MASTER

DISTRIBUTION OF SOLID FISSION PRODUCTS IN UO_2

by

J. H. McFadden
V. F. Baston
W. A. Yuill

Idaho Nuclear Corporation
Idaho Falls, Idaho

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

DISTRIBUTION OF SOLID FISSION PRODUCTS IN UO_2

I. INTRODUCTION

The migration of fission products and fissile materials, and the segregation of metallic ions in reactor fuel pins are problems of importance in reactor safety. Fission product migration and subsequent fission product release to the fuel-cladding gap are important safety considerations for both thermal and fast reactor fuel pins. Redistribution and segregation of fissile material will change the power generation profile in the fuel and will also affect the Doppler coefficient in mixed oxide fuels. Experimental data for fission product and plutonium migration have been presented by Bates^(1, 2). An analytical description of thermal diffusion in reactor fuels has been given by Wirtz⁽³⁾ and Beisswenger, et. al.^(4, 5). Christensen⁽⁶⁾ also has presented a model for fission product migration.

In this paper, the migration of fission products during reactor operation is described by a thermomigration model that has been used successfully to describe noble gas release from fuel pins during normal operation^(7, 8). The basic assumption in the derivation of this model is that the driving force for migration of fission products during reactor operation is a Gibbs-free-energy gradient, which is dependent on temperature and concentration gradients. Examples of forces contributing to the Gibbs-free-energy gradient and proportional to the thermal gradient are entropy effects, thermoelectric effects, and thermal stresses.

II. PHYSICAL MODEL FOR SOLID FISSION PRODUCTS

The physical model for the behavior of solid fission products in operating fuel pins is very similar to that proposed previously for noble gases⁽⁸⁾. The newly formed fission products, depending on their chemical properties, will either be soluble in the UO_2 fuel lattice or will migrate to cracks or fissures in the fuel pellet where they will precipitate as part of a metallic inclusion or low melting oxide melt. An important feature of the fuel pin, however, is that the precipitation of fission products in the fissures and cracks is at least partially reversible because of radiation effects. Fission fragments and ionizing radiation will in effect cause mixing among the various phases present. In addition, the inclusions containing phases of the precipitated fission products will be subject to the forces and stresses in the fuel, and will move into the hot regions of the pin over long periods of time.

The important consideration of such a physical model is that all the fission products in the fuel should be regarded as being subjected to the forces which exist in the UO_2 fuel lattice regardless of whether they are actually in the UO_2 lattice or in some phase.

III. ANALYTICAL DESCRIPTION

The time dependent diffusion equation for a fission product with concentration, $C(r, t)$, and effective decay constant, λ^* , produced at a rate of $P(r, t)$ is

$$\frac{dC(r, t)}{dt} = P(r, t) - \lambda^* C(r, t) + \nabla \cdot \left[\frac{D(r, t)}{RT(r, t)} \nabla C(r, t) - \nabla G(r, t) \right] \quad (1)$$

where: $T(r, t)$ = the absolute temperature,

R = the gas constant, and

$\nabla G(r, t)$ = the Gibbs-free-energy gradient.

The diffusivity, $D(r, t)$, of the isotope is

$$D(r, t) = D_0 \exp[-Q/RT(r, t)] \quad (2)$$

where: D_0 = the diffusion constant, and

Q = the activation energy for diffusion.

The Gibbs-free-energy gradient, $\nabla G(r, t)$ can be written as

$$\nabla G(r, t) = \left(\frac{\partial G}{\partial T} \right)_C \nabla T + \left(\frac{\partial G}{\partial C} \right)_T \nabla C \quad (3)$$

$$\text{or} \quad = \left(\frac{\partial G}{\partial T} \right)_C \nabla T + \frac{RT}{C} \nabla C \quad (4)$$

where $\left(\frac{\partial G}{\partial T} \right)_C$ includes all terms which are proportional to the thermal gradient.

The assumption that the driving force for atomic or ionic diffusion is the gradient of the free energy was first presented by Einstein⁽⁹⁾. Diffusion can occur under the condition of zero concentration gradient, if the free-energy is nonzero. In addition, Ficks law describes a special type of diffusion, and can be derived from Einstein's assumption by assuming the thermal gradient is zero.

The thermal gradient is an important term to include in this fission product migration model for two reasons. Since the thermal gradient in the outer region of the fuel is on the order of 4000 °K/cm, if a species has a partial molar entropy of ten entropy units at 1000 °K, the thermal gradient term contributes more to the Gibbs-free-energy gradient than the concentration gradient term, unless the concentration change across that region is greater than a factor of about 10⁷. The second reason for including the thermal gradient term is concerned with the direction of migration. Entropy affects the direction of migration in that chemical species formed as the result of an endothermic reaction in the lattice will concentrate in the high temperature region of the thermal gradient, whereas those formed in an exothermic reaction will migrate to the lower temperature region of the thermal gradient. A similar movement of ionic fission products occurs because of thermoelectric effects.

If the fuel rod has been operating for a time that is long compared to the half-life of the isotope being studied, steady state equilibrium will be established, $dC/dt = 0$, and Equation (1) is

$$V \cdot \left[\frac{D(r)C(r)}{RT(r)} \left[\left(\frac{\partial G}{\partial T} \right)_C VT + \frac{RT}{C} \nabla C \right] \right] - \lambda * C(r) = P(r) \quad (5)$$

where the expression for ∇G from Equation (4) has been substituted for the Gibbs-free-energy gradient. Approximate solutions to Equation (5) have been obtained by assuming a series solution of the form

$$C(r) = \sum_{n=0}^N a_n \cos \frac{n\pi r}{b} \quad (6)$$

where b is the radius of the fuel rod.

To solve Equation (5), the series, Equation (6), is substituted for $C(r)$, and each term is multiplied by

$$\cos \frac{m\pi r}{b}$$

and integrated over the volume element, rdr . Evaluation of these integrals results in a system of simultaneous linear equations, represented in matrix form by

$$Ax = B \quad (7)$$

where x is the column matrix of N coefficients, a_n , B is the column matrix whose terms are of the form

$$b_m = \int_0^b P(r) \cos \frac{m\pi r}{b} r dr, \quad (8)$$

and A is the N by N matrix composed of the integrated terms on the left hand side of Equation (5).

Equation (7) is solved for the coefficients, a_n , by means of a Gauss-elimination process, and the concentration profile is obtained by substitution of these coefficients into Equation (6) and evaluation of the summation.

IV. MIGRATION OF SR-90 AND CS-137

The method of solution of Equation (5) discussed in the previous section was used to describe the distribution of Sr-90 and Cs-137 in an operating UO₂ fuel rod of radius 1.7 cm⁽²⁾. The temperature distribution for this specimen (GEH-4-49) was calculated from data for preirradiated pins⁽¹⁰⁾ and is shown in Figure 1. The experimental distributions of Sr-90 and Cs-137 for this pin were taken from the work of Bates⁽²⁾ and are given in Figure 2. Since this specimen was irradiated for only 17 days and the analytical solution assumes $dC/dt = 0$, the experimental distributions for a specimen (APED-A-597) of 0.6 cm radius⁽²⁾, irradiated for a longer time at approximately the same linear power rating, are also given in Figure 2.

The analytical distributions for Sr-90 and Cs-137, based on a 15 term expansion of Equation (6), are shown in Figure 3. These distributions are assumed to be converged solutions, because the addition of more terms (up to $N=20$), does not change the values of the first 15 coefficients, a_n . The values of the physical parameters used in these calculations are given in Table I. The values of $(\partial G/\partial T)_C$, - 4cal/°K for Sr-90 and 5 cal/°K for

Figure 1. Temperature Distribution in 1.7-cm Radius Pin

Cs-137, used to calculate the distributions in Figure 3 are reasonable entropy values for the formation of oxides of strontium and cesium at 1000 °K. The effect of the sign difference of the values of $(\partial G/\partial T)_C$ is evident, with cesium moving toward the cooler regions of the fuel and strontium migrating toward the hotter region.

TABLE I

PARAMETERS FOR SR-90 AND CS-137 CALCULATIONS

Isotope	$\lambda^*(\text{sec}^{-1})$	$D_0^{(a)}(\text{cm}^2/\text{sec})$	$Q^{(a)}(\text{kcal/mol})$	$(\partial G/\partial T)(\text{cal}/^\circ\text{K})$
Sr-90	7.84×10^{-9}	4.5×10^{-7}	24.4	-4
CS-137	7.32×10^{-10}	8.53×10^{-9}	6.1	5

(a) Values from Oi and Takagi⁽¹¹⁾.

Figure 2. Experimental Distributions Sr-90 and Cs-137 From Bates

The magnitude of the experimental and calculated distributions are not the same. The reason for this discrepancy is that the production rate was based on a normalized radial power shape, which is proportional to the actual production rate for a particular isotope. In comparing the experimental and calculated distributions, notice should be taken that the shape of the experimental and calculated curves are the same and that the direction of migration; that is, up or down the thermal gradient, was correctly represented by the analytical method.

The Cs-137 curves in Figure 4, obtained by varying the value of $(\partial G/\partial T)_C$ as indicated in the figure, demonstrate the importance of including the thermal gradient term. Because of the complex chemical reactions occurring in a fuel pin during irradiation, physical properties such as stoichiometry and entropy are not constant in either space or time, and this lack of constancy should be considered whenever possible.

V. CONCLUSIONS

The calculated fission product distributions presented in this paper demonstrate that the thermomigration model for fission product distribution and release can be used to describe the distribution of fission products if the diffusivity and thermodynamic data for the isotope are known. The model also correctly accounts for the migration of strontium and cesium in opposite directions because of the difference in sign of $(\partial G/\partial T)_C$ for the two isotopes.

Figure 3. Analytical Distribution of Sr-90 and Cs-137 After Long Irradiation. ($b=0.6$ cm)

Figure 4. Cs-137 Distribution with $(\partial G / \partial T)$
As a Parameter ($b=0.6$ cm)

1. J. L. Bates, "Fission Product Distribution in Irradiated UO₂", Trans. Am. Nucl. Soc. 7, (1964) pp. 389.
2. J. L. Bates, Fission Product Distribution in Irradiated UO₂, BNWL-58 (March 1965).
3. K. Wirtz, "Thermal Diffusion in Nuclear Reactor Fuels", J. Am. Chem. Soc. 90, pp 3089-3090 (June 1968).
4. H. Beisswenger, M. Bober, and G. Schumacher, "Thermodiffusion in System UO₂-CeO₂", J. Nucl. Mater. 21, pp 38-52 (1967).
5. H. Beisswenger, M. Bober, and G. Schumacher, "Thermal Diffusion in UO₂-PuO₂ Mixtures", Proceedings of the IAEA Symposium on Plutonium as a Reactor Fuel, Vienna, pp 273-282 (1963).
6. W. F. Sheely (ed.), Reactor Fuels and Materials Development Program For Fuels and Materials Branch, Quarterly Progress Report, July-September 1969, BNWL-1223 (November 1969).
7. K. A. Dietz (ed.), Quarterly Technical Report Nuclear Safety Program Division, October 1 - December 31, 1969, IN-1320, pp 23-49 (March 1970).
8. W. A. Yuill, V. F. Baston, and J. H. McFadden, An Analytical Model Describing the Behavior of Fission Products in Operating Fuel Pins, IN-1467 (April 1971).
9. A. Einstein, "Uber die von der Molekular-Kinetischer Theorie der Wärme Geforderte Bewegung von in Ruhenden Flüssigkeiten Suspendierten Teilchen", Annalen der Physik (4) 17, p 549 (1905).
10. J. L. Bates, Vibrationally Compacted, Fused UO₂ Fuel Element: GEH-4-49, HW-64402-RD (March 1960).
11. N. Oi and J. Takagi, "Diffusion of Non-Gaseous Fission Products in UO₂ Single Crystals", Z. Naturforschg. 19a, pp 1331-1332 (1964).