in Element NUMEC C-6 with an initial O/M ratio of 1.98, exhibited only about half the amount of actinide redistribution as the other NUMEC elements (see Table I).

Initial fuel density will affect vapor-transport rates by limiting the vapor path, as mentioned previously. Inasmuch as the density in all the fuels changes during restructuring, the initial density may affect only the

rates, and may not have a strong effect on the final actinide distribution. For example, a high fuel density would slow the vapor-transport process, but it would also affect uranium and plutonium transport equally and therefore might not change the final distribution, even though the restructuring time would be increased. In any event, no significant variation was seen in either central-void size or actinide redistribution as a function of initial fuel density.

Several direct observations have been reported^{8,10} in support of the suggestion that preferential evaporation of uranium-bearing species is the controlling mechanism for actinide redistribution in nearly stoichiometric mixed-oxide fuel. In the present study, we have examined the pellet-interface region of a fuel element (NUMEC C-11) irradiated to an average burnup of 9.7 at. % at 12.5 kW/ft. This fuel element was fabricated from dished-end pellets such that vapor transport through the 5-mil interface gap²³ would be possible. Both radial and longitudinal microprobe traces were obtained along this interface region at the locations shown in Fig. 8.

Fig. 8. Location of Microprobe Traces Taken on Dished-end Pellet-interface Region of Fuel Element NUMEC C-11. Neg. No. MSD-56347.

The results of the interface-gap examination are shown in Fig. 9. In Fig. 9(a) straight lines have been drawn at 17.9 wt %, the initial plutonium concentration, and it is clear that the minimum plutonium concentration (maximum uranium concentration) near the pellet interface (traces 2 and 3) is lower than the usual minimum in the matrix (traces 1 and 4). The position of this minimum has also shifted toward the cooler region of the fuel. The minimum plutonium concentration is about 6 wt % below the normal minimum (trace 5), whereas no longitudinal actinide variation was

observed near the central void (trace 6). We believe that this decrease in plutonium concentration, as shown in trace 5, is due to preferential evaporation of uranium-rich species from the fuel near the central void and condensation of the uranium-rich vapor in the cooler portion of the pellet-interface gap.

Fig. 9. Plutonium Distribution along Six Traces Indicated in Fig. 8. The straight-line segment in (a) at 17.9 wt % Pu is included for reference. Neg. Nos. MSD-56348 and -56349.

B. Other Diffusion Mechanisms

Segregation of uranium and plutonium can also occur by a surface-diffusion or volume-diffusion mechanism. The flux equations for these mechanisms are similar to Eq. 3, except that a heat of transport Q^* replaces the heat of vaporization ΔH . The quantity Q^* has not been measured for the oxides of interest, and even its sign is uncertain. If, however, the effective

Q^* 's for uranium and plutonium are different, segregation would be possible. It has been argued⁷ that Q^* for uranium and plutonium will not be significantly different because of the chemical similarity between uranium and plutonium. However, atomic movement is a thermally activated process during both solid-state diffusion and vaporization. Thus, it seems likely that if the equilibrium vapor pressures are different, as demonstrated in Refs. 10, 27, 28, and 30, the Q^* 's could also be different.

It has been suggested^{10,31} that temperature-gradient volume diffusion is a long-term process wherein progressive redistribution occurs after the vapor-transport process has ceased to be effective. Experimental evidence from the present study does not support this theory. The high-burnup NUMEC fuel elements had two to three times greater burnup than the ANL fuel elements listed in Table I, but they did not show significantly greater redistribution of the actinides. Differences in operating temperature between these fuel elements caused by different power ratings may invalidate this comparison. However, sections of the PNL fuel elements experienced temperatures and temperature gradients similar to some of the restructured fuels, while accumulating burnups as much as 3.5 at. %, but no actinide redistribution could be detected in the PNL fuels where vapor transport did not occur.

In principle, a solid-state diffusion mechanism could lead to actinide segregation, but the experimental evidence indicates that segregation by vapor transport is dominant. A distinction can be made between the temperature-gradient-diffusion term, which could lead to segregation, and the concentration-gradient-diffusion term, which leads to homogenization. Even if the former is ineffective because of similarities in the Q^* 's for uranium and plutonium, the latter could be important. Back diffusion in the concentration gradient will occur, but it is not necessary to assume this is important to explain the results observed. Furthermore, the results of surface-relaxation measurements by Maiya³² indicate that solid-state mechanisms are not effective at high temperatures in producing long-range mass transport in UO_2 . These measurements were designed to separate the effects of the various transport mechanisms, and they showed that at temperatures above 1660°C vapor transport was responsible for the surface shape changes.

C. Segregation in Molten Fuel

If a fuel element is operated so that a portion of the fuel is molten, an additional segregation mechanism is possible. In the molten fuel, the actinide concentration will be uniform. During normal freezing, the first solid to appear will have a concentration different from the concentration of the liquid. For moderately hypostoichiometric $(U_{0.8}Pu_{0.2})O_{2-x}$, the phase diagram³³ indicates that the first solid to freeze will be uranium-rich, leaving behind a plutonium-rich liquid. Therefore the central region, which

would be the last to freeze, would be plutonium-rich. The exact shape of the concentration profile, however, will depend on the freezing rate and the degree of mixing that results from diffusion or thermal convection in the liquid.³⁴

The fuel elements described in Table II were operated at high linear power ratings and had molten centers during some portion of their irradiation history. Thus, it can be expected that actinide segregation would occur by both the normal freezing and the vapor-transport mechanisms described previously. In addition, some axial relocation of the molten fuel was observed in these elements,³⁵ so it is not surprising that the maximum plutonium concentrations listed in Table II varied. It is clear, however, that increases in plutonium concentration in excess of 100% can occur when fuel melting takes place.

D. Axial Redistribution

Actinide segregation can occur by the vapor-transport process operating axially through the central void. It seems likely, however, that axial transport would occur so as to minimize both concentration and temperature gradients along the wall of the central cavity. If a temperature gradient existed, material would evaporate from the hot areas and condense on the cooler areas of the void wall. Even though uranium might be preferentially evaporated, fissile plutonium would also be transported, changing the power profile and reducing the axial temperature gradient. Once temperature uniformity had been achieved, vapor transport in a concentration gradient (first term in Eq. 3) would cause a reduction of the concentration differences along the wall.

Fuel-centerline temperatures, as shown in Fig. 5, exhibit a tendency toward isothermal conditions along the wall of the central void; i.e., the temperature differences between the top, middle, and bottom sections are much less after restructuring. Furthermore, any axial transport that has occurred is not taken into account in the temperature calculation; therefore, it is possible that temperature differences along the wall of the void are less than indicated in Table I. Except for the top section of NUMEC C-15, the data listed in Table I show considerable consistency between concentrations at the top, middle, and bottom sections, even though the initial temperatures, burnups, and linear power ratings were substantially different for these sections.

An attempt was made to test for axial segregation by performing a mass-balance analysis on the data for the three NUMEC elements. The mass of plutonium per unit length of fuel within a region bounded by radii r_1 and r_2 is

$$Pu \text{ (mass)} = \int_{r_1}^{r_2} Pu \text{ (wt \%)} 2\pi r \rho \, dr, \quad (5)$$

where $Pu \text{ (wt \%)}$ is the measured concentration of plutonium, which varies with radius, and ρ is the density of the mixed-oxide fuel. Since the microprobe data were obtained on fully dense locations in the fuel, ρ is the theoretical density. The mass of plutonium originally in this volume of fuel is

$$Pu \text{ (mass)} = \int_{r_1}^{r_2} (17.9) 2\pi r \rho \, dr, \quad (6)$$

where 17.9 is the wt % of plutonium in $(U_{0.8}Pu_{0.2})O_2$. If the ratio of Eq. 5 to Eq. 6 is greater than unity, a relative gain in the amount of plutonium in that region is indicated. Because the microprobe data were obtained at fully dense points in the fuel, absolute values of net gains or losses of material from the radial sections are not detectable. A plutonium-mass ratio greater than unity can therefore be due to a net gain of plutonium, a net loss of uranium, or a combination of both.

Results of this relative mass-balance method are shown in Fig. 10. Mass ratios were evaluated from the microprobe data using suitable sums to replace the integrals in Eqs. 5 and 6. The region over which the sums were performed was bounded by the central void and the cool end of the columnar grains, eliminating the uncertainties from the measurements in the colder regions where no significant actinide migration occurs.

Fig 10

Total Mass of Plutonium in Radial Section after Irradiation, Compared with Initial Total Mass Neg Nos. MSD-56350, -56351, and -56352.

The error bars in Fig. 10 show the root-mean-square deviations of the three measurements represented by each point. The accuracy of the mass ratios is no better than the 4% uncertainty of the maximum concentration values. Therefore, the results for NUMEC C-6 and C-11 do not indicate any significant axial redistribution. However, the results for NUMEC C-15 indicate a relative gain of plutonium in the top section. Inasmuch as the top section of NUMEC C-15 had the highest plutonium concentration of any nonmelted fuel element we examined, it is concluded that this section experienced actinide segregation by axial transport, which did not occur in the other fuel elements. The high plutonium concentration in the top section of NUMEC C-15 is unusual, and the reasons are not understood.

V. CONCLUSIONS

Measured radial actinide distributions in 11 mixed-oxide fuel elements irradiated in EBR-II established that the plutonium concentrations were higher near the central void when segregation occurred. Redistribution of uranium and plutonium is closely tied to central-void formation, and for peak linear power ratings less than 11 kW/ft, no central void was formed and no actinide segregation occurred. In nearly stoichiometric restructured fuels, plutonium concentrations near the central void were typically 35-50% higher than the initial value, and for fuels that experienced center melting (>20 kW/ft), increases greater than 100% were sometimes measured. Mixed-oxide fuels with burnups to 11 at. % were examined, but no dependence of actinide segregation on burnup was seen.

These results are consistent with a vapor-transport mechanism in which uranium is preferentially evaporated from the hot central region of the fuel and transported, by means of porosity, down the temperature gradient. The redistribution process is effectively stopped when central-void formation lowers the centerline temperature. Equilibrium conditions for the concentration gradient probably do not apply. Flux equations for actinide transport in the vapor phase were presented, and the basis of a quantitative model was outlined.

Direct evidence that supports a preferential vapor-transport mechanism was found in the pellet-interface region of a fuel fabricated from dished-end pellets, where an enhanced uranium concentration occurred in the cool portion of the interface gap. No indication of solid-state diffusion contributing to actinide segregation was seen in several cases where it might have been expected. A relative mass-balance analysis indicated that axial redistribution of the actinides occurred in one of the fuel sections examined.

Although a large quantity of experimental data has been accumulated, the conclusions should be treated with some reservation because the number

of fuel and operating variables is large. The relation between actinide redistribution and central-void formation must be examined more closely so that effects of restructuring and O/M ratio can be clearly separated. Restructured fuels with initial densities $\approx 92\%$ TD should also be examined to study fuel-density effects. The effect of initial fuel O/M ratio is expected to be important, and mixed-oxide fuels with a wide range of O/M ratios are currently being examined. Thus an understanding of actinide redistribution in terms of a vapor-transport mechanism is emerging, but further experimental and analytical work is required to clarify the effects of fuel variables and to develop a detailed model that will accurately predict actinide distributions under various fabrication and operational conditions.

APPENDIX

Effect of Actinide Redistribution on Allowable
Power Rating and Doppler Broadening

by

W. T. Sha and P. R. Huebotter

The tendency for radial redistribution of uranium and plutonium in mixed-oxide fuel elements has a potential effect on two important considerations in fast-reactor core design: (1) allowable power rating, and (2) Doppler broadening. As an adjunct to the ongoing empirical and theoretical effort to characterize and understand the redistribution phenomenon, its engineering significance was assessed³⁶ and is reported in detail here.

1. Allowable Power Rating

As a result of radial actinide redistribution, the plutonium concentration increases near the fuel-element centerline, and the profile of radial power generation in fuel elements of the FTR and future LMFBR's will be skewed accordingly. Maximum fuel temperature will be higher for the same linear power than in an otherwise identical element with homogeneous U-Pu distribution, or in an element with actinide heterogeneities but high uranium enrichment, e.g., mixed-oxide elements currently being irradiated in EBR-II. For a given limiting fuel temperature (i.e., the fuel solidus), therefore, the allowable linear power rating must be reduced if this effect occurs.

a. Analysis

To determine how seriously U-Pu redistribution can affect allowable power rating, calculations based on two "limiting" cases* of radial redistribution were performed, assuming they occurred in an LMFBR fuel element with 0.25-in. cladding OD by 0.015-in. wall thickness and a fuel smeared density of 85% TD. Case A, based on results from fuel element GE-F2Z,³⁷ involves a moderate degree of U-Pu redistribution that is typical of pellet-type fuel elements operated at power ratings in the 12- to 16-kW/ft range. Case B, based on results from the bottom section of Element SOV-1 (see Table II),²² involves considerably more radial segregation, which is apparently typical of low smeared density and linear power above the current range of interest.

The heat-transfer analysis used the VOID³⁸ computer program to locate the columnar, equiaxed, and undisturbed fuel regions after

*The two cases do not represent theoretical limits, but rather "typical" and "high" degrees of redistribution, and afford a basis for interpolation and extrapolation within reason.

restructuring. Fuel densities indigenous to these regions, their interface temperatures, and thermal-conductivity expressions were based on work by Baily and co-workers.^{39,40} The radial heat-generation profile was determined by S_8 transport theory⁴¹ and was found to be closely proportional to the radial plutonium mass profile. With the calculated radial heat-generation profile, the THTB⁴² computer program was used to calculate steady-state and transient temperature distributions. (The transient temperatures were used later in the analysis of Doppler broadening.) The core-midplane sodium temperature was taken as 900°F. The radial plutonium-distribution patterns of limiting Cases A and B were assumed to follow the expression $y(r) = c_i(b - ar)$, where i designates regions after fuel restructuring; c_i was evaluated by region, based on the local-to-average fuel densities; and the constants a and b were chosen to describe the experimental measurements of plutonium concentration. For limiting Case A, the values of a and b are 10.66 and 1.8, and corresponding values for Case B are 2.76 and 1.22.

b. Results and Discussion

To consider the effect of U-Pu radial segregation in proper perspective, it must be presented in context with other determinants of

Fig. 11. Effects of Plutonium Redistribution, Fuel Restructuring, and Contact Heat-transfer Coefficient on Allowable Power Rating of LMFBR Mixed-oxide Fuel Elements, Neg. No. MSD-56353.

allowable power rating and the uncertainties therein, an imposing assignment not completely discharged in the present study. However, Fig. 11 shows the sensitivity of allowable power rating to at least the first-order determinants. As expected, the allowable power rating is strongly dependent on the contact heat-transfer coefficient, which was varied from 500 to 2000 Btu/hr-ft²-°F, in this study. This range of values is worth 3-4 kW/ft in allowable power rating; that is, a coefficient of 2000 permits an element to be operated at 3-4 kW/ft higher than an identical element with a coefficient of 500.

Allowable power rating is greatly assisted by the fuel restructuring process. The 4- to 5-kW/ft benefit shown in Fig. 11 is, in roughly equal proportions, due to the geometric benefit from the central hole and the improvement in thermal conductivity that results from higher fuel density after restructuring.³⁹ In LMFBR fuel-element design practice, the allowable

power rating is always evaluated for the restructured case, and the bottom curve in Fig. 11 has no significance unless restructuring kinetics are slow in relation to the time scale for normal reactor startup. Some evidence exists that restructuring at temperatures approaching the solidus occurs in minutes. If so, it is probably unnecessary to be concerned about inadvertent fuel melting due to too rapid startup of a reactor that contains unrestructured fuel.

Uncertainty regarding the (U,Pu)O₂ solidus temperature and the apparent dependence of this property on burnup, stoichiometry, and U/Pu ratio, create a range of values that are taken as the design-limit temperature. This range is 2650-2800°C, which is worth 0.5-1.5 kW/ft in allowable power rating, as shown in Fig. 11.

Figure 11 also shows the effect of U-Pu redistribution on allowable power rating. The penalty for a small amount of redistribution (Case A) is about 0.5-0.8 kW/ft, depending on the contact heat-transfer coefficient and the temperature assigned as the design limit. For a large amount of plutonium redistribution (Case B), the penalty ranges from 1.8 to 3.2 kW/ft.

2. Doppler Broadening

The Doppler effect, the most important prompt negative-reactivity feedback effect in large ceramic-fueled fast reactors, arises from the temperature sensitivity of the ²³⁸U parasitic-capture cross section. Simply stated, as the average temperature of ²³⁸U increases, its capture probability increases; thus, the effective neutron multiplication decreases. In principle, U-Pu segregation, coupled with the low thermal conductivity of mixed-oxide fuel, introduces a time lag between the increased rate of plutonium heat generation in a power excursion and uranium heating.

a. Analysis

The effect of plutonium redistribution on Doppler broadening was investigated based on the following assumptions:

- (1) The Doppler coefficient can be expressed in the simple form

$$\frac{dk}{dT} = -\frac{a}{T}, \quad (7)$$

where a is a constant that may be determined experimentally or by detailed neutronic calculation for a given reactor design. Doppler saturation effects are neglected.

- (2) The effect of plutonium redistribution on the value of a is assumed negligible.

- (3) No plutonium segregation is present in the axial direction.
- (4) The effect of Doppler-reactivity feedback on reactor power is neglected.
- (5) The dynamic response of a reactor may be represented by a single-pin analysis.

Average uranium temperatures* for homogeneous (U,Pu)O₂ and for limiting Cases A and B were calculated during three power transients with initial conditions represented by a linear power rating of 12 kW/ft and a contact heat-transfer coefficient of 1000 Btu/hr-ft²-°F. The three transients are described by $P(t) = P(0) \exp(xt)$, where P is reactor power, t is time (sec), and x is 0.01, 1.0, and 1000, which represents mild, rapid, and very rapid (accident condition) transients.

b. Results and Discussion

The effects of radial plutonium redistribution on the neutron multiplication factor, from zero power to full power (12 kW/ft) and during the three hypothetical power transients that start from full power, are shown in Fig. 12. From these results the following observations can be made:

- (1) During the reactor startup operation (zero to full power), the Doppler effect will be greater (more negative) for a core with radial plutonium redistribution in the fuel elements than for an identical core without plutonium redistribution. With full reactor power typified by fuel elements at 12 kW/ft, and extensive plutonium redistribution represented by Case B, the difference in startup Doppler effect is $\approx 0.04(a)$.**

Fig. 12

Effects of Plutonium Redistribution on Neutron Multiplication Factor Evaluated for Mixed-oxide Fuel Taken from Zero to Full Power and during Three Power Transients. Neg. No. MSD-56354

*Since the Doppler effect is mainly due to the resonance broadening of ²³⁸U, the average uranium temperature was used to compute the change in neutron multiplication.

**If a is assigned the value of 0.005 and the effective delayed-neutron fraction β is assigned the value of 0.003, the difference in startup Doppler is $\approx 7 \text{ d}$.

(2) For a mild power transient from full power ($x = 0.01$), the effect of plutonium redistribution on Doppler feedback is negligible.

(3) For a rapid power transient from full power ($x = 1$ or a 1-sec period), the effect of plutonium redistribution on Doppler feedback is noticeable, but not significant--a few cents in the first 2 sec, by which time extensive core damage would have occurred. The minor irregularities in the lines in Fig. 12 are due to latent heat effects and the fact that the thermal arrests occur at slightly different times during the transient for the homogeneous plutonium case and the redistributed plutonium cases.

(4) For a very rapid power transient from full power ($x = 1000$ or a 0.001-sec period), the effect of plutonium redistribution on Doppler feedback is noticeable, but minor. The analysis was taken to 0.01 sec, by which time the total Doppler reactivity swing was about 20 β less negative for Case B than for a homogeneous distribution of plutonium. It is unnecessary to carry the analysis further, because after 0.01 sec, the average uranium temperature is 8000-9000°C, the core disassembly process has started, and the accident (as well as the uncertainties in analyzing the accident) is dominated by fuel movement, sodium voiding, fuel-coolant interactions, and other processes. By comparison with these phenomena, the impact of plutonium redistribution, reflected through the role the Doppler effect plays in the accident, is unimportant.

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