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**THE ROLE OF FISSION PRODUCTS
IN THE SWELLING OF IRRADIATED
 UO_2 AND $(\text{U}, \text{Pu})\text{O}_2$ FUEL**

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ADVANCED PRODUCTS OPERATION

GENERAL ELECTRIC

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THE ROLE OF FISSION PRODUCTS IN THE SWELLING
OF IRRADIATED UO_2 AND $(U, Pu)O_2$ FUEL

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SECTION I

INTRODUCTION

Up to now, the studies of the "swelling" or volume increase of fuels under irradiation have been almost entirely devoted to the behavior of gaseous fission products. It is generally admitted that to a large extent, gas bubble distribution, migration, and coalescence under a thermal gradient determine the swelling rate. It has also been emphasized that solid fission products contribute significantly to the swelling, but no detailed justification is given for the orders of magnitude reported. Data concerning the location of solid fission products in irradiated fuels, and consequently directly connected to the swelling problem, have become available only recently.

The contribution of the solid fission products to the swelling of irradiated UO_2 or mixed oxide (U, Pu) O_2 fuel was studied on the basis of the analytical results obtained. A tentative model was devised to account for the portion of the increased volume which is due to the accumulation of solid fission products as a function of irradiation exposure.

It is the purpose of this report to present the analytical steps involved in synthe-

sizing the model for the swelling process of UO_2 or mixed oxides which is due to solid fission products.

The report is divided in four main sections.

- a. Definition of the elements resulting from uranium and plutonium fission and evaluation of their concentration in the fuel irradiated under specific conditions.
- b. Study of the behavior of the fission products in the irradiated fuel and identification of the compounds they contribute to form.
- c. Estimation of the partial volume of the compounds associated with each fission product.
- d. Calculation of swelling rates by summation of the partial volumes at a given burnup.

SECTION II

THE FISSION PRODUCTS OF URANIUM AND PLUTONIUM

Under irradiation, the uranium and plutonium atoms fission into one pair of "fission product" atoms. Some of these fission products are stable and are accumulated in the fuel, others are radioactive and

decay into new species; still others capture neutrons and generate in turn stable or unstable species. Therefore, the composition of the fuel during irradiation follows a rather complicated pattern.

The distribution of the elements resulting from uranium and plutonium fission induced by thermal, ^(1,2) FCR, ⁽³⁾ and fast, ⁽⁴⁾ neutron spectra are available from the literature. Typical fission product spectra or fission yield are given in Sections IV in Table 4-1 and 4-2.

The fission products generated from uranium and plutonium fission are basically the same in nature but their respective concentration in noble metals for instance, can differ widely from U-235 to Pu-239 fission yield. In FCR or fast flux, the situation is more complicated by the fact that U-238 is fissioning and data as precise as that for U-235 are not available. The same is also true for higher mass isotopes of plutonium. As we shall see later, from the point of view of solid fission products, there is little difference for uranium fission yield whatever the neutron spectrum considered. The situation is also similar for plutonium fission. Under these conditions, it has been assumed that for a given neutron spectrum, the fission

yields for the solid fission products are the same for U-235 and U-238 and for Pu-239, Pu-240, Pu-241, and Pu-242.

Since the concentration of one given element in the fuel changes constantly during the irradiation, the operating conditions must be specified: Composition of the fuel density in fissile material, characteristics of neutron flux, irradiation and cooling time, etc.

If one assumes a constant fission rate for practical purposes, the burnup achieved is a linear function of the irradiation time. Under these conditions at a given burnup level, the relative concentrations of each solid fission product resulting from U-235 fission do not differ significantly whatever the neutron spectrum is—thermal, FCR, or fast. The same is true for Pu-239 fission. It will be shown later for several cases that when radioactive equilibrium is reached for a specific element, its concentration and dependent properties increase linearly with the burnup level.

SECTION III

BEHAVIOR OF FISSION PRODUCTS IN IRRADIATED OXIDE FUELS

A considerable number of observed microstructures of oxide fuels irradiated at various burnups and in different conditions are reported in literature. The irradiated fuel consist of an oxide matrix more or less restructured when compared to the original structure. In the irradiated state, oxides exhibit inclusions, gas bubbles, and in some cases, interaction between the fuel and the cladding materials.

3.1 EXPERIMENTAL DATA RELATED TO THE BEHAVIOR OF FISSION PRODUCTS IN THE IRRADIATED FUEL MATRIX

Early experiments have shown that the matrix of irradiated oxide fuel is not homogeneous.

- a. Bleiberg, et al., ⁽⁵⁾ have concluded from metallographic examination of UO_2 based fuels irradiated in a wide

burnup range that the fission products are accumulated at the grain boundaries. In particular, the grain boundaries increase in thickness as the irradiation proceeds and they present an enhanced sensitivity to the chemical etchants used in metallography. A sub-grain formation is noted to occur in high burnup specimens, indicating short path diffusion of the fission products and local accumulation inside the grain of the matrix.

In the same work, ⁽⁵⁾ reference is made to experiments performed by Padden, where by successive acid leaching of irradiated fuels, it was shown that Zr, Ce, Sr, and Cs were concentrated at the grain boundaries.

- b. Recently, Bradbury, et al., ⁽⁶⁾ have investigated, by electron microprobe technique, the fission products which could be expected in irradiated UO_2 samples according to their importance in the fission yield. In this study, only Nd was detected in the matrix, although its fission yield is comparable to other fission products such as Zr and Ce, which are all known to be very soluble in UO_2 from out-of-pile experiments. Other fission products were found segregated in inclusions which will be considered in the next section.

3.2 EXPERIMENTAL DATA RELATED TO THE BEHAVIOR OF FISSION PRODUCTS AND INCLUSIONS OBSERVED IN IRRADIATED FUEL

It has been observed that fuels irradiated at high temperatures contain inclusions. Information concerning their composition is rather contradictory, at least from early UO_2 irradiation results.

- a. On the basis of their metallographic appearance, Bleiberg and Lustman ⁽⁵⁾ have reported that they were likely

metallic and uranium based alloys containing nonvolatile fission products such as Nb, Zr, etc. The resistance of these inclusions to the attack of etchants used in metallography was explained on the basis of the decreased chemical activity of uranium resulting from alloying with these elements.

- b. X-ray diffraction patterns, obtained by Bates ⁽⁷⁾ on a section of irradiated fuel, exhibited extra lines in the diffraction pattern of UO_2 which could be indexed as characteristic of the beta uranium structure. On this basis, it was concluded that the inclusions were beta uranium alloys stabilized by fission products.
- c. From further experiments performed on a very large inclusion extracted from UO_2 fuel and consequently devoid from any matrix effect, Lustman ⁽⁸⁾ concluded that these kinds of inclusions "are basically metallic in nature." The spectrographic analysis has shown that the major constituents of the inclusions are Ru, Mo, Rh, and a small quantity of Pd, and they did not contain either uranium or zirconium.
- d. In the same experiments mentioned above, Bradbury, et al., ⁽⁶⁾ examined thin slices of irradiated UO_2 by an x-ray microprobe technique. Two types of inclusions were identified.

1. The Barium-free inclusions possibly metallic and containing Mo, Tc, Ru, and Rh in which a concentration of 40 percent of uranium is given as a maximum limit. It is considered, however, that the UO_2 matrix could be responsible for the uranium observed since when scanning the sample under the electron beam of the microprobe, the inclusions exhibit a net depletion in uranium compared to the oxide matrix.

2. The Barium containing inclusions in which zirconium and strontium are often associated. Possible formation of perovskite type compounds such as barium zirconate (BaO_3Zr) is strongly suggested but had not been verified experimentally at that time. Mo, Ce, and Y have also been observed in these inclusions.

Using x-ray diffraction techniques, Aitken et al.,⁽⁹⁾ have definitely identified BaO_3Zr in synthetic fissia samples sintered at 1400°C . The existence of this type of compound in the irradiated fuels is, therefore, no longer questionable.

It is important to note that although the two kinds of inclusions differ widely in their structural material, they have not been differentiated metallographically.

- e. In a recent work performed on inclusions extracted from UO_2 and $(\text{U}, \text{Pu})\text{O}_2$ fuels partially molten during irradiations, Davies et al.,⁽¹⁰⁾ provided some information for the first time about the inclusions in irradiated mixed oxide fuel $(\text{U}, \text{Pu})\text{O}_2$. Based on resistivity measurements, it was concluded that the inclusions recovered were definitely metallic in both UO_2 and mixed oxide fuels. From chemical analysis, it was found that they contain only very small quantities of uranium or plutonium and no zirconium. The composition of those inclusions is basically the same for both UO_2 and $(\text{U}, \text{Pu})\text{O}_2$ fuels with the major components being Mo, Ru, Rh, and Pd. The presence of Sb has also been detected, and it was, therefore, suggested that all the elements ranging from Mo to Sb could be reduced as a metal.

It should be emphasized that from both the works of Lustman⁽⁸⁾ and Davies⁽⁹⁾

which were performed on big inclusions devoid from any matrix effect, it was concluded that the metallic inclusions do not contain uranium and plutonium. This conclusion is in contradiction with the results of Bates and Bradbury who worked on sections of irradiated fuel.

3.3 THEORETICAL BEHAVIOR OF SOLID FISSION PRODUCTS IN IRRADIATED FUELS

It appears from the experimental results mentioned above that the oxide fuel after irradiation still consists of an oxide matrix or heterogeneous structure where metallic and nonmetallic inclusions are segregated. From thermodynamic considerations, it can be established that the presence of metallic inclusions is justified in an irradiated oxide fuel matrix.

Because each uranium or plutonium atom fission generates two fission product atoms and liberates simultaneously two oxygen atoms, the relative oxidation behavior of the oxide matrix nonfissioned and of the fission products must be compared. The fission products of uranium or plutonium can be divided into two classes by considering the relative stability of the oxides in terms of their relative free energy of formation as tabulated by Glassner.⁽¹¹⁾ Those which can form oxides of greater or comparable stability to that of the initial oxide fuel matrix, and those which can form oxides less stable than the same matrix. For a given element for which several oxides are known to exist, the oxide which has the highest free energy will be formed first, the others only existing as unstable transient species. If the oxygen activity increases this oxide can now be transformed into a formerly less stable one, etc.

The most probable valence of the fission products is, of course, determined by the nature of the oxide which is the most stable in the operating conditions, for instance $3+$ in a sesquioxide, etc. Dividing the

solid fission products in two main categories, as shown in Figure 3-1, we have:

a. In the first category, the fission product atoms: Y, Zr, La, and all the rare earths Ce, Pr, Nd, Pm, Sm, Eu, Gd, can form oxides of greater stability than the initial matrix UO_2 or $(\text{U}, \text{Pu})\text{O}_2$. They must be oxidized at their most stable valence by preference to any other fission product. They could reduce the fuel matrix if there were not enough oxygen for this process; they generate oxides of crystal structure close to that of the matrix and can form extensive solid solutions with it. They will be considered as the "soluble fission products"—Sr and Ba can form stable oxides belonging to that category which are known to be completely insolubles in UO_2 from out-of-pile experiments, ⁽¹¹⁾ but we have seen that they contribute to the formation of Zirconates, thus reducing the quantity of "soluble" Zr available.

b. In the second category, the remaining fission products can form oxides that are considerably less stable than the matrix as long as the matrix does not become strongly hyperstoichiometric. As a consequence, the remainder of the oxygen atoms (left only when fission products of the first category are oxidized) can be dissolved in the matrix to some extent before oxidizing the fission products of the second category. The fission products in this category can be further divided into:

1. Alkaline metals Rb and Cs—their oxides are very unstable at moderate temperature (1000°).
2. Metals or elements exhibiting some metallic character—their oxides are easily reduced. (As, Ge, Nb,

Mo, Tc, Ru, Rh, Pd, Ag, Cd, In, Sn, and Sb.)

c. The behavior of some of the fission products, Br, I, Se, Te, not mentioned up to now, is hard to predict, but they fortunately interest minor fractions of the fission yield. It should be noted, however, that some can form refractory ionic compounds.

3.4 DISCUSSION

3.4.1 Matrix

Apparently there is very poor agreement between experimental results and the behavior expected from thermodynamic consideration, at least for the fission products of the first category.

The concentrations of each soluble solid fission product (first category) accumulated during irradiation were calculated, using the fission product spectra for U-235 and assuming a linear burnup as a function of the time. Table 3-1 summarizes the results for UO_2 irradiated in thermal, FCR, and fast neutron flux at about 3 and 10 percent burnup, respectively. Because the concentration achieved for one specific element is only time (or burnup) dependent and does not differ significantly from one fission spectra to another, reference can be made to the UO_2 sample irradiated at about 5 percent burnup which was investigated by Bradbury, et al.

It is shown from Table 3-1 that at burnups as high as 100,000 MWd/Te (i.e., 10.5 atomic percent fission) the total concentration of soluble fission products is only 7 atomic percent. When each one is considered separately, only Nd, soluble Zr, and Ce are in noticeable concentration. If the absence of all the other soluble fission products is explained, that of Zr and Ce in the matrix when Nd was observed could be considered as abnormal.

FIGURE 3-1. STANDARD FREE ENERGY OF FORMATION OF FISSION PRODUCT OXIDES

However, in Bradbury's experiment, the sample examined was highly radioactive and the sensitivity of the microprobe was lowered to a threshold of detection of about 0.5 to 1 weight percent. In conclusion, the concentration achieved for the major component Nd was just sufficient to be detected if homogeneously distributed.

The sample examined had cooled a long time, radioactive species had decayed, and the picture observed may not be exactly representative; since Nd is at the end of several beta decay schemes its concentration would have increased. Some of these elements have gaseous precursors momentarily dragged in as gas bubbles to the grain boundaries. When the given but small amount generated for a given burnup is considered, a higher concentration of fission products at the grain boundaries (as observed by Padden) is related to a depletion of the matrix (as observed by Bradbury). In conclusion, the discrepancy between theoretical and experimental behavior for the soluble fission products (first category) is due mainly to the low concentrations achieved for each element even at the high burnup considered.

3.4.2 Inclusions

Apparently, for all the components contributing to the formation of inclusions, the agreement is better. Although some precision is needed about the role of oxygen formerly associated with U or Pu fissioned, it has been shown that the less oxidizable species of the fission yield can coexist in an oxide matrix, but no information is given for the amount of fission products reduced as a metal. The presence of uranium in metallic inclusion is not firmly established and needs to be verified.

The presence of nonmetallic inclusion (ZrO_3Ba) was unexpected; it is logical a posteriori since BaO and SrO are very stable and reactive oxides, but are completely insoluble in UO_2 . In this type of inclusions,

Mo, Ce, Y have been definitely identified, but these elements are respective decay products of Zr, Ba, and Sr, and their presence is normal if a sample is investigated after a long cooling time as it was in that experiment, although it has been suggested by Aitken⁽¹²⁾ that Ce could be partially substituted in zirconate compounds. Once again, except for uranium in metallic inclusions, there is no longer any discrepancy between theory and experiment.

3.4.3 Others

The role of the alkali metals Rb and Cs remains unknown. It is likely that if the M_2O type oxides are formed they are strongly dissociated, and the metals which are volatiles concentrate in the cold parts of the fuel or even escape if its surface temperature is too high. The existence of cesium rich deposits often observed on cold parts of the cladding support this point of view at least partially. However, it has been observed that only 20 percent of the cesium is released from UO_2 irradiated and operated 30 percent molten for several months.⁽³⁾ This suggests that Rb and Cs could participate in the formation of some unknown compounds.

3.5 CONCLUSIONS RELATIVE TO THE BEHAVIOR OF FISSION PRODUCTS IN UO_2 AND (U, Pu) O_2 IRRADIATED FUELS

The behavior of the elements generated by fission for both UO_2 and (U, Pu) O_2 is summarized in Table 3-2. It must be considered that although they are based on experimental results confirmed by theory, there could be some local deviation from these rules.

For instance, the part of Zr involved in the formation of zirconates has been arbitrarily taken as equal to the amount of Sr and Ba present although some of these latter are radioactive and decay in other species.

TABLE 3-1
 CONCENTRATION ATOM PERCENT SOLUBLE FISSION PRODUCTS
 IN IRRADIATED UO_2 (20 Percent Enriched)

(100 Percent Dense Medium. Burnup of 100,000 MWd/Te
 Achieved in 365 days or 37,000 MWd/Te in 135 days.)

Fission Product Spectra U-235	FCR ⁽²⁾	Fast ⁽³⁾	Fast ⁽³⁾	Thermal ⁽¹⁾
Burnup (MWd/Te)	100,000	100,000	37,000	37,000
Irradiation Time (days)	365	365	135	135
Y	0.63	0.48	0.19	0.21
Zr soluble*	1.33	1.51	0.52	0.52
La	0.63	0.67	0.25	0.24
Ce	1.84	1.54	0.61	0.72
Pr	0.67	0.53	0.17	0.19
Nd	1.78	1.98	0.66	0.66
Pm	--	0.30	0.11	0.09
Sm	0.22	0.26	0.08	0.09
Eu	--	>0.01	>0.01	>0.01
Gd	--	0.02	--	--
Total soluble $\frac{\text{FP}}{(\text{FP} + \text{U})}$	7.10%	7.30%	2.67%	2.72%

* Zr soluble defined as the Zr in excess over the Ba+Sr quantity.

TABLE 3-2
 BEHAVIOR OF FISSION PRODUCTS IN UO_2 AND $(\text{U}, \text{Pu})\text{O}_2$ IRRADIATED FUELS

A. First Category: Fission products oxides more stable than MO_2 matrix

- 1) "Soluble" fission products
 Zr (soluble), Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd.
- 2) Nonmetallic inclusion
 BaO_3Zr , SrO_3Zr

B. Second Category: Fission product oxides less stable than MO_2 matrix

- 3) Metallic inclusions: Ge, As, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, In, Sn, and Sb
 Presence of U or Pu to establish
- 4) Volatile elements Rb, Cs, and I
- 5) Ionic compounds Br, Se, Te

C. Third Category: Gaseous fission products

Kr, Xe

As suggested by Aitken⁽¹²⁾ there is some possibility of substitution of rare earth atoms in place of Zr in the zirconate lattice.

Among the elements participating in the formation of metallic precipitates only Mo, Tc, Ru, Rh, and Pd, (which are the major components of the fission yield in a proportion of 95 percent) have been defi-

nately identified. It is assumed, however, that all the other similar elements are also reduced.

Although it has been emphasized that the behavior of one element could not follow a rigid picture, these conclusions derived from experience agree fairly well with what can be predicted from theoretical considerations.

SECTION IV

CHEMICAL EFFECTS ASSOCIATED WITH THE ACCUMULATION OF FISSION PRODUCTS IN IRRADIATED UO_2 AND $(\text{U}, \text{Pu})\text{O}_2$ FUELS

As one U^{4+} or Pu^{4+} ion is fissioned, it generates a pair of fission product atoms and at the same time, two oxygen O^{2-} ions (or $4e^-$) are momentarily liberated. Accordingly, the average valence of the pair of fission product atoms is above or less than $4+$, there will be some respective oxygen in defect or in excess to oxidize the fission products. In this latter case, some oxygen is available to dissolve either into the oxide matrix or to oxidize the cladding material according to their respective affinity. For a swelling calculation, this aspect cannot be neglected because the volume change related to the generation of one pair of fission products from the fissioned atoms (which cease to exist) is not going to be the same if for instance the fission product is reduced as a metal of high density or forms an oxide of low density.

4.1 DEFINITION OF AN AVERAGE VALENCE PER AVERAGE FISSION PRODUCT ATOM

The relative oxidation behavior of the fission products and of the matrix have been considered in Section III in which the fission products were divided in two main categories:

- Those which form very stable oxides and are preferentially oxidized;
- Those which form oxides less stable than a UO_2 or $(\text{U}, \text{Pu})\text{O}_2$ matrix even hyperstoichiometric.

The amount of oxygen available to dissolve in the matrix or to oxidize the fission products of the second category can be estimated by calculating the valence change between the M^{4+} ion fissioned and the average valence of the two fission products generated. When the concept of Robinson⁽¹³⁾ and Childs⁽¹⁴⁾ is used, the average valence per fission product atoms can be defined as:

$$\bar{\gamma} = \frac{\sum_i \beta_i \gamma_i}{\sum_i \beta_i} \quad (1)$$

where

β_i is the fission yield percent for the element of subscript i

γ_i is the valence of the same element i

$\sum \beta_i$ represents twice the number of fissions.

The choice of the valence used in the calculations is listed in Tables 4-1 and 4-2 and is justified from the following considerations.

- a. For the fission products of the first category (Section III), the valence is taken as that of the cation in the most stable compound (i.e., the compound which has the highest standard free energy of formation).

Zr soluble from ZrO_2 $\gamma = 4+$

(Ce excepted) all the rare earth form M_2O_3 $\gamma = 3+$

Since CeO_2 has stability comparable to UO_2 and ZrO_2 , it has been considered that Ce forms CeO_2 with $\gamma = 4+$ rather than Ce_2O_3 although this latter is more stable at lower oxygen activities.

- b. For the fission products of the second category, two possibilities have been considered, the first being identical to that chosen above, although the oxygen would dissolve in the matrix at some extent rather than oxidize them at this valence. As suggested by experience, the second possibility is to take a valence equal to zero for elements found in metallic inclusions since they do not consume oxygen. In this category, it is observed that Rb and Cs have been considered to be at the valence +1, although we cannot predict if they form suboxides M_2O or participate in the formation of more complex compounds. Whatever the situation, if some Rb or Cs is volatilized as a metal after dissociation of their oxide, it is likely they reoxidize on the cold parts of the cladding.

The average valences for fission product atoms resulting from U-235 and Pu-239 have been calculated for a fast neutron spectrum using fission yield spectra of Burris and Dillon.⁽⁴⁾ These calculations shown in Tables 4-1 and 4-2 have been made for the

two extreme possibilities mentioned above, where the fission products of the second category are reduced or not in the metallic state.

The same type of calculation has been done using the fission spectra of U-235 and Pu-239 irradiated in thermal, FCR, and fast flux. The results are listed in Table 4-3. It is shown that in fast flux, the average valence per fission product atom resulting from U-235 fission is the same whatever the irradiation time above 1 month. The situation for fast Pu-239 fission is similar.

This confirms in another manner the fact established before (Table 3-1) with a reactor operating at steady-state conditions, i.e., with a constant local fission rate, an almost linear accumulation of fission products is to be expected in the fuel as a function of time. On the basis of small differences observed in the yield spectra for fast and thermal irradiation performed during the same duration, it can be concluded that for solid fission contribution, the effects are the same whatever the neutron flux considered, fast or thermal.

4.2 REDISTRIBUTION OF OXYGEN ATOMS RELEASED BY U AND Pu FISSION

Each Pu^{4+} ion fissioned generates two fission product atoms of average valence $\bar{\gamma}^+$, and at the same time liberates two oxygen ions²⁻. Through the use of thermodynamic principles, it is possible to determine how the oxygen available is redistributed to the fission products.

Table 4-3 shows that for one Pu fission, the average valence of the two fission products generated will be $2\bar{\gamma}_1 = 2 \times 2.55^+$, assuming that all the fission products are oxidized to their most stable valences. By utilizing the available oxygen freed from the fission of U and Pu, it can be shown that there are not enough oxygen atoms available from the fission process to oxidize all available species that compete for oxygen:

$5.10^+ + 4^- - 1.10^+ \text{ or } 0.55^-$
not compensated (2)

$2(\text{Fp})^{2.55+} + 2(0^{--}) - 0.556(0^{--})$
lacking per fission (3)

In other words, the number of oxygen ions lacking per fission is precisely $(\bar{\gamma}_1 - 2)$.

Only the most stable oxides will be formed (first category of fission products) while some of the less oxidizable species will be reduced to the elemental state (second category of fission products listed in Table 3-2), considering the standard free energies of formation.

If as suggested from chemical analysis of metallic precipitates, it is assumed that all the less oxidizable fission products (elements of the periodic chart ranging from Nb or Mo to Sb) are reduced to the metallic state, an average valence per fission product atom $\bar{\gamma}_2 = 1.29^+$ is calculated.

By using the same treatment as above, it is shown that $(2 - \bar{\gamma}_2) = 0.61$ oxygen ions are in excess once all the other fission products (rare earths, Zr, etc.) are oxidized to their most stable valences. In these conditions, depending on the relative values of the potential of dissolution of oxygen in the mixed oxide or the free energy of formation of the fission products oxides for Nb, Mo, etc., and Sb, the $(2 - \bar{\gamma}_2)$ oxygen ions available from fission will be either dissolved in the mixed oxide matrix or will form oxides with the most oxidizable species Nb, Mo, etc.

As shown by Markin, et al., (15) up to a valence number equal to 4.2 for the uranium, the oxygen potential of hyperstoichiometric mixed oxide has very little temperature dependence (at least between 500° and 1500°C). The free energies of formation of Mo oxides are of the same order of magnitude at low temperature but decrease rapidly with in-

creasing temperature. Hence, whether the available oxygen dissolves the mixed oxide or oxidizes the Mo will depend strongly on the local temperature.

In a LMFBR fuel element operating with the central temperature about 2200°C and the surface temperature 1000°C, all the Nb is oxidized and all the molybdenum can be reduced to the metallic state while the matrix becomes increasingly hyperstoichiometric.

For fuel elements operated at low power, this tendency could be reversed in the cooler outer portion of the fuel, i.e., the oxygen liberated by fission could oxidize the molybdenum to some extent rather than dissolving in the matrix. This fact is important because a small fraction of the radius located at the periphery will correspond to an appreciable fraction of the fuel and the volume of oxide MoO_2 or MoO_3 per atom of molybdenum is greater than the volume of the same element in the metallic state. Thus, the presence of stable molybdenum oxides will lead to additional swelling in the cooler fuel regions.

4.3 EVOLUTION OF STOICHIOMETRY IN THE OXIDE FUELS UNDER IRRADIATION

Table 4-2 shows that, considering the presence of metallic precipitates in irradiated fuels, the average valences per fission product generated are respectively $\bar{\gamma}_2 = 1.7^+$ and $\bar{\gamma}_2 = 1.3^+$ for U and Pu fission. This means that the amount of oxygen $(2 - \bar{\gamma})$ with $\bar{\gamma} < 2$, released by fission is higher for Pu. This is due to the higher fission yield in semi-noble metals (Mo, Ru, Pd) for the Pu compared to U fission: When considering a fuel operated at sufficiently high temperature so that all the elements ranging from Mo to Nb are in the metallic state, the changes in stoichiometry of the fuel matrix under irradiation can be calculated as a function of the burnup.

TABLE 4-1
FISSION PRODUCT SPECTRA FOR U-235 IRRADIATED 1 YEAR IN A FAST
NEUTRON SPECTRUM AND COOLED 15 DAYS

Calculation of the Average Valence Per Fission Product Atom			
Element (Fission Product i)	Fission Yield % (β_i)	Valence (γ_i)	Fission Yield $\times$ Valence ($\beta_i \times \gamma_i$)
Ge	0.005	4 ⁺	0.020 ⁺
As	0.002	3 ⁺	0.006 ⁺
Se	0.396	2 ⁻	0.792 ⁻
Br	0.133	1 ⁻	0.133 ⁻
Kr	2.907	0	0.000
Rb	3.776	1 ⁺	3.776 ⁺
Sr	8.623	2 ⁺	17.246 ⁺
Y	4.454	3 ⁺	13.362 ⁺
Zr	28.958	4 ⁺	115.832 ⁺
Nb	0.872	4 ⁺ or 0	1.088 ⁺ or 0
Mo	24.005	4 ⁺ or 0	96.020 ⁺ or 0
Tc	6.198	4 ⁺ or 0	24.792 ⁺ or 0
Ru	14.938	4 ⁺ or 0	59.752 ⁺ or 0
Rh	3.517	3 ⁺ or 0	10.551 ⁺ or 0
Pd	1.688	2 ⁺ or 0	3.376 ⁺ or 0
Ag	0.088	1 ⁺ or 0	0.088 ⁺ or 0
Cd	0.240	2 ⁺ or 0	0.480 ⁺ or 0
In	0.045	3 ⁺ or 0	0.135 ⁺ or 0
Sn	0.334	4 ⁺ or 0	1.336 ⁺ or 0
Sb	0.218	3 ⁺ or 0	0.654 ⁺ or 0
Te	0.218	2 ⁻	4.360 ⁻
I	1.046	1 ⁻	1.046 ⁻
Xe	22.188	0	0.000
Cs	18.761	1 ⁺	18.761 ⁺
Ba	6.316	2 ⁺	12.632 ⁺
La	6.270	3 ⁺	18.810 ⁺
Ce	14.369	4 ⁺	57.476 ⁺
Pr	4.943	3 ⁺	14.829 ⁺
Nd	18.049	3 ⁺	54.147 ⁺
Pm	2.765	3 ⁺	8.295 ⁺
Sm	2.417	3 ⁺	7.241 ⁺
Eu	0.025	3 ⁺	0.075 ⁺
Gd	0.166	3 ⁺	0.498 ⁺

$$\sum_i \beta_i = 200.80$$

$$(1) \sum_i \beta_i \times \gamma_i = 534.96 \text{ all the elements are oxidized.}$$

$$(2) \sum_i \beta_i \times \gamma_i = 336.66 \text{ Nb to Sb are reduced.}$$

$$\bar{\gamma}_1 = 2.66^+ \text{ if all the elements are oxidized.}$$

$$\bar{\gamma}_2 = 1.68^+ \text{ if Mo to Sb are reduced (i.e., at valence 0).}$$

Although the "soluble" fission products (rare earths, Zr, etc.) are not homogeneously distributed in the mixed oxide matrix, it is likely that they go into substitutional solid solution in the cation sublattice of the mixed oxide matrix even if high local concentration gradients exist. In this condition, the oxygen ions available from fission are reallocated not only among nonfissioned U and Pu but also among the soluble fission products.

The calculations given in Appendix A have been performed using the two extreme hypotheses (a) none and (b) all fission products are in solid solution in the matrix to show that the conclusions do not differ significantly.

The final results displayed in Table 4-4 show an almost linear increase of the "integrated" stoichiometry as a function of the burn-up. This is a direct consequence of the almost linear accumulation of the soluble fission products.

TABLE 4-2
FISSION PRODUCT SPECTRA FROM Pu-239 IRRADIATED 1 YEAR IN FAST
NEUTRON SPECTRUM AND COOLED 15 DAYS

Calculation of the Average Valence Per Fission Product Atom			
Element (Fission Product i)	Fission Yield % (β_i)	Valence (γ_i)	Fission Yield $\times$ Valence ($\beta_i \times \gamma_i$)
Se	0.008	2 ⁻	0.016 ⁻
Kr	0.902	0	0.000
Rb	1.066	1 ⁺	1.066 ⁺
Sr	3.853	2 ⁺	7.706 ⁺
Y	2.040	3 ⁺	6.120 ⁺
Zr	19.762	4 ⁺	79.048 ⁺
Nb	0.678	4 ⁺ or 0	2.712 ⁺ or 0
Mo	20.269	4 ⁺ or 0	81.076 ⁺ or 0
Tc	5.898	4 ⁺ or 0	23.592 ⁺ or 0
Ru	24.376	4 ⁺ or 0	97.504 ⁺ or 0
Rh	5.654	3 ⁺ or 0	16.962 ⁺ or 0
Pd	15.660	2 ⁺ or 0	31.320 ⁺ or 0
Ag	1.704	1 ⁺ or 0	1.704 ⁺ or 0
Cd	0.977	2 ⁺ or 0	1.954 ⁺ or 0
In	0.093	3 ⁺ or 0	0.279 ⁺ or 0
Sn	0.222	4 ⁺ or 0	0.888 ⁺ or 0
Sb	0.367	3 ⁺ or 0	1.091 ⁺ or 0
Te	4.602	2 ⁻	9.204 ⁻
I	2.392	1 ⁻	2.392 ⁻
Xe	23.935	0	0.000
Cs	17.810	1 ⁺	17.810 ⁺
Ba	5.722	2 ⁺	11.444 ⁺
La	5.317	3 ⁺	15.951 ⁺
Ce	12.066	4 ⁺	48.264 ⁺
Pr	4.391	3 ⁺	13.173 ⁺
Nd	16.088	3 ⁺	48.264 ⁺
Pm	2.178	3 ⁺	6.534 ⁺
Sm	4.276	3 ⁺	13.178 ⁺
Eu	0.628	3 ⁺	1.884 ⁺
Gd	0.133	3 ⁺	0.399 ⁺
$\Sigma_i \beta_i = 203.52$		(1) $\Sigma_i \beta_i \times \gamma_i = 518.31^+$	all the elements oxidized.
		(2) $\Sigma_i \beta_i \times \gamma_i = 161.94^+$	Mo to Sb reduced.
$\bar{\gamma}_1 = 2.55^+$ if all the elements are oxidized.			
$\bar{\gamma}_2 = 1.29^+$ if Mo to Sb are reduced (i.o., at valence 0).			

Whatever the fission spectrum, fast or thermal, used for the calculation, the conclusions are the same and the difference in results are too low to be significant.

4.4 OXIDATION OF THE CLADDING MATERIAL AS A FACTOR LIMITING THE EVOLUTION OF THE STOICHIOMETRY OF THE FUEL UNDER IRRADIATION

The term of stoichiometry such as used in the preceding section is in fact improper and should be replaced by "integrated stoichiometry through a cross section of fuel

rod." When equilibrium is reached in an irradiated fuel pin there is an extremely low partial pressure of oxygen in equilibrium with oxide rings of various stoichiometry following the temperature profile (radial and axial). It would be logical to consider that with a fuel operating with a central temperature of about 2200°C and a surface temperature of 800°–1000°C, the oxide will be slightly hypostoichiometric at the center and increasingly hyperstoichiometric as progressing toward the periphery. This situation would be accentuated in thermal flux where the fission rate is higher at the

TABLE 4-3
AVERAGE VALENCE $\bar{\nu}$ PER FISSION PRODUCT ATOM GENERATED BY U-235 OR Pu-239
FISSION AS CALCULATED FROM FISSION YIELD SPECTRA REFERENCED

Neutron Spectrum		FCR	Fast				Thermal
Average Valence Per Average Fission Product Atom		Davis ⁽³⁾ Irradiation 1 Year	Burris-Dillon ⁽⁴⁾ Irradiated 1 Year Cooled 15 Days	Burris-Dillon ⁽⁴⁾ Irradiated 135 Days Cooled 15 Days	Burris-Dillon ⁽⁴⁾ Irradiated 85 Days Cooled 15 Days	Burris-Dillon ⁽⁴⁾ Irradiated 30 Days Cooled 15 Days	Reference (8) Irradiated 135 Days Cooled 15 Days
U-235 Fission	No Reduction	2.67 ⁺	2.66 ⁺	2.69 ⁺	2.60 ⁺	2.59 ⁺	2.50 ⁺
	Mo to Sb Reduced	1.76 ⁺	1.68 ⁺	1.74 ⁺	1.67 ⁺	1.68 ⁺	1.72 ⁺
Pu-239	No Reduction	2.57 ⁺	2.55 ⁺	2.57 ⁺	2.58 ⁺	2.58 ⁺	-
	Mo to Sb Reduced	1.22 ⁺	1.29 ⁺	1.33 ⁺	1.34 ⁺	1.34 ⁺	-

surface than in the center. However, if radial variation of the stoichiometry is to be expected because of purely thermal and fissioning effects, the presence of a cladding and its affinity for oxygen cannot be ignored.

Irradiation experiments have shown that a few hours after the beginning of operation the fuel is restructured and the initial gap between the fuel and the cladding can no longer exist at the operating temperature. With increasing burnup, the contact fuel-cladding is improved and this is favorable to eventual chemical reactions.

By comparing the respective values of the potential of dissolution of oxygen in mixed oxide of various compositions, and the free energy of formation of oxidation products in equilibrium with the stainless steel, Markin, et al., ⁽¹⁵⁾ have determined the limits of the compatibility of stainless steels and mixed oxide. When a stainless steel cladding with an inner wall temperature of about 700°C and a fuel surface temperature of 900°—1000°C, is considered, it is concluded that the stoichiometry of the fuel (UO₂ or mixed oxide 20 percent Pu) must be maintained nearly equal to 2.00. If the oxygen composition is higher, it is removed and it is free to oxidize the cladding, forming iron and chromium oxides.

In this case the oxidization process is kinetics-dependent and these conditions are only realized for sufficiently long-term irradiations. If this situation is reached with a stainless steel cladding, it will be more severe when a Zircaloy cladding is used. For instance, after irradiation of UO₂ in Zircaloy cladding, Rubin, et al., ⁽¹⁶⁾ have observed layers of grey phase at the cladding-fuel interface with the thickness of this layer increasing with the burnup. In this experiment, a number of 1.2×10^{20} oxygen molecules was estimated to generate an equivalent layer of ZrO₂ at the surface of the fuel compartment in which 6.53×10^{20} fissions occurred.

This corresponds to a release of
$$\frac{2 \times 1.2 \times 10^{20}}{6.53 \times 10^{20}} = 0.36 \text{ oxygen atom per}$$
 fission evaluated. This figure is in good agreement with $2 - \bar{\gamma}_2 = 0.28$ as was calculated in Table 4-3 for thermal fission. This oxygen release by the fission explains the presence of oxidation layers at the fuel-cladding interface after irradiation when out-of-pile compatibility tests are negative. Because the oxygen release is an almost linear function of the burnup, the thickness of the layer must also increase regularly with burnup provided that oxidation is not the controlling step.

TABLE 4-4
THEORETICAL EVOLUTION OF THE OXIDE FUEL STOICHIOMETRY UNDER
IRRADIATION PERFORMED IN AN INERT CLADDING

Irradiation Time (days)	137		365	
Burnup Achieved (MWd/Te)	37,000		100,000	
U-235 Fission	2.012	2.004*	2.040	2.015*
Pu-239 Fission	2.028	2.020*	2.085	2.060*

*All the soluble fission products in solid solution.

SECTION V

ESTIMATION OF THE VOLUME OF FUEL ASSOCIATED WITH THE NONFISSIONED
ATOMS OF THE MATRIX AND THE SOLID FISSION PRODUCTS

In preceding sections, it has been shown that the fission products participate in the formation of a rather limited number of compounds for which the properties are generally well known. Once the concentration of the solid fission products is calculated for a given burnup level, the only data needed to evaluate the swelling of the fuel associated with their generation refers to the volume of each specie (oxide, molecule, metallic atom) in which the corresponding fission product is involved. For this purpose, the crystallographic data provide the most accurate basis.

The volume of oxide associated with one cation (U or Pu nonfissioned and soluble fission product) with one molecule (Zirconates) with one atom (metallic fission product) has been simply calculated as the volume of the unit cell divided by the number of molecules or atoms in the unit cell. This is an extension of the classic Friedel method used to calculate the so called radius of the sphere of the "equivalent volume." This method provides a measure of the space effectively occupied by a large number of atoms or molecules and is the only point of interest in this analysis.

The precision in crystallographic measurements is often better than a thousandth of Angstrom and the volume of one given specie can be estimated with an accuracy better than that relative to its concentration such as calculated from the fission yield.

5.1 VOLUME ASSOCIATED WITH THE FUEL MATRIX AND THE SOLUBLE FISSION PRODUCTS

For increasing burnup, the unit cell of the mixed oxide under irradiation will evolve as follows:

Fission of the plutonium:	Unit cell increase
Conversion of U-238 into plutonium (breeding):	Unit cell decrease
Substitution of soluble fission products in cation lattice:	Unit cell decrease
Introduction of oxygen in anion lattice:	Unit cell decrease

The following breeding ratios were considered:

~0.8 for graphite or heavy water moderated reactor
 ~0.5 for boiling water reactors
 ~0.85 for the internal breeding ratio of FCR core 1963 reference design. (17)

5.1.1 Evolution of the Unit Cell of Irradiated UO_2

The presence of U-235 substituted for U-238 in the cation sublattice of UO_2 does not affect the lattice parameter which is $a = 5.470 \text{ \AA}$ for $\text{O/M} = 2.00$ with an enrichment of 20 percent. The unit cell contains four UO_2 molecules and the volume of oxide per cation U^{4+} is:

$$V = \left(\frac{5.470}{4} \right)^3 \text{ \AA}^3$$

$$= 40.93 \times 10^{-24} \text{ cc} \quad (4)$$

Independent of the V ions nonfissioned, the only cations which contribute as stable oxides to the formation of the oxide matrix are the "soluble fission products" and the plutonium converted from U-238. These can be classified as follows:

- a. Pu, Zr, and Ce form stable FCC fluorite type dioxides isostructural with UO_2 and their unit cell is smaller than that of UO_2 . By assuming the formation of ideal solid solutions, it can be shown

(Table 5-1) that the contraction of the unit cell of UO_2 associated with the substitution of Pu, Zr, and Ce in the cation sublattice is only $5 \times 10^{-3} \text{ \AA}$ at 100,000 MWd/Te burnup level.

- b. La, Pr, Nd, Pm, Sm, Eu, and Gd can form stable sesquioxides of various crystal structure (generally hexagonal A or BCC C-Type). They also can be accommodated in the cation sublattice of UO_2 with a simultaneous valence increase of uranium valence from U^{4+} to U^{5+} or U^{6+} .

Because of the regulating action of the cladding, the stoichiometry in equilibrium with the cladding should remain close to 2.00 for the same temperature conditions specified above, assuming similar properties for (U-Pu) oxides and (U-rare earths) oxides solid solutions.

Crystallographic data available from systems $(\text{U}, \text{Gd})\text{O}_2$,⁽¹⁸⁾ and $(\text{U}, \text{Y})_2$ ⁽¹⁹⁾ show that these FCC fluorite solid solution structures behave ideally with a large concentration range of rare earths substituted in the cation sublattice of UO_2 . In this condition, except for Ce and Pr, the lattice parameter of a hypothetical REO_2 FCC fluorite structure can be extrapolated, and, from this the partial volume of oxide associated with the rare earth in the UO_2 - REO_2 solid solution can be calculated.

The solid solutions $(\text{U}, \text{RE})\text{O}_2$ have not been investigated for all the rare earths which are the fission products of interest. The lattice parameter of the hypothetical RE_2O_3 structure has been evaluated in another manner.

The U_3O_8 and RE_2O_3 form, on a large but limited concentration range, solid solution of FCC fluorite structure as does UO_2 . For a solution of 43 M/O U_3O_8 + 57 M/O

RE_2O_3 a final composition $(\text{U}_{43}\text{RE}_{57})\text{O}_{2.00}$ has precisely a stoichiometry equal to 2.00 and can be considered as part of the system $(\text{U}, \text{RE})\text{O}_2$.

We have found that for Y and Gd the lattice parameter extrapolated from UO_2 and $(\text{U}_{43}\text{RE}_{57})\text{O}_{2.00}$ is the same as that extrapolated from the known $(\text{U}, \text{RE})\text{O}_2$ solid solutions, within an accuracy sufficient for our volume evaluation. This treatment was extended to the other rare earths (except for Pr and Ce which form dioxides), using data of Hund et al.,^(20, 21) relative to fluorite phases in U_3O_8 - RE_2O_3 systems.

The corresponding volumes of oxide per cation associated with each rare earth in the UO_2 structure are listed in Table 5-1.

At the 100,000 MWd/Te burnup level, the final contraction expected for a solid solution of all the cations (Pu, Zr, RE) would be $11 \times 10^{-3} \text{ \AA}$. It has been shown experimentally that an appreciable amount of the fission products is in fact segregated at the grain boundary. This means that the matrix which constitutes a majority of the area sampled in an x-ray diffraction equipment can appear depleted.

Experience shows also that other cations are released because of a gaseous precursor effect and are found as a sublimate decay product in the cooler parts of the fuel pin. These do not contribute to a contraction of the matrix. The concentrations, as listed in Table 5-1 are overestimated and the observed lattice parameter contraction should be less than $11 \times 10^{-3} \text{ \AA}$. This is in basic agreement with x-ray diffraction experiments performed by Bleiberg et al.,⁽⁵⁾ on UO_2 irradiated in Zircaloy cladding. At burnup levels up to 150,000 MWd/Te it was observed that within an accuracy limit of $\pm 5 \times 10^{-3} \text{ \AA}$ the lattice parameter of UO_2 remained constant at a value of 5.470 $\text{ \AA}$. Although they did not mention

specifically the fact shown in Figure 5-1, a curve was reported where it can be shown that the lattice parameter of samples annealed after irradiation decrease systematically as a linear function of the burnup. For instance, at 25×10^{20} fission/cc, (100,000 MWd/Te) for what we assume to correspond to a complete solid solution of the fission products, a contraction of about 10×10^{-3} Å is reported versus 11×10^{-3} Å calculated above.

From the agreement between calculations and experimental data, it can be considered that up to a burnup of about 150,000 MWd/Te the lattice parameter of UO_2 is constant at 7×10^{-3} Å, which represents an error of only 0.37 percent on the estimation on the volume of the whole matrix for a 100 percent dense medium.

5.1.2 Evolution of the Unit Cell of the Irradiated Mixed Oxide

In the case of a mixed oxide fuel $(\text{U}, \text{Pu})\text{O}_2$ with a plutonium composition between 20 to 30 percent, it can be shown that the contraction of the initial unit cell to be expected after irradiation at a given burnup level is lower than that previously evaluated for UO_2 .

A 100 percent dense fuel $(\text{U}_{0.8} \text{Pu}_{0.2})\text{O}_{2.00}$ with depleted U that is irradiated to 10 percent burnup* represents a case where only the Pu atoms have been fissioned. Since only Pu atoms have been fissioned, the 10 percent atoms fissioned represent half of the initial quantity of plutonium. For a breeding ratio of 0.5 the 10 Pu fissioned are partly replaced by 5 atoms corresponding to the conversion of U-238 into Pu.

* Expressed as the fraction of atoms fissioned versus the initial total number of heavy U + Pu.

TABLE 5-1
COMPOSITION OF UO_2 IRRADIATED TO 100,000 MWd/Te AND OXIDE VOLUME PER CATION
IN FLUORITE $(\text{U}, \text{M})\text{O}_2$ STRUCTURE EXTRAPOLATED FROM
CRYSTALLOGRAPHIC DATA (18, 19, 20, 21)

Cation	Valence in Fluorite (U, M) O_2 Structure	Volume of Oxide Per Cation $\times 10^{-24}$ cc (Extrapolated in Fluorite Structure for O/M = 2.00)	Maximum Concentration % Cation in the Matrix
U	4+ and 5+ or 6+	40.93	Matrix nonfissioned 86.96
Pu	4+	39.28	Conversion U** 5.35
Zr soluble**	4+	34.50	1.46
Ce	4+	39.61	1.97
La	3+	43.30	0.65
Pr	3+ or 4+	39.23	0.51
Nd	3+	40.04	1.82
Pm	3+	39.37	0.25
Sm	3+	38.69	0.25
Eu	3+	38.07	0.19
Gd	3+	37.56	0.02
Y	3+	35.36	0.57

* Concentration calculated for an assumed breeding ratio equal to 0.5.

** Zr soluble defined as the Zr quantity in excess over (Ba + Sr) in the fission yield.

FIGURE 5-1. LATTICE PARAMETER OF IRRADIATED UO_2

The final Pu/U ratio at 10 percent burnup is:

$$\frac{10 \text{ Pu Nonfissioned} + 5 \text{ Pu Conversion}}{80 \text{ U-238} - 5 \text{ Pu Conversion}} = 0.2 \quad (5)$$

The final U/Pu ratio is the same as for the starting material and in this case the breeding of Pu does not contribute to the contraction of the unit cell like in UO_2 where it represented $5 \times 10^{-3} \text{ \AA}$ i.e., 50 percent. The only cations which can contribute to the contraction of the unit cell are the soluble fission products Zr and rare earths. The 10 Pu atoms fissioned generate 20 fission products atoms among which 5.7 are soluble instead of 6.7 for U fission. In these conditions, the contraction of the unit cell of $(\text{U}_{80}\text{Pu}_{20})\text{O}_{2.00}$ should be at the maximum of $5 \times 10^{-3} \text{ \AA}$ when all the soluble fission products are homogeneously distributed in solid solution.

5.1.3 Conclusion

The lattice parameter of the oxide fuels considered change very slightly under irradiation up to high burnup levels whatever the amount of fission products in solid solution. The effective volume of solid material which constitutes the matrix can be calculated with an accuracy better than 0.3 percent by taking the total number of cations in the matrix and multiplying by the volume of oxide associated with each cation (we recall this volume was taken as one-quarter of the volume of the unit cell of the starting material) since it was shown that the lattice parameter of the matrix was little affected by radiation.

5.2 VOLUME ASSOCIATED WITH THE METALLIC FISSION PRODUCTS AND CONSTITUTION OF THE INSOLUBLE METALLIC PRECIPITATES

The results of the investigations concerning the white metallic inclusions observed in irradiated fuels has been reviewed

and explained from theoretical considerations in Section III. It was concluded that the elements likely to be found in the metallic state are As, Ge, Mo, Tc, Ru, Rh, Pd, Ag, Cd, In, Sn, and Sb. The presence of U which could not be firmly established will be discussed after calculation of the volume associated to each metallic atom either elemental or alloyed.

5.2.1 Calculations of the Atomic Volume Associated with the Metallic Fission Products

The accuracy of crystallographic data for pure metals is higher than for the oxides, and determination of lattice parameter are currently achieved with a precision better than 0.01 percent. For instance, in an FCC metal of lattice parameter a , the volume of the unit cell is $V = a^3$; since the unit cell contains four atoms the equivalent volume association with one atom is:

$$v = \frac{a^3}{4} \quad (6)$$

assimilating this volume to a sphere, Friedel has defined a radius of equivalent sphere as:

$$R = \frac{3a^{3-1/3}}{16\pi} \quad (7)$$

The Friedel radii were calculated from the x-ray data compilation of Pearson⁽²²⁾ for the corresponding "metallic" pure elements and are listed in Table 5-2 with the classical radii accepted values for single covalent bonds or metallic bond distances. It is observed that these latter values are significantly lower than Friedel radii, but it is emphasized that they represent the specific nature of the bond between atoms rather than the volume they occupy as is the case for Friedel radii.

TABLE 5-2
FRIEDEL RADII AND "EQUIVALENT VOLUMES" OF THE PURE OR ALLOYED ELEMENTS
PARTICIPATING TO THE FORMATION OF METALLIC INCLUSIONS

Element	Classical Metallic or Covalent Bond	Friedel Radii Å for		Atomic Volume (Å ³) Pure Elemental	Average Atomic Volume (Å ³) Alloyed Element
		Pure Elemental	Alloyed Element		
Nb	1.43	1.62	1.57	17.97	16.23
Mo	1.36	1.56	1.55	15.59	15.49
Tc	1.30	1.50	1.50	14.21	14.21
Ru	1.33	1.48	1.48	13.57	13.57
Rh	1.34	1.49	1.49	13.77	13.77
Pd	1.38	1.52	1.52	14.79	14.65
Ag	1.44	1.62	1.59	17.75	16.77
Cd	1.49	1.73	1.63	21.58	18.30
In	1.62	1.84	1.65	26.14	19.00
Sn	1.40	1.86	1.66	26.88	19.20
Sb	1.41	1.93	1.71	30.23	21.0

Since it can be expected that these elements will not remain separately but will form multicomponent alloys, the equivalent volume of each of these elements has been calculated from existing crystallographic data related to binary solid solutions, intermetallic compounds, etc. An illustration of this kind of treatment is shown in Figure 5-2 where the equivalent volume as defined above has been plotted for several solid solution of Ag, Cd, Sn (minor components of the fission yield) in Pd (major component).

In the family of elements Pd-Ag, Cd, and Sn, several important features are shown:

- a. Both the volume of solvent Pd and solute Ag, etc., are constant over a very large concentration range (far beyond to that to be considered taking into account the respective proportions of each component versus Pd in the fission yield).
- b. The volume of the solvent is the same as for pure element.
- c. Over a large concentration range both the volume of the solvent and solute atoms are independent of the crystal structure of the phase in which the ele-

ment is involved; Pd and Cd for instance occupy the same "equivalent volume" in the FCC (Pd-Cd) phase and in the tetragonal (Pd-Cd) phase.

In another family of Pd alloys with Mo and Nb, for instance, the new value found for Pd differs only slightly from that presently calculated with (Ag, Cd, Sn, etc.). An average value has been taken from that found in each family of atoms, taking into account both the respective concentration of the elements in the fission yields and their solubility limits. As shown in Table 5-2, for metallic bonds the values of Friedel radii differ only slightly depending on whether the element is pure elemental or alloyed; fortunately, this is the case for the elements Mo, Tc, Ru, Rh, and Pd, which are the major components of the fission yield in a proportion of 95 percent. The discrepancy between Friedel radii (pure and alloyed) becomes striking with elements such as In, Sn, and Sb, which in pure form exhibit covalent bonds but can exhibit a metallic character when in solid solution or in intermetallic compounds. Since we deal with alloys, the metallic radii have been used in our calculations for those elements but their fission yield is so low that the average volume per metallic fission product generated would not be affected.

FIGURE 5-2. DETERMINATION OF THE ATOMIC VOLUMES OF METALS FROM CRYSTALLOGRAPHIC DATA

5.2.2 Calculation of the Average Volume Per Metallic Fission Product Atom

The average volume per solid fission product atom participating to the formation of the insoluble metallic inclusions can be defined as:

$$\bar{v} = \frac{\sum_i \beta_i v_i}{\sum_i v_i} \quad (8)$$

where

β_i is the fission yield of the metallic element i
 v_i is the equivalent alloyed volume (Table 5-2) of the same element i .

Once again, it can be shown from Table 5-3 that whatever the neutron flux considered—thermal, FCR, or fast—there is for practical purpose no difference between the values obtained.

It was shown that for the major components of the fission yield Mo, Ru, Rh, and Pd (no data available for Tc) no difference in equivalent volume was observed whether the element was present as a pure metal or alloyed with other metallic fission products. It was mentioned that the discrepancy for In, Sn, and Sb occurred probably because that at low concentration those elements exhibit a metallic character. If their presence was not taken into account the average volume values listed in Table 5-4 would be changed only 0.5 percent. The validity of the above volume estimation can be established by comparison of calculated and measured densities of metallic inclusions.

5.2.3 Calculation of the Density of the Metallic Inclusions

Once the average volume $\bar{v}$ per metallic fission product atom and the average mass $\bar{m}$ per atom are determined, the average density $\bar{\rho} = \frac{\bar{m}}{\bar{v}}$ can be calculated.

TABLE 5-3
AVERAGE VOLUME PER FISSION PRODUCT ATOM PARTICIPATING TO THE FORMATION OF METALLIC INCLUSIONS ASSUMING NO URANIUM PRESENT

Neutron Spectrum	Fast	FCR	Thermal
Irradiation Time (days)	135 Cooled 15	365	135 Cooled 15
$\bar{v} \text{ (cc)} \times 10^{-23}$ U-235 fission	1.470	1.469	1.471
$\bar{v} \text{ (cc)} \times 10^{-23}$ Pu-239 fission	1.456	1.454	--

TABLE 5-4
COMPARISON BETWEEN CALCULATED AND MEASURED DENSITIES OF METALLIC INCLUSIONS EXTRACTED FROM UO_2 AND $(\text{U}, \text{Pu})\text{O}_2$ FUELS OPERATED MOLTEN DURING IRRADIATION

Atom Fissioned	Average Mass Per Metal Atom $\bar{m} \times 10^{-22} \text{ gr}$	Average Mass Per Metal Atom $\bar{v} \times 10^{-23} \text{ cc}$	Average Density $\bar{\rho} = \frac{\bar{m}}{\bar{v}} \times \text{gr/cc}$	J. Davies' Measured Density $\rho \times \text{gr/cc}$
U-235	1.658	1.469	11.30 ± 0.05	11.3 ± 0.1
Pu-239	1.693	1.454	11.65 ± 0.05	12.0 ± 0.4

The average mass per metallic fission product is defined in a similar manner as the volume $\bar{v}$ was, with the same denominations.

$$\bar{m} = \frac{\sum_i \beta_i m_i}{\sum_i \beta_i} \quad (9)$$

But for a given element i , the mass m_i differs from that measured with natural abundance specimens and this has been taken into account in our calculation.

The results of the density calculations in Table 5-4 can be compared with the experimental data of J. Davies⁽¹⁰⁾ relative to large metallic inclusions extracted from UO_2 and $(\text{U}, \text{Pu})\text{O}_2$ fuels operated partially molten during irradiation.

The above calculation refers to inclusions in which each component is present in the proportions of the fission yield. These conditions were realized in the experiment referred to⁽¹⁰⁾ as shown by the agreement between calculated and measured isotopic abundance for the molybdenum.

Because the UO_2 was operated molten a long time and the mixed oxide only during a transient experiment, the agreement between experiment and calculation is better for the inclusion extracted from UO_2 .

As shown in Appendix B, the mass of metallic inclusions recovered from UO_2 is exactly that generated by the volume of fuel estimated molten by α and β - γ autoradiography techniques.⁽¹⁰⁾

The close agreement between the calculations and the experimental results confirms the validity of the assumptions and that of the Friedel method used for these calculations.

Without taking into account the results of chemical analysis^(8, 10) which confirmed the

quasi-absence of uranium in metallic inclusions extracted from irradiated UO_2 (and therefore divided from any interference from the matrix), the densities measurement suggests that these inclusions do not include beta-uranium alloys.

Ninety to 95 uranium atom percent is necessary to stabilize the beta-uranium phase at a density close to 18.8 gr/cc. If 11.3 gr/cc is taken as the density of the inclusions with zero uranium content, the experimental error on density measurement admitted by Davies corresponds to a maximum concentration of 1.5 atom percent uranium.

5.3 VOLUME ASSOCIATED WITH NONMETALLIC INCLUSIONS

On the basis of out-of-pile experiments performed on synthetic fissia by Aitken,⁽⁹⁾ the assumption of Bradbury⁽⁶⁾ concerning the possible formation of perovskite compounds has been used in this model. Although the existence of compounds such as $\text{UO}_3(\text{Ba}, \text{Sr})$ (which have the same volume as ZrO_3Ba and are partially soluble in each other) is reported,⁽²³⁾ this has not been considered because for each Ba associated to each U in UO_3Ba there exists one ZrO_2 available for the matrix.

In the same manner, the existence of other perovskite compounds such as SnO_3Cd , CeO_3Cd ⁽²⁴⁾ is reported, that could play a role. Since the fission yield in Cd and Sn is low this possibility has been ignored.

For the stabilized high temperature forms, the partial volumes per molecule of zirconate calculated from crystallographic data are:

$$\text{ZrO}_3\text{Ba} = 72.82 \times 10^{24} \text{ cc}$$

$$\text{ZrO}_3\text{Sr} = 69.00 \times 10^{24} \text{ cc}$$

5.4 VOLUME ASSOCIATED WITH THE OTHER FISSION PRODUCTS

In this last category are the elements such as:

Br, I.
Se, Te.
Rb, Cs.

Very little is known about their behavior in the fuel and it is impossible to predict what kind of chemical compounds they can generate. It has been mentioned above that both Rb and Cs have gaseous precursors and can be released this way from the fuel. The oxides Rb_2O and Cs_2O are unstable and are dissociated at a great extent even at moderate temperature. The metal Rb and Cs liberated are very volatile and can also escape from the fuel.

Both these mechanisms can explain the quantities of Rb and Cs found condensed in the cold parts of the cladding of operating fuel. On the basis of the agreement between the calculated and experimental value of oxygen released per fission Rb and Cs re-

main at the valence 1^+ , since their oxides (M_2O type) are unstable. The participation of these elements to the formation of some more complex oxygenated compounds should be considered. The uncertainty relative to the behavior of Cs is the same as for Br, I, Se, and Te. It has been considered that some of them can form stable ionic compounds. The volume occupied by all these elements has been calculated using the corresponding ionic radii of Pauling listed below:

<u>Elements</u>	<u>Ionic Radius Å</u>
Br-	1.95
I-	2.16
Se--	1.98
Te--	2.21
Rb+	1.48
Cs+	1.69
O--	1.40

Some oxygen is associated with these elements and the corresponding value of ionic radius of oxygen is plotted with that of the fission products.

Unfortunately, this method of volume evaluation is a first approximation rather than a measure as was done above.

SECTION VI

SWELLING RATES ASSOCIATED WITH THE SOLID FISSION PRODUCTS GENERATION

6.1 CALCULATION

Once the composition of the fuel irradiated in specific conditions is known (i.e., the nature of the fission products and their respective concentration at a given burnup) the solid fission products are shared among the category of compounds in which they are involved.

- Stable oxides soluble in the matrix (or segregated into).
- Metallic inclusion.

- Nonmetallic inclusions.
- Other fission products.

The swelling consecutive to the accumulation of the fission products in fuel is calculated as follows:

- The summation of the partial volumes associated with each kind of fission products whatever the compound they contribute to form, gives a positive "solid" contribution $(\Delta V/V)^+$, since it represents a volume which did not exist before irradiation.

- b. The difference between the volume associated with the matrix before and after irradiation gives a negative "solid" contribution $(\Delta V/V)^-$ because it represents the volume of oxide destroyed by U and Pu fission.

- c. The minimum swelling occurs when the negative contribution is completely compensated by the positive, and the maximum swelling occurs when there is no compensation. An example of this kind of treatment is shown in

Table 6-1 for UO_2 -20 percent enriched irradiated 1 year at 100,000 MWd/Te burnup level.

Similar types of calculations referring to UO_2 and $(\text{U}_{80}\text{Pu}_{20})\text{O}_2$ fuels irradiated at various burnup levels show that the absolute volume changes increase linearly as a function of the burnup. Under these conditions it is possible to define a swelling rate in terms of atom percent burnup or fission density such as displayed in Table 6-2.

TABLE 6-1
SWELLING RATES FOR SOLID FISSION PRODUCT GENERATION IN $\text{UO}_{2.00}$
20 PERCENT ENRICHED IRRADIATED 365 DAYS AT 100,000 MWd/Te BURNUP
LEVEL 100 PERCENT DENSE MEDIUM

	Fission Product* Yield Per 100 Fissions Reference (4)	Atoms Per cc $\times 10^{20}$	Volume cc Per Fp $\times 10^{-24}$ cc	Partial Volume cc Per cc of Fuel
U nonfissioned		218.93	40.93	0.8960 ± 0.0030
Soluble Fp	67.48	17.11		$+0.0700 \pm 0.0002$
Fp metallic (inclusions)	52.14	13.22	14.73	$+0.0195 \pm 0.0001$
Fp Zirconates				
ZrO_3Sr	8.62	2.19	69.00	$+0.0151 \pm 0.0001$
ZrO_3Ba	6.32	1.60	73.70	$+0.0118 \pm 0.0001$
Fp others	26.30	6.67		$+0.0207 \pm 0.0010$
Fp volume generation (maximum positive contribution)		$\left(\frac{\Delta V}{V}\right)^+ = 13.70\%$	{ 1.32% per at.% burnup 0.54% per 10^{20} fiss/cc	
Volume of oxide destroyed (negative contribution)		$1 - 0.896 = \left(\frac{\Delta V}{V}\right)^- = 10.40\%$	{ -1.00% per at.% burnup -0.41% per 10^{20} fiss/cc	
Minimum swelling expected Positive + negative contribution		$13.70 - 10.40 = 3.3\%$	{ +0.32% per at.% burnup +0.13% per 10^{20} fiss/cc	

* To obtain a total fission yield of 200 percent versus U fissioned, it is recalled that the gaseous fission products should be added plus insoluble Zr already taken into account since associated with Ba or Sr in Zirconates.

TABLE 6-2
SWELLING RATES ASSOCIATED WITH SOLID FISSION PRODUCTS GENERATION

	(U ₈₀ Pu ₂₀)O _{2.00} (U Depleted) Pu-239 Fission	UO _{2.00} (20% Enriched) U-235 Fission
Negative contribution $\left(\frac{\Delta V}{V}\right)^-$ or (Fission or destruction of the matrix)	-0.97% per at. % burnup -0.39% per 10 ²⁰ fiss/cc	-1.00% per at. % burnup -0.41% per 10 ²⁰ fiss/cc
Maximum positive contribution $\left(\frac{\Delta V}{V}\right)^+$ or (Generation of fission products)	+ 1.27% per at. % burnup + 0.51% per 10 ²⁰ fiss/cc	+ 1.32% per at. % burnup + 0.54% per 10 ²⁰ fiss/cc
Total minimum solid contribution or $\left(\frac{\Delta V}{V}\right)^+ \left(\frac{\Delta V}{V}\right)^-$	+ 0.30% per at. % burnup + 0.12% per 10 ²⁰ fiss/cc	+ 0.32% per at. % burnup + 0.13% per 10 ²⁰ fiss/cc

SECTION VII

DISCUSSION

From the examination of final results displayed in Table 6-2 for UO₂ enriched in U-235 and the mixed oxide 20 percent PuO₂ made with UO₂ depleted in U-235, it appears that no difference is observed in the swelling rates.

This situation comes mainly from the fact that Pu fission generates more noble metals but less zirconates than U fission and are compensate for each other.

The evaluation of realistic situations is greatly improved, assuming as it is generally done, that the fission yield of U-238 does not significantly differ from the fast fission yield of U-235 at least for solid fission products.

Although U-238 accounts for 10 percent of the fissions in the mixed oxide fuel of the 1000 MWe FCR, this was not considered in the calculation in Table 6-2; but on the basis

of similar "solid" swelling rates for U and Pu the conclusions are unchanged. The results as displayed are simple figures which need to be commented further.

It is noted that all the calculations were made using room temperature data. This way of doing it is realistic so long as no attempt is made to interpret the radial deformation of the cladding as a consequence of the only swelling. The deformation of the cladding is more a complex problem associated with the differential thermal expansion of the cladding-fuel system, the restructuring of the fuel under thermal gradient, the discontinuous density decrease if the melting point of the fuel is reached, and gaseous swelling. Except when the fission gas release becomes important, it is artificial to separate the contribution of the solid and gaseous fission products to the overall swelling rate.

The rare gas fission product atoms occupy some space in the matrix. Since x-ray diffraction line broadening measurements on unirradiated fuels⁽⁵⁾ show that they are not in interstitial position, the space available from U or Pu fission can act as a trap for the gas atoms, as well as the initial porosity which always exists. Even if there were no fission gas to occupy some of the voids created by fissions and the porosity, there is no reason for which all the space available should be filled before a volume increase of the fuel would be observed.

If one considers the only "solid" contribution, it is emphasized that there is no unique number, as shown in Table 6-1. At

a given burnup, the kinetics of annihilation of the volume of oxide destroyed by fission and the positive volume associated with the generation of fission products is strongly dependent on:

- a. The irradiation conditions (pressurized cladding or not, temperature)
- b. The fuel pin design (strong, thick cladding, fuel-cladding gap, density of the fuel).
- c. The properties of the fuel (plasticity, initial stoichiometry) and the total solid contribution can vary between the two limits specified.

SECTION VIII

CONCLUSION

If one considers the relative thermodynamic behavior of the irradiated oxide matrix, the fission products and the cladding, it can be shown that about 0.3 and 0.7 oxygen atom are available per uranium or plutonium fission, respectively. The oxygen available from fission can either be dissolved in the oxide matrix or oxidize the stainless steel cladding, depending on the initial stoichiometry of the fuel so that a final equilibrium stoichiometry is reached at approximately $O/M = 2.00$. This may explain the presence of oxidation layers observed at the fuel-cladding interface, and the increasing thickness of this layer with burnup.

The initial advantage of using a hypostiochiometric fuel of better thermal conductivity may diminish or disappear with increasing burnup, depending upon operational thermal history of a given fuel element.

Because of available oxygen from the fission process, and its reaction with the in-

terior of the cladding, out-of-reactor compatibility tests of oxide fuels with cladding are of questionable value.

The concentration of each fission product at a given burnup was calculated, using the conventional fission yield for thermal or fast fission of uranium or plutonium. The volume occupied by each fission product atom or molecule was assumed to be equal to the volume of the corresponding unit cell (from available crystallographic data) divided by the number of atoms or molecules in the unit cell.

By summation of the partial volumes associated with the fission product and the volume of the matrix nonfissioned, the net volume changes ΔV at several burnup and swelling rates $\Delta V/V$ percent as a function of fission density are calculated.

The volume of material associated with the generation of solid fission product

replaces the volume of oxide matrix fissioned. If one assumes a complete utilization of the vacancies created, the maximum solid fission product swelling rate will be 0.13 percent $\Delta V/V$ per 10^{20} fission/cc for UO_2 or $(Pu_{0.2}U_{0.8})O_{2.0}$. If none of the vacancies are consumed, the swelling rate

will be as high as 0.54 percent $\Delta V/V$ per 10^{20} fission/cc. An average figure, derived from irradiations performed in different conditions, is $\Delta V/V = 0.35$ percent/ 10^{20} fission/cc, almost the average of the two limits calculated above.

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APPENDIX A

EVOLUTION OF INTEGRATED STOICHIOMETRY OF IRRADIATED
UO₂ IN AN INERT CLADDING

Fuel Composition: UO₂ 20 percent enriched
 Burnup Achieved: 100,000 MWd/Te in 365 days fast fission⁽⁴⁾

a. Calculation of Fission Density

One unit cell of UO₂ ($a = 5.470 \text{ \AA}$) of volume $V = 163.74 \times 10^{-24} \text{ cc}$ contains 4 UO₂ molecules. A 100 percent dense medium contains $\frac{4 \text{ U atoms}}{163.74 \times 10^{-24} \text{ cc}} = 244.29 \times 10^{20} \text{ U atoms}$ per cc of oxide. If one assumes that a total energy of 205 MeV is released per fission, 1 MWd/Te is equivalent to 2.634×10^{15} fissions per gram of U.

For an oxide of this composition a density of 10.93 gr/cc is calculated from the volume and the mass of the unit cell; we have, therefore:

$$\frac{237.4}{269.4} \times 10.93 = 9.63 \text{ gr U per cc of oxide,}$$

[100,000 MWd/Te corresponds to $(2.634 \times 10^{20}) \times (9.63) = 25.363 \times 10^{20}$ fission per cc of oxide].

At the end of irradiation, we have (assimilating Pu, Am, etc., to U for their behavior versus oxygen) 218.93×10^{20} U nonfissioned with a double corresponding number of oxygen ions associated.

As shown in Table 4-4, for the irradiation conditions specified above, the average valence per fission product atom is $\bar{\nu} 1.677+$. Since two fission product atoms are in presence of two oxygen freed by U 4+ fission, the oxygen available to dissolve in the lattice of the oxide is $(2 - \bar{\nu}_2)$ ion per fission (with $\bar{\nu} < 2$).

Therefore, the number of oxygen ions which have dissolved in the lattice of UO₂ is $25.363 \times 10^{20} \frac{\text{fission}}{\text{cc}} \times 0.343 \frac{\text{oxygen released}}{\text{fission}} = 8.192 \times 10^{20} \frac{\text{oxygen}}{\text{cc}}$.

b. Stoichiometry Achieved When None of Soluble Fission Products are in Solid Solution in UO₂ Matrix

The extra oxygen is only relocated on the nonfissioned U atoms.

Oxygen associated with U nonfissioned	$8.19 \times 10^{20} \text{ at./cc}$
Oxygen liberated and available to dissolve	$446.04 \times 10^{20} \text{ at./cc}$
Total oxygen	$218.93 \times 10^{20} \text{ at./cc}$
O/M = 2.040	

c. Stoichiometry Achieved When All the Soluble Fission Products are in Solid Solution in UO₂ Matrix

Although experimental results show that even soluble fission products are found segregated at the grain boundaries, this highly improbable case has been considered to check at what extent the precedent result is affected.

The concentration in soluble fission products accumulated at this burnup and the corresponding quantity of oxygen associated with them are simply introduced in the preceding calculation.

	Fission Yield* (β_i)	Valence	
		(ν_i)	(β_i) $\times$ (ν_i)
Zr soluble	14.02	4+	56.08+
Ce	14.37	4+	57.48+
Y+ La+ trivalent RE	39.09	3+	177.27+
	$\Sigma_i \beta_i = 67.48$		$\Sigma_i \beta_i \nu_i = 230.83+$

$$\bar{\nu}_{\text{soluble}} = \frac{\Sigma_i \beta_i \times \nu_i}{\Sigma_i \beta_i} = 3.42+$$

The amount of soluble fission product accumulated represent 67.5 percent of the number of fissions which have occurred, and one average soluble fission product of average valence $\bar{\nu}_{\text{sol}} = 3.42+$ is associated with 1.71 oxygen ion (O^{--}).

$$\begin{aligned} \text{Number of soluble atoms} &= 0.675 \times 25,363 \times 10^{20} = 17.114 \times 10^{20} \\ \text{Oxygen associated with soluble atoms} &= 17.114 \times 10^{20} \times 1.71 = 29.27 \times 10^{20} \end{aligned}$$

Metal atoms ($\times 10^{20}$)		Oxygen atoms ($\times 10^{20}$)	
U nonfissioned	218.927	with U nonfissioned	437.854
Soluble Fp	17.114	with soluble Fp	29.272
Cations in the matrix	236.04	available from fission	8.192
		Total oxygen ions	475.32
$O/M = \frac{O}{U + Fp} = 2.014$			

APPENDIX B

ESTIMATION OF THE VOLUME OF FUEL MOLTEN DURING IRRADIATION
FROM THE WEIGHT OF METALLIC INCLUSIONS RECOVERED

a. UO₂—Rod 12 GV⁽²⁵⁾

Enrichment 3.5 percent

Fuel vibratory compacted smeared density 85 percent

Weight of oxide 897 gr

Average burnup achieved 19,500 MWd/Te

1. Theoretical Density of UO₂

The unit cell of lattice parameter $a = 5.470 \text{ \AA}$ and of volume $V = a^3 = 163.667 \times 10^{-24} \text{ cc}$ contains 4 UO₂ mol. The theoretical density of that UO₂ is:

$$\rho_{th} = \frac{4 \times 269.9 \text{ gr}}{(6.023 \times 10^{23}) \times (163.667 \times 10^{-24}) \text{ cc}}$$

2. Fission Density

If one assumes 205 MeV energy released per fission, 1 MWd/Te is equivalent to 2.634×10^{15} fiss/gr U.

At 19,500 MWd/Te burnup level, there are $19,500 \text{ MWd/Te} \times 2.634 \times 10^{15} \text{ fiss/gr U} \times \text{Te/MWd} \times 8.20 \text{ gr U/cc UO}_2 = 4.212 \times 10^{20} \text{ fiss/cc UO}_2$ for that UO₂ 85 percent smeared.

3. Calculation of Weight of Inclusion Per Gram of Fuel at this Burnup

The fission yield for the elements reduced at the metallic state represent 49 percent of the number of the fissions. [For GETR core fission yield Reference (4) can be used.]

The average mass $\bar{m}$ calculated is (Section VI) $\bar{m} = 1.66 \times 10^{-22} \text{ gr metal/metallic Fp}$. We have: $4.21 \times 10^{20} \text{ fiss/cc UO}_2 \times 0.49 \text{ metallic Fp/fiss} \times 1.66 \times 10^{-22} \text{ gr/metallic Fp} = 0.034 \text{ gr inclusion/cc UO}_2$.

4. Evaluation of the Volume Molten

To generate 1 gr of inclusion 29.5 cc of fuel are necessary. The total volume of fuel occupy:

$$897 \text{ gr} \times \frac{1}{8.20} \text{ cc/gr} = 109 \text{ cc.}$$

The volume of fuel having generated 1 gr inclusion represents $29.5/109 = 27$ percent of the total volume in good agreement with the 30 percent as evaluated by α and $\beta - \gamma$ autoradiography techniques. (The 30 percent represents the integrated value over the whole length of the rod.)⁽¹⁰⁾

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