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MODELS FOR FISSION-GAS RELEASE FROM COATED FUEL PARTICLES

J. W. Prados
J. L. Scott

OAK RIDGE NATIONAL LABORATORY
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John W. Prados and James L. Scott

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MODELS FOR FISSION-GAS RELEASE FROM COATED FUEL PARTICLES

John W. Prados[1] and James L. Scott

ABSTRACT

Mathematical relations are presented for estimating the release fractions of gaseous fission products from coated fuel particles and fuel elements containing them. The relations are based on simplified models of the release process, with particular emphasis on the following mechanisms: (a) recoil, (b) diffusion from fuel, (c) diffusion through particle coating, and (d) diffusion through fuel element matrix. The characteristics of fission-gas release by these mechanisms, acting singly and in combination, are considered, and the application of the theoretical relations to experiment planning and interpretation is discussed. Special attention is given to methods for analysis of data from continuous, in-pile (sweep capsule) release experiments and neutron-activation release experiments.

INTRODUCTION

One type of fuel element of current interest to gas-cooled reactor technology consists of small particles of ceramic fuel (e.g., uranium carbide) coated with a layer of low-permeability pyrolytic graphite and dispersed in a graphite matrix.[2-4] The pyrolytic-carbon coatings are to contain the gaseous fission products released from the fuel, and thus prevent excessive contamination of the coolant gas while avoiding the

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[1]Consultant from the University of Tennessee.

[2]Oak Ridge National Laboratory Staff, "Conceptual Design of the Pebble-Bed Reactor Experiment," USAEC Report ORNL-TM-201, May 17, 1962.

[3]"Fuel-Element Development Program for the Pebble-Bed Reactor — Final Report," USAEC Report NYO-9064, New York Operations Office, April 30, 1961.

[4]C. A. Klein, "Pyrolytic Graphite," Intern. Sci. Technol., 1(8): 60 (1962).

poorer neutron economy inherent in the use of metallic fuel cladding. Unfortunately, the coatings now available are only partially successful in retaining the fission products and allow a significant fraction to escape.

Experimental studies are under way at the Oak Ridge National Laboratory[5-7] and elsewhere[8,9] aimed at (a) defining the fission-gas escape mechanisms from coated particles and the fuel elements containing them and (b) establishing manufacturing specifications for coated-particle fuel elements necessary to maintain fission-product-release rates at acceptable levels. Rational interpretation of results from these studies will require physical and mathematical models of the release mechanisms. The development and experimental confirmation of such models are essential if test results are to be used with any confidence to predict fission-gas-release rates as functions of fuel properties and reactor operating conditions. Models are also needed to test experimental release data for possible mechanism and to suggest critical experiments to distinguish between mechanisms.

PURPOSE

The purpose of this report is to present mathematical relationships for calculating steady-state fission-gas-release rates from coated fuel particles. These relationships are based on several postulated release mechanisms, though the absence of a well-defined physical concept of the release process has limited consideration to relatively simple models.

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[5]Oak Ridge National Laboratory, "GCRP Quar. Prog. Rep. Sept. 30, 1961," USAEC Report ORNL-3210, pp. 133–62.

[6]Oak Ridge National Laboratory, "GCRP Quar. Prog. Rep. Dec. 31, 1961," USAEC Report ORNL-3254, pp. 137–65.

[7]Oak Ridge National Laboratory, "GCRP Quar. Prog. Rep. March 31, 1962," USAEC Report ORNL-3302, pp. 172–220.

[8]E. E. Anderson, P. E. Gethard, and L. R. Zumwalt, "Steady-State Release Fractions of Krypton and Xenon Fission Products at High-Temperature from $(U,Th)C_2$–Graphite Fuel Matrix in Out-of-Pile Experiments," USAEC Report GA-3211, General Atomic, June 15, 1962.

[9]R. J. Burian, R. L. Ritzman, J. E. Gates, and R. F. Dickerson, "Evaluation of Irradiated Alumina-Coated UO_2 Particles Dispersed in Graphite," USAEC Report BMI-1572, Battelle Memorial Institute, March 22, 1962.

As experimental release data accumulate, it may be necessary to employ more sophisticated release models or combinations of the present models to provide an adequate representation of the release process. Although the relations presented in the following pages are approximate and untested, the approach used in their development should be equally valuable in more sophisticated and complex analyses.

MECHANISMS OF RELEASE

An enlarged cross section of a pyrolytic-carbon-coated UC_2 particle is shown in Fig. 1. The dark region surrounding the central UC_2 region is a layer of high-permeability carbon which provides a gas holdup volume between fuel and low-permeability coating. In a fuel element containing such particles, a gaseous fission product escaping to the coolant stream must travel from its point of generation to the fuel particle surface, through the coating surrounding the particle, and thence through the matrix to the external surface of the fuel element. The release process may thus be analyzed as three sequential steps: (a) release from fuel to void volume between fuel particle and coating, (b) transport across coating to matrix material, and (c) transport through matrix pores to external surface of the fuel element. One might anticipate that many cases would arise where one of these steps is sufficiently slow relative to the others that its characteristics will control the overall rate of fission-gas release.

Possible mechanisms for each step will now be discussed individually. The mathematical description of the various release mechanisms involves a multitude of symbols. Each is defined when it is first introduced, but the definitions are not repeated with each new equation for sake of brevity. As an aid to the reader who has forgotten the meaning of one of the symbols, a complete listing immediately follows the Appendix.

Release from Fuel

The most probable mechanisms proposed for fission-product escape from the fuel are recoil, diffusion, and chemical attack on the fuel. The characteristics of release by each of these mechanisms are considered briefly below.

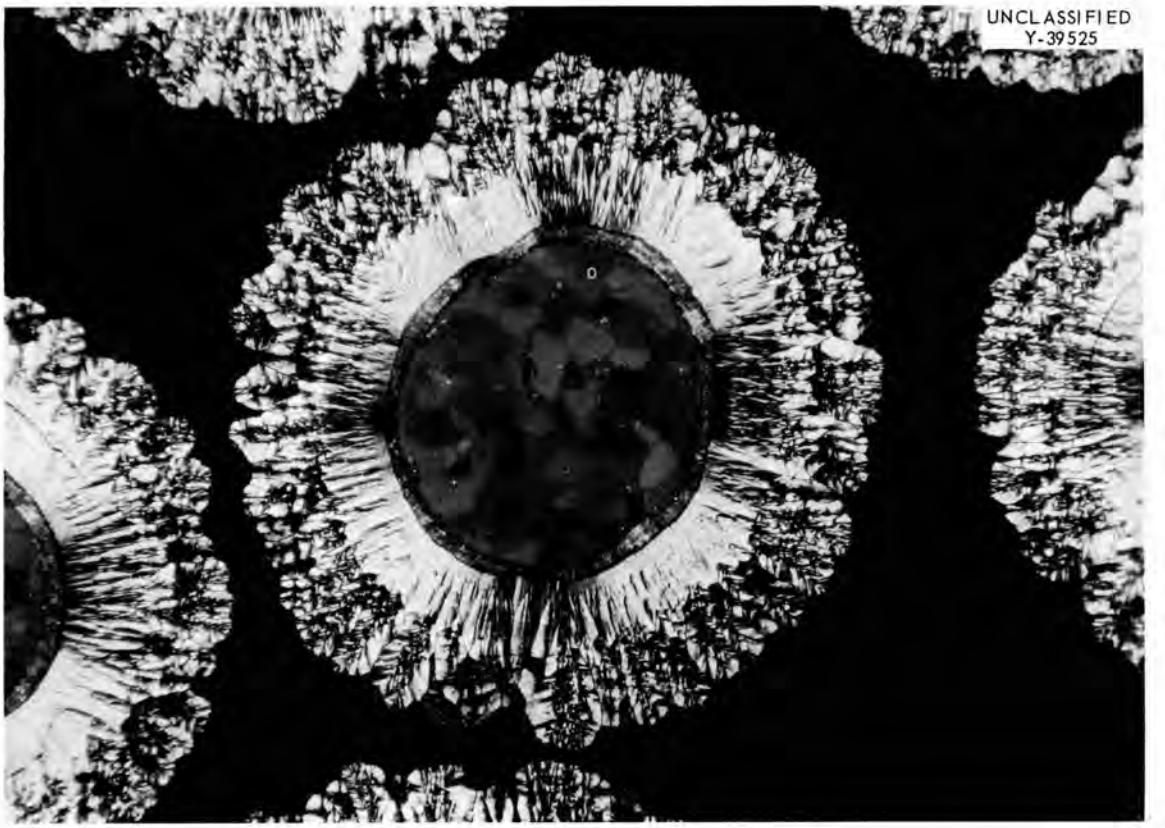

Fig. 1. Typical Polarized Light Microstructure of Particles from Lot HTM-1. As-polished. 200X. Reduced 4%.

Recoil

For a fission product to escape by recoil from the fuel, it must originate in a fission within a distance, R, of the fuel surface. The recoil range, R, is the distance traveled by a fission fragment in the fuel material. Not all fission fragments originating within a distance, R, of the surface will escape, since they may not be moving normal to the surface. However, one can derive an expression for the average fraction of fission products that escape by recoil under the assumptions that fissions occur uniformly throughout the fuel and that the fragments move in random directions from the point of fission. The relation for computing fractional release by recoil from spherical fuel particles as given by White et al.[10] and derived in the Appendix is:

$$f_R = \frac{3}{4}\left(\frac{R}{a}\right) - \frac{1}{16}\left(\frac{R}{a}\right)^3 \qquad (1)$$

where

f_R = fraction of fission products produced that are released by recoil,

R = recoil range (length), and

a = radius of fuel particle (length).

For the fission products of interest in release studies, the recoil range in uranium carbide will be taken as constant at six microns.

Diffusion

The fraction of a given radioactive fission-product species released by diffusion from a fuel particle under steady-state conditions may be estimated from a relatively simple relation based on the following assumptions: (a) the species of interest is generated uniformly throughout the fuel, (b) the movement of the species through the fuel follows Fick's law

[10] D. W. White, A. P. Beard, and A. H. Willis, "Irradiation Behavior of Dispersion Fuels," USAEC Report KAPL-P-1849, Knolls Atomic Power Laboratory, Nov. 18, 1957, p. 15.

with a constant diffusion coefficient, and (c) the solubility of the species in the fuel material is sufficiently low that its concentration may be considered zero at the outer fuel surface. The resulting equation for the fraction released from the fuel by diffusion has been presented by Cottrell et al.[11] and is also developed in the Appendix.

$$f_D = \frac{3}{\phi^2} (\phi \text{ ctnh } \phi - 1) \tag{2}$$

where

$\phi = \sqrt{\frac{\lambda a^2}{D}}$

f_D = fraction of a given fission product generated in the fuel that is released by diffusion at steady state,

λ = decay constant for fission product $(\text{time})^{-1}$, and

D = Fick's law diffusion constant for fission product $\frac{(\text{length})^2}{(\text{time})}$.

A plot of f_D vs ϕ from Eq. (2) is shown in Fig. 2. It will be noted that if ϕ is greater than about 10, $(\phi \text{ ctnh } \phi - 1) \rightarrow \phi$, and f_D is given by the limiting form:

$$f_D \cong 3\sqrt{\frac{D}{\lambda a^2}} \qquad \left(\text{for} \sqrt{\frac{\lambda a^2}{D}} > 10\right) . \tag{3}$$

The analysis leading to Eqs. (2) and (3) must be modified if the released species has a relatively long-lived precursor which also diffuses out of the fuel, as with the parent-daughter pairs, I^{135}–Xe^{135} and I^{133}–Xe^{133}. Since the concentration distribution of the parent is not uniform throughout the fuel, the rate of production of the daughter will also be nonuniform. Modified relations for the fractional release by diffusion by both parent and daughter are derived in the Appendix and the results are as follows:

---

[11] W. B. Cottrell, H. N. Culver, J. L. Scott, and M. M. Yarosh, "Fission-Product Release from UO_2," USAEC Report ORNL-2935, Oak Ridge National Laboratory, Sept. 13, 1960.

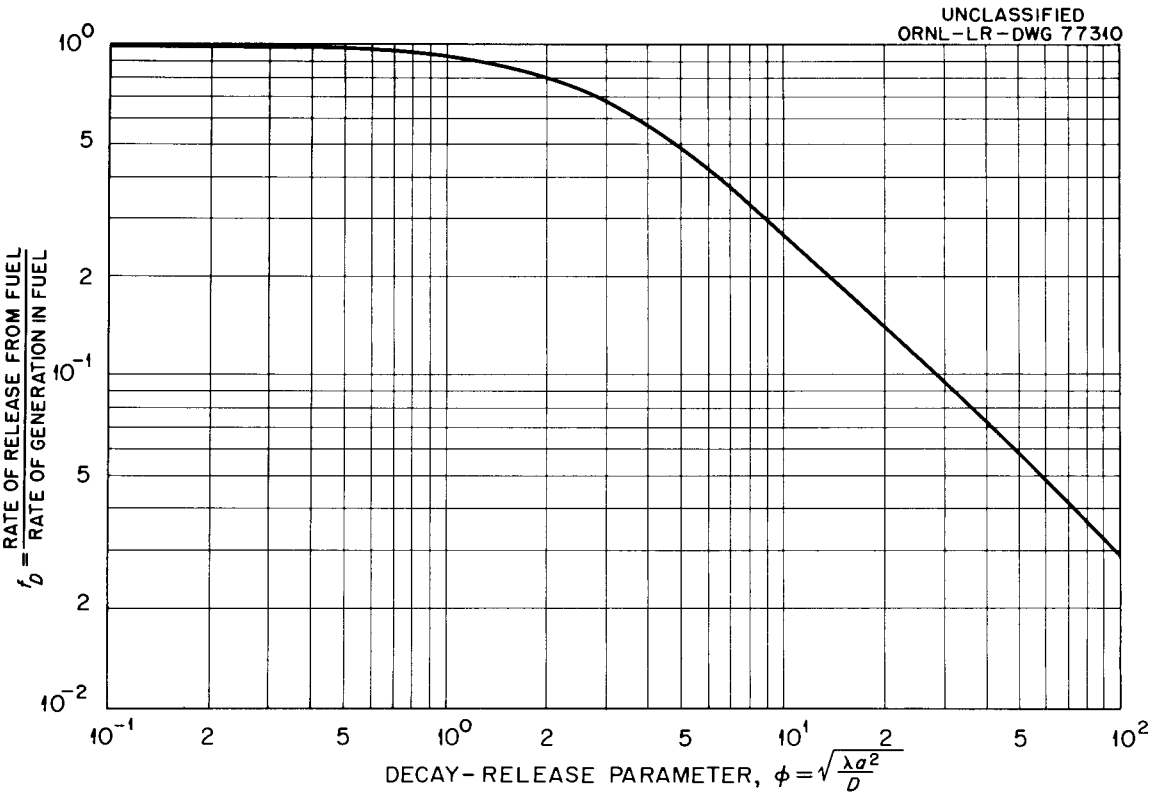

Fig. 2. Fractional Release from Fuel by Diffusion, f_D, Versus Decay-Release Parameter, ϕ.

$$f_{DA} = \frac{3}{\phi_A^2} (\phi_A \text{ ctnh } \phi_A - 1) \tag{4}$$

$$f_{DB} = \frac{3}{\phi_B^2} \left(\frac{\eta^2}{\eta^2-1} \phi_B \text{ ctnh } \phi_B - \frac{\eta}{\eta^2-1} \phi_B \text{ ctnh } (\eta\phi_B) - 1 \right), \tag{5}$$

where

$$\eta = \frac{\phi_A}{\phi_B} = \sqrt{\frac{D_B\lambda_A}{D_A\lambda_B}}$$

subscript A refers to parent species,

subscript B refers to daughter species.

For the case where both ϕ_A and ϕ_B are large, the equations reduce to

$$f_{DA} = 3 \sqrt{\frac{\lambda_A a^2}{D_A}} \tag{6}$$

$$f_{DB} = 3\sqrt{\frac{\lambda_B a^2}{D_B}} \left(\frac{\eta}{\eta+1}\right) . \tag{7}$$

These equations describing diffusional release from the fuel also apply, at least semiquantitatively, to regions other than the fuel, where fission products may be produced. Apparent fission-product generation outside the fuel would occur if all or most of the products released by recoil became imbedded in the porous carbon surrounding the fuel. The products could then diffuse from the carbon to the open pore volume, and the fractional release by this mechanism would approximately equal the product, $f_R f_D$. The diffusion coefficient for fission-product diffusion in carbon would be used to compute f_D, and the radius, a, would be that of an equivalent sphere with the same free surface-to-volume ratio as the porous carbon.[11]

Other Mechanisms

Other mechanisms have been proposed whereby fission products may escape from the fuel material. One of these is the "knock-out" process

suggested by Lewis.[12] Here it is considered that a fission product, escaping from the fuel by recoil, may release additional fission products either by direct impact or by transient vaporization of the surrounding matter. A satisfactory analysis leading to an equation for predicting the fraction of a given species released by this mechanism has not been carried out, due to the many uncertain factors associated with the process. Among the unknowns, are the effective "diameter" of a recoil track; whether all volatile fission products in the track are "vaporized," and if so, whether some "condense" back into the fuel before they can escape; and whether a significant homogenization of internal-fission-product concentrations is produced by mixing along those tracks which do not penetrate to the surface. Additional attempts to analyze this process quantitatively are planned for the future.

Another mechanism which may play a role in the release of fission products from fuel particles is chemical reaction. If oxygen is introduced into the system, either by desorption of CO or CO_2 from the graphite, back-diffusion of air through leaks, or in-leakage of steam from the boiler, the resulting impurities in the helium will tend to convert UC_2 in particles with defective coatings to UO_2, by one of the following reactions:

$$UC_2 + 2H_2O \rightarrow UO_2 + \text{mixed hydrocarbons } (CH_4,\ C_2H_4,\ \text{etc.}) \tag{8a}$$

$$UC_2 + 2CO \rightarrow UO_2 + 4C \tag{8b}$$

$$UC_2 + CO_2 \rightarrow UO_2 + 3C\ . \tag{8c}$$

For all of the above reactions, the free-energy change is a large negative number at room temperature and becomes more positive as the temperature increases. Thus, the driving force for the reactions increases with decreasing temperature, but the rates of reaction decrease with decreasing temperature. The maximum rates of reaction would be expected to occur in the range 400 to 1000°C depending on the particular reaction taking place and the partial pressure of the gaseous impurity. Thus oxidation might be particularly troublesome during shutdowns or reactor scrams.

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[12] W. B. Lewis, "The Return of Escaped Fission Product Gases to UO_2," USAEC Report DM-58, Atomic Energy Commission of Canada, Ltd., Chalk River, Jan. 21, 1960.

The oxidation of UC_2 to UO_2 would have two major effects. First, as the carbide is converted to the oxide, an interface would sweep out the reacted volume of fuel. This interface probably serves as a short-circuit diffusion path for the release of volatile-fission products, so that the rate of release would be equal to the rate of oxidation. During the oxidation process the release would be characterized by long-lived species. The second effect is the expansion which is associated with the oxidation process. It is probable that the oxide would spall off the carbide as it is formed. Subsequent reconversion to carbide could then occur if the reactor temperature is increased, or if the renegade impurity gas is removed from the system. The net result would be a notable decrease in the particle size of the carbide and an enhanced release of short-lived species by the processes previously described.

Release from Coatings

Once a gaseous fission product has been released to the open pore volume surrounding the fuel material of a coated particle, it must still cross the low-permeability coating before it can escape. Transport through the coating could occur by diffusion of the product through the pores of the coating and cracking of the coating, either from internal pressure buildup or damage sustained during fabrication. These processes will be considered in later sections.

A third escape mechanism recently discovered[13] is the diffusion of uranium out of the fuel, through the coatings, and into the fuel element matrix. Should this occur at a significant rate, saturation of the fuel element matrix with uranium could result, and part of the fissions would occur within and external to the coatings. The fission products would presumably escape from the graphite matrix to its open pores by recoil and diffusion, and release rates should be given by equations of the form for diffusion from the fuel itself.

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[13] J. L. Scott, R. E. Adams, and R. A. Bowman, "Met. and Ceram. Div. Ann. Prog. Rep. May 31, 1962," USAEC Report ORNL-3313, Oak Ridge National Laboratory, p. 26.

Diffusion Through Coatings

It is assumed that transport of gaseous fission products through an undamaged low-permeability coating is primarily by Knudsen diffusion[14] with flux proportional to the gradient of the partial pressure (or concentration) of the diffusing species. Except for geometry, the mathematical analysis closely parallels that presented earlier by one of the authors.[15] Raines and Goldwaithe[16] have presented similar treatments in which solid-phase diffusion rather than gas permeation is considered the primary mechanism for fission-product transport across the coating. The differential equation describing steady-state diffusion and radioactive decay of a fission product in a spherical shell has been solved in the Appendix to yield an expression for the fraction of a fission product released from the fuel that escapes from the coating.

$$f_C = \frac{1}{\frac{a}{b}\sinh\psi\left[\frac{\delta}{b-a}\left(\frac{\epsilon_s}{\epsilon}\right)\psi + \frac{b-a}{\psi a} + \operatorname{ctnh}\psi\right]} \tag{9}$$

where

$$\psi = \sqrt{\frac{\lambda\epsilon(b-a)^2}{K}},$$

f_C = fraction of a fission product released from fuel particles that escape from the coatings,

a = radius of fuel particle (length),

b = outer radius of coating (length),

δ = thickness of high-permeability shell between fuel and coating (length),

ϵ_s = open porosity of high-permeability shell $\frac{\text{(open pore volume)}}{\text{(total volume)}}$,

ϵ = open porosity of low-permeability coating $\frac{\text{(open pore volume)}}{\text{(total volume)}}$, and

K = permeability of coating $\frac{(\text{length})^2}{(\text{time})}$.

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[14] P. C. Carman, pp. 3, 69 in Flow of Gases Through Porous Media, Academic Press, New York, 1956.

[15] J. W. Prados, "A Model for Fission-Gas Release from Porous Fuels in Low-Permeability Containers," USAEC Report ORNL-3168, Oak Ridge National Laboratory, Aug. 11, 1961.

[16] G. E. Raines and W. H. Goldwaithe, "In-Pile Fission-Gas-Release Behavior of Alumina-Coated UO_2 Particles Irradiated to High Burnup," USAEC Report BMI-1552, Battelle Memorial Institute, Nov. 6, 1961.

Four quantities must be specified to fix the value of f_C from Eq. (9); the parameter ψ, the ratio of the porosities of the high-permeability shell and low-permeability coating, and two geometrical ratios involving the dimensions of coating, shell, and fuel. Although too many variables appear to permit a convenient general plot of Eq. (9), one can observe the effects of coating and fission-product properties on the fractional release by plotting f_C vs ψ for fixed values of the geometrical and porosity ratios. Such a curve is shown in Fig. 3 based on dimensions typical of coated particles under test at the Oak Ridge National Laboratory (ORNL). The following data were assumed to apply:

$$a = 100\ \mu,$$
$$b = 182\ \mu,$$
$$\delta = 12\ \mu,$$
$$\frac{\epsilon_s}{\epsilon} = 5 \text{ (rough estimate).}$$

For large values of ψ, $\sinh \psi \rightarrow \frac{e^{\psi}}{2}$, and $\operatorname{ctnh} \psi \rightarrow 1$. The resulting equation:

$$f_C = \frac{2\left(\frac{b}{a}\right) e^{-\psi}}{\frac{\delta}{b-a}\left(\frac{\epsilon_s}{\epsilon}\right)\psi + \frac{b-a}{\psi a} + 1} \tag{10}$$

predicts approximately exponential dependence of f_C on ψ since the terms in the denominator will depend much less strongly on ψ than will $e^{-\psi}$.

The coating diffusion equations have not been solved for a parent-daughter pair.

Comparison of Figs. 2 and 3 illustrates the intrinsic difference in the diffusional release characteristics of fuel and coating at large values of the controlling parameters. For large values of ϕ, the fractional release from the fuel is inversely proportional to ϕ; for large values of ψ, the fractional release from the coatings decreases much more drastically, approximately as the negative exponential of ψ. Both ψ and ϕ may be given approximately the same physical interpretation; as a measure of the relative rates of radioactive decay and diffusive flow. Both are defined as the square root of the decay constant divided by a diffusion rate parameter.

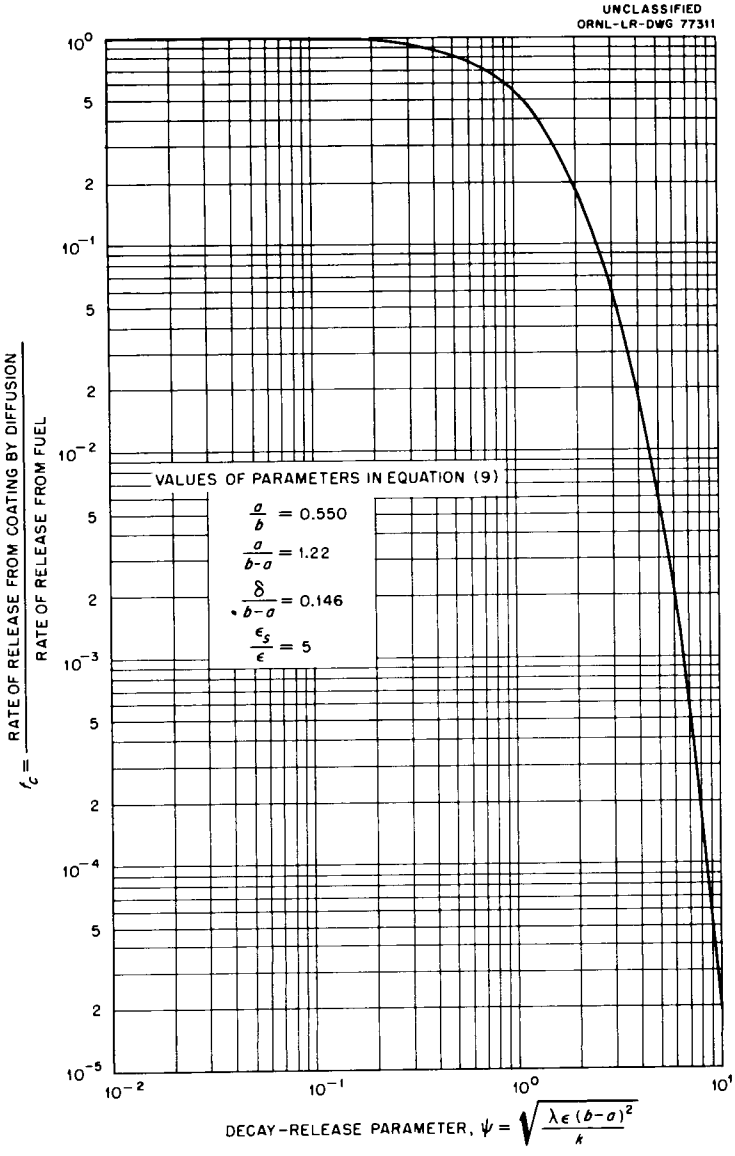

Fig. 3. Fractional Release by Diffusion Through Coatings Versus Decay-Release Parameter, ψ.

The significant difference between the nature of dependence on half-life of the escaping species predicted by the two mechanisms of "fuel" and "coating" diffusion may provide a means of distinguishing between their relative importance in a given release experiment.

The strong decrease of release fraction with increasing ψ, illustrated in Fig. 3, emphasizes the potential ability of particle coatings to eliminate significant gaseous fission-product escape. To perform this task, however, coatings must have sufficiently low gas permeability to keep ψ in the range 5 to 10 or above for all species of interest; further, they must be durable under reactor conditions and provide an effective barrier for uranium diffusion.

Release from Cracked Particles

Experiments performed on coated particles to date have indicated that the coatings do not always maintain their integrity. Cracking and rupture of some coatings appear to occur during particle manufacture and fuel element fabrication, as well as during irradiation and/or post-irradiation heat treatment.

Since only a relatively small fraction (2 to 10%) of the coatings appear to fail during most experiments, it has been assumed that improved control of manufacturing techniques could eventually reduce the rate of failure to zero. One may ask, however, whether buildup of fission-product gases in the void volume between the fuel and coating can eventually lead to pressures sufficient to cause widespread coating ruptures.

The maximum expected severity of the pressure buildup can be calculated under the assumptions that the coating is a uniform spherical shell of material with yield stress, Y, and that the fission gas released from the fuel does not decay or diffuse across the coating. Decay can be ignored because the stable xenon and krypton species create most of the pressure. The assumption that diffusion of stable species through the coating does not occur should lead to a conservative estimate of the maximum pressure buildup. The resulting equation relates the fuel burnup necessary to produce coating failure to the properties of the coated particle and fission gas.

$$Bu = \frac{2\delta\epsilon_s Y\left[1 - \left(\frac{a}{b}\right)^3\right]}{af_F n' ZR^*T} \left\{ 1 + \frac{P_o}{\frac{2}{3}Y\left[1 - \left(\frac{a}{b}\right)^3\right]} \right\} , \tag{11}$$

where

Bu = percent burnup of fuel $= 100 \dfrac{\text{(fuel atoms fissioned)}}{\text{(fuel atoms initially present)}}$,

Y = yield stress of coating material $\dfrac{\text{(force)}}{\text{(area)}}$,

f_F = total fraction of fission gas released from fuel by all mechanisms,

$n' = \dfrac{\text{moles of fission gas produced}}{\text{percent burnup-volume of fuel}}$,

Z = gas compressibility factor $= \dfrac{PV}{nR^*T}$,

R^* = universal gas constant $\dfrac{\text{(pressure - volume)}}{\text{(mole - degree)}}$,

T = absolute temperature (degrees), and

P_o = pressure external to coating $\dfrac{\text{(force)}}{\text{(area)}}$.

The compressibility factor, Z, is a function of gas temperature and pressure, and may be calculated with reasonable accuracy from generalized methods based on the Law of Corresponding States.[17] The absolute internal pressure, P, at failure may be calculated from the relation[18]

$$P = P^o + \frac{2}{3}Y\left[1 - \left(\frac{a}{b}\right)^3\right] . \tag{12}$$

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[17] J. H. Perry (ed.), pp. 352–5 in Chemical Engineers' Handbook, 3d ed., McGraw-Hill Co., Inc., New York, 1950.

[18] Rodney Hill, p. 98 in The Mathematical Theory of Plasticity, Oxford University Press, London, 1950.

The burnup necessary to cause coating failure is shown in Fig. 4 as a function of coating yield stress and fractional release from the fuel for coated particles with the same dimensions as employed in Fig. 3. A temperature of 1000°C, shell porosity of 0.25, n' of 1.35×10^{-4} $\frac{\text{(g-moles of gas)}}{\text{(percent burnup-cm}^3\text{)}}$ and zero external pressure were assumed. One sees that for low-release fractions ($f_F < 0.02$) and coatings of reasonable strength ($Y > 1000$ psi), significant burnup may be attained without danger of rupture from internal pressure. For higher release fractions, however, a reasonable probability of coating rupture through internal pressure buildup may exist.

One should note that allowable burnups calculated from Eq. (11) are quite sensitive to the assumed thickness and porosity of the high permeability shell between particle and coating. In the example chosen, the thickness, δ, was an average value measured from several photomicrographs; the porosity, ϵ_s, was estimated conservatively at a typical value for reactor-grade graphite.

Release from Fuel Elements

Fission-product gases released from the coated particles must still migrate through the graphite fuel element matrix before entering the coolant. This is thought to occur primarily by gaseous diffusion through the open pores of the matrix. The total fraction of gaseous fission product produced that will be released to the coolant is given by an expression of the form:

$$f_T = f_P f_C f_E \,, \tag{13}$$

where

f_T = fraction of a fission product produced that escapes from fuel element,

f_P = fraction of a fission product produced that escapes from fuel particles (by all mechanisms),

f_E = fraction of a fission product released from coated particles that escapes from fuel elements.

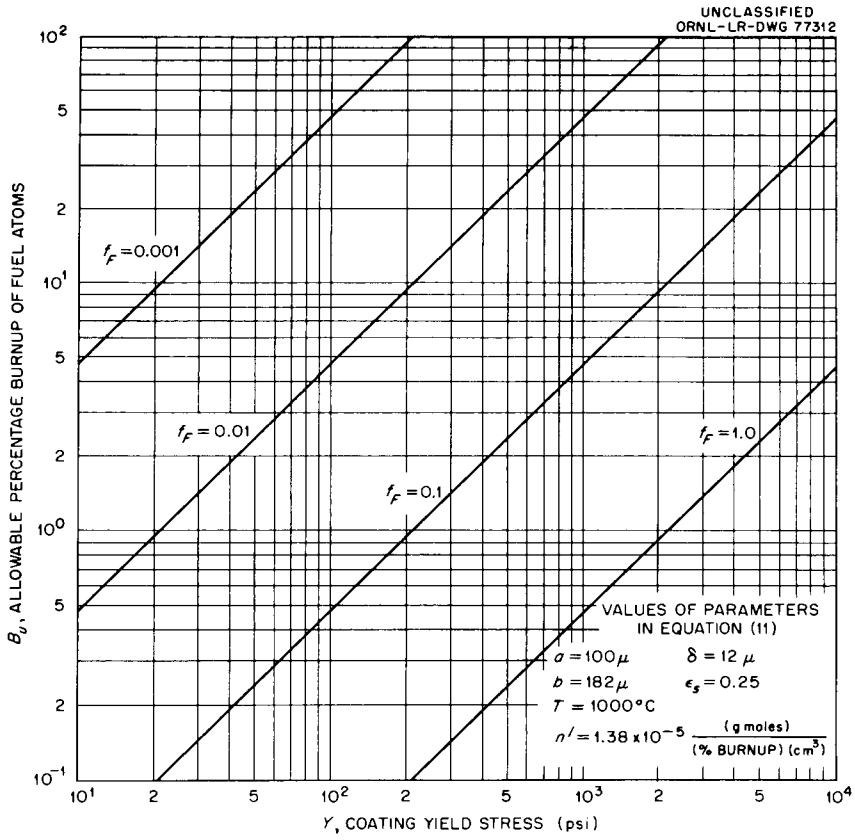

Fig. 4. Allowable Percentage Burnup Versus Coating Yield Stress for Different Fractional Releases from the Fuel.

Often, the factors on the right-hand side of Eq. (13) are independent of each other. However, where gas-phase diffusion through the coating pores is the primary mechanism for transport through the coatings and the diffusional resistance of the matrix itself is significant, f_C may depend on f_E. In such a case it will be desirable to solve the diffusion-decay equations for coating and matrix simultaneously, to obtain an expression for the product $f_C f_E$.

The fraction escaping through the fuel element matrix, f_E, will depend on the permeability and porosity distribution throughout the fuel element, and possibly on the release characteristics of the coated fuel particles themselves. These factors will rarely be known with sufficient accuracy to justify a detailed analysis of fission-gas transport in the element. Hence, only three special (and in a sense, limiting) cases will be considered here for a spherical fuel element: (a) fuel element matrix of uniformly high porosity and permeability (e.g., reactor-grade graphite); (b) fuel element matrix of high permeability and porosity except for an unfueled impregnated surface layer of low permeability and porosity; and (c) fuel element matrix uniformly impregnated to produce a low permeability and porosity throughout.

Uniform High-Permeability Matrix

For a matrix of uniformly high permeability, say $10^{-2} \rightarrow 10^{\circ}$ cm^2/sec, the rate of fission-product-gas flow through the pores would be rapid, relative to the rate of release from the coated fuel particles, and at steady state essentially all gas released from the particles would escape. Hence f_E would be near unity.

High-Permeability Matrix with Low-Permeability Coating

Here it is presumed that there is no significant resistance to diffusion, and hence uniform fission-gas pressure, within the high-permeability region, but that transport through the low-permeability coating can occur only by Knudsen flow with flux given by a Fick's law-type expression. The mathematical analysis of this situation is quite similar to that for gas transport across the coatings and may be found in the Appendix. The resulting equation for f_E is almost identical in form with Eq. (9).

$$f_E = \frac{1}{\frac{A}{B}\sinh \Psi \left[\frac{\Psi}{3}\left(\frac{A}{B-A}\right)\frac{\epsilon_E}{\epsilon_L} + \frac{B-A}{A\Psi} + \operatorname{ctnh} \Psi\right]} , \tag{14}$$

where

$$\Psi = \sqrt{\frac{\lambda\epsilon_L (B-A)^2}{K_L}} ,$$

B = outer radius of low-permeability layer surrounding fuel element (length),

A = radius of fuel element (length),

ϵ_E = open porosity of bulk fuel element matrix $\frac{\text{(open pore volume)}}{\text{(total volume)}}$,

ϵ_L = open porosity of outer, low-permeability layer $\frac{\text{(open pore volume)}}{\text{(total volume)}}$,

K_L = permeability of outer low-permeability layer $\frac{(\text{length})^2}{\text{(time)}}$.

The form of dependence of the fuel element release fraction on Ψ would be similar to that of the coating release fraction on ψ, although the actual magnitudes of the fractions might differ widely. Equation (14) reduces to the form of Eq. (10) for values of $\Psi > 5$.

Uniform Low-Permeability Matrix

A rigorous mathematical analysis of fission-gas release from a fuel element of uniform, low permeability containing many small sources of fission gas (coated particles) would be a formidable task and would require a numerical solution for the calculation of f_E. However, results of reasonable accuracy follow from a much simpler model in which the discrete fuel particles are replaced by a hypothetical fission-gas source distributed uniformly throughout the fuel element. As shown in the Appendix, the mathematical treatment for this model reduces to that for a single uniform fuel sphere, and the fraction of the fission gas escaping from the fuel element, f_E, is given by

$$f_E = \frac{3}{\Phi^2}\left[\Phi \text{ ctnh } \Phi - 1\right], \tag{15}$$

where

$$\Phi = \sqrt{\frac{\lambda \epsilon_E A^2}{K_E}},$$

A = fuel element radius (length),

K_E = permeability of fuel element matrix $\frac{(\text{length})^2}{(\text{time})}$.

Equation (15) reduces to the form of Eq. (3) for $\Phi > 10$. One may read values of f_E as a function of Φ directly from Fig. 1, by replacing f_D with f_E and ϕ with Φ.

Effect of Neutron Capture on Decay Constant

Application of any of the preceding equations to a fission-product species with appreciable neutron-capture cross section requires use of an "effective decay constant", $\lambda + \sigma_a \phi'$, rather than λ alone. Here, σ_a is the neutron-capture cross section for the species of interest, usually expressed in (cm^2) and ϕ' is the reactor flux at the fuel location, (neutrons)/(cm^2)(sec). The $\sigma_a \phi'$ correction is negligible for most gaseous fission products of interest, except Xe^{135}.

EXPERIMENTAL METHODS FOR TESTING FISSION-GAS-RELEASE MODELS

Experimental fission-gas-release data are usually obtained by one of two techniques: continuous steady-state, in-pile experiments[19] (sweep-capsule experiments) and neutron-activation experiments.[20] In the steady-state experiments, the fuel specimen is irradiated continuously in a flowing stream of inert gas which is subsequently analyzed for fission-product activity. The neutron-activation tests consist of two parts: an

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[19]R. M. Carroll and C. D. Baumann, "Experiment on Continuous Release of Fission Gas During Irradiation," USAEC Report ORNL-3050, Oak Ridge National Laboratory, Feb. 9, 1961.

[20]Oak Ridge National Laboratory, "GCRP Quar. Prog. Rep. Dec. 31, 1959," USAEC Report ORNL-2888, pp. 68–72.

irradiation period conducted at low temperature to inhibit diffusional release, followed by an out-of-pile anneal at a controlled elevated temperature. Released fission gas is collected either by means of a vacuum-cold trap system or an inert-gas sweep. The gas is then analyzed as in the case of the continuous experiments.

The continuous release experiments are more convenient for observing the effects of reactor flux and irradiation time on the release parameters. They are also more satisfactory for studying recoil and combined recoil-diffusion release processes. However, the neutron-activation tests provide closer control of specimen temperature (a necessity when studying diffusional effects), and usually yield more reproducible results than the continuous in-pile tests. The neutron-activation tests are of particular value for observing the rates of individual diffusional release processes, as from uncoated fuel particles, uranium-saturated graphite matrix material, etc.

The analysis of results from these types of tests will now be discussed.

Continuous In-Pile Experiments

Since the continuous in-pile experiments normally operate near steady-state conditions for long periods of time, the equations previously developed for steady-state release may be used directly for data analysis and comparison. The data are usually obtained as an average concentration, C, of a given fission product at some analysis point in the flowing gas downstream from the fuel specimen and outside of the reactor. If the sweep gas is assumed to be well-mixed in a small volume surrounding the specimen, a simple relation for the steady-state release rate, R_T, of a given fission product in terms of its concentration, C, in the sweep gas, is derived in the Appendix as:

$$R_T = (Q + \lambda V_C) e^{\frac{\lambda V_L}{Q}} C , \tag{16}$$

where

R_T = release rate of given fission product from the specimen $\frac{(\text{moles})}{(\text{time})}$,

Q = volumetric flow rate of inert sweep gas $\frac{(\text{volume})}{(\text{time})}$,

V_C = volume of gas in chamber surrounding specimen (volume),

V_L = volume of sweep line from fuel specimen to sample point (volume),

C = average concentration of component in gas at sample point $\frac{(\text{moles})}{(\text{volume})}$.

With some sweep-capsule designs, baffles permit a portion of the capsule volume to act as a delay line rather than a mixing chamber. In such instances, that portion of the capsule volume should be incorporated in V_L rather than V_C. For practical purposes the effect is usually negligible, and in fact, the term λV_C may usually be omitted altogether, since $\lambda V_C \ll Q$.

To determine the overall fractional release of the given component from the fuel specimen it is necessary to know its steady-state rate of formation. This may be calculated from the relation

$$B_T = \left[\frac{m_F x_U x_E \sigma_F \phi'}{M_F}\right] \gamma \ , \tag{17}$$

where

B_T = production rate of a given fission product $\frac{(\text{moles})}{(\text{time})}$,

m_F = mass of fuel material (mass),

x_U = mass fraction of chemical fuel species in fuel material, e.g., $\frac{(\text{mass of U})}{(\text{mass of } UC_2)}$,

x_E = fractional enrichment of fuel species in fissionable isotope, e.g., $\frac{(\text{mass of } U^{235})}{(\text{mass of total U})}$,

σ_F = fission cross section of fissionable species (5.39×10^{-22} cm^2 for U^{235}),

ϕ' = neutron flux at fuel $\frac{(\text{neutrons})}{(\text{area})(\text{time})}$,

γ = fission yield of component, atoms formed/fission,

M_F = atomic weight of fissionable atoms (235 for U^{235}).

The overall release fraction from the fuel specimen is then simply computed for the fission product of interest as

$$f_T = \frac{R_T}{B_T} . \tag{18}$$

It may be noted in passing that Eq. (18) permits prediction of fission-product release rates from fuel elements under reactor operating conditions from known B_T and f_T. The factors required for calculating B_T from Eq. (17) are usually known. The prediction of f_T, however, will require an experimentally confirmed mathematical model of the release process.

Neutron-Activation Tests

Since the neutron-activation tests involve an unsteady-state release of fission gas, their interpretation is not as direct as that of the continuous in-pile experiments. Usually one wishes to examine a specific step in the release process, believed to be diffusional in nature, and to obtain a diffusion coefficient or related rate-determining parameter describing the process. The analyses presented here are directed toward this end.

During initial low-temperature irradiation, diffusive release should be negligible, but a portion of the generated fission gas may escape by recoil, knock-out, or chemical attack on the fuel. Some gas may be released to the void space surrounding the specimen and some may be adsorbed on the specimen surface. To prevent loss of information on the magnitude of this release, the specimen should be sealed in a gas-tight enclosure prior to irradiation.

When a previously irradiated fuel specimen is heated to the annealing temperature in the test apparatus, an initial rapid release, or "burst," of fission gas is usually observed. Subsequently, release occurs at a much slower rate. The initial burst may consist of gas released by recoil or chemical reaction during irradiation and subsequently adsorbed on the fuel, or of release by further chemical reaction at the elevated temperatures in the test apparatus. The burst could be associated with the rapid annealing of surface defects produced by fission-fragment damage.

It has also been postulated that the initial burst represents true fission-product diffusion, and the subsequent low rate of release is caused by the clustering of xenon and krypton atoms in the matrix rendering them immobile. That release occurs at all is attributed to dissociation of unstable clusters. On heating from a low to a higher temperature, an additional burst would be observed because the low-temperature clusters are unstable at the higher temperature. For this reason they dissociate and reform larger clusters. The burst is associated with the escape of mobile fission products during the redistribution.

The slow release following the burst is frequently found to occur at a rate inversely proportional to the square root of time. As shown in the Appendix, this would be predicted for a diffusional process provided the overall release fraction remains small (< 0.1).

The raw data from a neutron-activation experiment will be the activity of collected gas as a function of time. Usually a single isotopic species is monitored and the activity is determined by counting characteristic radiation emitted by the species, e.g., the 80 kv gamma radiation emitted by Xe^{133}. From the measured activity of the gas, the amount present in the collection apparatus can be determined.

The start of the experiment, $t = 0$, is taken as the time at which the previously irradiated specimen is brought up to operating temperature in the annealing furnace. The release fraction for the transient release is defined as the ratio of the amount of the monitored fission product actually outside the specimen at time, t, divided by the amount which would have been present within the specimen at t if no release had occurred.[21]

$$f_G = \frac{n}{n_o e^{-\lambda t}} \quad , \tag{19}$$

[21]W. B. Cottrell, H. N. Culver, J. L. Scott, and M. M. Yarosh, "Fission-Product Release from UO_2," USAEC Report ORNL-2935, Oak Ridge National Laboratory, Sept. 13, 1960.

where

f_G = fraction of a given fission product released during anneal period,

n = moles of a fission product which have been released during anneal and not yet decayed,

n_o = moles of fission product present in specimen at start of anneal period,

t = time measured from start of anneal period.

One may calculate n_o from the relation[22]

$$n_o = \frac{B_T}{\lambda}\left(1 - e^{-\lambda t_R}\right) e^{-\lambda t_C} - n_E , \tag{20}$$

where

n_E = moles of fission product external to fuel specimen at start of anneal period, i.e., which have been released during irradiation and have not decayed or been adsorbed,

t_R = irradiation time (time),

t_C = time between end of irradiation and start of anneal period, "cooling time" (time).

If the species monitored is the daughter in a parent-daughter chain (as with $I^{133} \rightarrow Xe^{133}$), n_o must be calculated from the expression[22]

$$n_o = \frac{B_T \lambda_A}{\lambda_A - \lambda_B}\left[\left(\frac{1 - e^{-\lambda_B t_R}}{\lambda_B}\right) e^{-\lambda_B t_C} - \left(\frac{1 - e^{-\lambda_A t_R}}{\lambda_A}\right) e^{-\lambda_A t_C}\right] - n_E , \tag{21}$$

where

subscript A refers to parent species,

subscript B refers to daughter species.

In either case, B_o may be calculated from Eq. (17). One may measure n_E by puncturing the specimen container and collecting the released fission gas just prior to the anneal period.

The fraction, f_I, of fission gas released during the irradiation period may provide information on release by recoil and related processes.

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[22]Harold Etherington (ed.), p. 7–15 in Nuclear Engineering Handbook, McGraw-Hill Co., Inc., New York, 1958.

One may calculate f_I from

$$f_I = \frac{n_E}{n_o + n_E} \quad . \tag{22}$$

After the irradiation is completed and the specimen has been heated to operating temperature, the release data during a neutron-activation test may be expressed by a relation of the form

$$f_G = f_H + f_S \ , \tag{23}$$

where

f_H = fraction released during initial rapid burst, usually within the first few hours of the test,

f_S = fraction released during slow release period following burst.

As predicted by diffusion theory, f_S will frequently be proportional to the square root of time measured from the start of the test. The slow release may be expressed in the following form, so long as total release fractions are small (< 0.1).

$$f_S = 6\sqrt{\frac{Dt}{\pi a^2}} \quad . \tag{24}$$

Where the surface area (and hence "equivalent sphere" radius) of the specimen is unknown or poorly defined, it is customary to express results in terms of a diffusional release parameter, D', defined as the ratio D/a^2. Results conforming to the form of Eq. (24) have been observed for uncoated fuel particles, for coated particles whose coatings have ruptured, and for coated particles subjected to prior heat treatment to induce diffusion of uranium through the coatings.[23]

Values of D or D' can be obtained from experimental data by plotting f_G vs $\sqrt{t}$ and reading the slope of the curve after the initial burst is over.

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[23] J. L. Scott, R. E. Adams, and R. A. Bowman, "Met. and Ceram. Div. Ann. Prog. Rep. May 31, 1962," USAEC Report ORNL-3313, Oak Ridge National Laboratory, p. 27.

An extensive straight-line portion is usually observed whose slope is taken as

$$6\sqrt{\frac{D}{\pi a^2}} .$$

Alternately, one may plot $(f_G - f_H)^2$ vs t, and again a straight line should result, with slope,

$$\frac{36D}{\pi a^2} .$$

One may find f_H by extrapolation of the slowly rising portion of the f_G vs $\sqrt{t}$ curve to zero time.

Sometimes it is desirable to change the temperature level during a neutron-activation test in order to observe the effect of temperature on D (or D′). The predicted form for small diffusional release in such a case is developed in the Appendix and given as:

$$f_S = 6\sqrt{\frac{t'}{\pi a^2}} , \tag{25}$$

where

$$t' = \int_0^t D(\bar{t})d\bar{t}$$

$\bar{t}$ = dummy time variable of integration.

For the case where annealing temperature is changed from one constant value to another at times t_1 and t_2 during the anneal, the f_S vs t relation is shown to be:

$$f_S = \begin{cases} \dfrac{6}{\sqrt{\pi a^2}}\sqrt{Dt} & 0 < t < t_1 \\[2ex] \dfrac{6}{\sqrt{\pi a^2}}\sqrt{D_1 t_1 + D_2(t-t_1)} & t_1 < t < t_2 \\[2ex] \dfrac{6}{\sqrt{\pi a^2}}\sqrt{D_1 t_1 + D_2(t_2-t_1) + D_3(t-t_2)} & t > t_2 \end{cases} \tag{26}$$

where

D_1, D_2, D_3 = diffusion coefficients during constant-temperature periods $\frac{(\text{length})^2}{(\text{time})}$.

One may thus obtain D_1, D_2, and D_3 from a single plot of f_S^2 vs t. The slope of the first linear portion will be

$$\frac{36D_1}{\pi a^2},$$

of the second will be

$$\frac{36D_2}{\pi a^2},$$

and of the third will be

$$\frac{36D_3}{\pi a^2}.$$

Interpretation of neutron-activation test results in terms of diffusion through particle coatings will require development of solutions for transient diffusion and decay processes in the fuel and coating. In general, these will be complex in form and difficult to employ for data treatment. For special restrictions on ranges of variables covered, however, it may be possible to obtain simplified release equations yielding, perhaps, a linear f_S vs $\sqrt{t}$ relation for diffusion through the coatings. Work on the development of such equations will be pursued should evidence accumulate that coating diffusion is an important mechanism in the release from coated particles.

INTERPRETATION OF TEST RESULTS: MODEL CHARACTERISTICS

Fission-gas-release fractions predicted by the developed models exhibit characteristic relationships with the properties of the fuel, coating, fuel element matrix, and escaping fission gas. These relationships may help one distinguish between possible controlling mechanisms of fission-gas release, by comparison of experimental-release-fraction dependence on system properties with that predicted for the several mechanisms under consideration. Unfortunately, comparison of results from a single series of experiments may not fix the controlling mechanism of release, since: (a) the release may not be controlled by a single mechanism, and (b) several mechanisms may show the same form of dependence

on the properties being examined. Even so, such comparisons will usually eliminate certain possibilities from consideration and may indicate the experiments necessary to establish a satisfactory model for release.

A convenient starting point for attempts to distinguish between release mechanisms is the comparison of overall steady-state-release fractions of different noble-gas isotopes.[24] The diffusivities of the noble gases (or their rates of permeation in porous solids) should be of comparable size, and differences in their release fractions should be due primarily to the differences in their half-lives, which vary up to a hundred-fold.

Possible forms of this release fraction—half-life dependence will now be considered, together with the mechanisms they suggest. It should be noted that the half-life, τ, is inversely proportional to the decay constant, λ.

Release Fraction Independent of Half-Life

Observed release fractions of the different noble-gas species essentially independent of half-life would indicate that diffusive mechanisms do not control the rate of release. Half-life independent release fractions would strongly suggest that: (a) the major portion of the fission gas was released by recoil, either from the fuel particles themselves or from fissions in uranium which had diffused across the particle coating and into the fuel element matrix; (b) a significant fraction of the escaping fission fragments did <u>not</u> remain imbedded in shell, coating, or matrix sufficiently long to decay; (c) if uranium had not diffused out of the particles, a number of cracked coatings should exist; and (d) no significant diffusional resistance was provided by the fuel element matrix itself.

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[24] J. W. Prados, "A Model for Fission-Gas Release from Porous Fuels in Low-Permeability Containers," USAEC Report ORNL-3168, Oak Ridge National Laboratory, Aug. 11, 1961.

Release Fraction Proportional to Square Root of Half-Life

Release fractions which are proportional to the square roots of the half-lives of the escaping species indicate that diffusion phenomena control the release. At least four possible mechanisms might show this form of half-life dependence, acting singly or in parallel: (a) release by diffusion from the fuel itself and out through cracked particle coatings; (b) release from the fuel by recoil, imbedding the recoil fission fragments in the high-permeability carbon shell between fuel and coating, and subsequent escape of the fission products by diffusion from the shell across broken particle coatings; (c) diffusion of uranium out of the fuel into the fuel element matrix and escape of fission products from the matrix by diffusion; and (d) rapid escape of fission products from the fuel by recoil and through broken coatings; thence slow diffusive transport through a uniform, low-permeability fuel element matrix.

Mechanisms (a), (b), and (c) above may well act simultaneously and still give release fractions proportional to the square roots of the half-lives. To distinguish between them would require independent evidence, e.g., calculation of the recoil fraction might aid in distinguishing between (a) and (b); and extended heat treatment with subsequent chemical analysis of the fuel element matrix might eliminate mechanism (c) or confirm its existence. Diffusion data on uncoated particles from neutron-activation tests can greatly assist in establishing the correct mechanisms in such cases.

Release Fraction Directly Proportional to Half-Life

It is possible that the mechanisms (a), (b), and/or (c) above might operate in series with mechanism (d); release might occur by solid-phase diffusion from the region of fission into the fine-pore structure of a low-permeability fuel element, and thence by gas-phase diffusion out of the element. Under such conditions, Eq. (13) indicates that the release fractions might well be proportional to the first powers of the half-lives rather than their square roots.

A second mechanism which could lead to a proportionality between release fraction and half-life would be chemical attack on the fuel particles themselves, presumably by coolant impurities which enter through

previously failed coatings. If the rate of reaction were constant and other mechanisms of release were relatively unimportant, a linear dependence of release fraction on half-life could result.

Release Fraction, A Linear Function of the One-Half and Three-Halves Powers of Half-Life

Raines and Goldwaithe[25] have shown that if particle coatings fail at a slow, constant rate, and if release rates from the fuel follow a square root dependence on half-life, then release fraction can be a linear function of the one-half and three-halves powers of half-life. An outline of their reasoning follows.

From a material balance, the steady-state concentration of an escaping fission product in the free volume, V_f, between fuel and coating is equal to $R_a/\lambda V_f$, if one neglects transfer across the coating. If the rate at which coatings fail is taken as $\dot{N}_f \frac{\text{particles}}{\text{time}}$, and if a coating failure releases all gas from the free volume then the rate of fission-product release through the failed coatings would be $\dot{N}_f V_f \left(\frac{R_a}{\lambda V_f}\right)$ or $\dot{N}_f R_a/\lambda$. The rate of fission-product release through previously failed coatings would be given by the product, $R_a N_f$, where N_f is the number of failed coatings at any given time. The total release rate would then be the sum, $N_f R_a + \dot{N}_f R_a/\lambda$, and for small values of the parameter ϕ, the total fraction released would would be given by

$$f_T = 3\, N_f \sqrt{\frac{D}{a^2}}\, \frac{1}{\lambda^{1/2}} + 3\, \dot{N}_f \sqrt{\frac{D}{a^2}}\, \frac{1}{\lambda^{3/2}} \,. \tag{27}$$

Hence, over a limited time interval it is seen that the release fraction could be given by a linear combination of the one-half and three-halves powers of the half-lives of the escaping species. Data presented by Raines and Goldwaithe[25] appear to follow this pattern. One would not expect the relation to hold over long periods of time, however, due to changes in N_f and $\dot{N}_f$.

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[25] G. E. Raines and W. H. Goldwaithe, "In-Pile Fission-Gas-Release Behavior of Alumina-Coated UO_2 Particles Irradiated to High Burnup," USAEC Report BMI-1552, Battelle Memorial Institute, Nov. 6, 1961.

Other Forms of Release Fraction—Half-Life Dependence

One would not expect to observe the simple release fraction—half-life relations of the types noted previously in all cases. In some, the release fractions may show less half-life dependence than the square root proportionality; in others, the fractions may show an extremely strong, almost exponential dependence on half-lives. In the former cases, one might suspect combined release mechanisms involving both diffusional and direct recoil release; in the latter, gas diffusion through particle or fuel element coatings may provide a significant fraction of the resistance to release.

Each case must be tested against all reasonable mechanisms and combinations thereof. Since release models based on combined mechanisms usually involve at least one adjustable parameter, it may be relatively easy to fit several models to the results of a single experiment. Hence, the model(s) must be tested for consistency with information beyond overall release fraction—half-life relationships.

DISCUSSION

Possible mechanisms for the release of gaseous fission products from coated-particle fuel elements have been considered, and mathematical relationships developed for predicting the fraction of a given fission product released by each mechanism as a function of system parameters. These relations are based on simplified models of the release processes and by no means cover all possible mechanisms, nor do they permit unequivocal specification of a given mechanism even when observed fission-gas-release behavior conforms to one of the postulated models. They do, however, provide a rational basis for the interpretation of data and the planning of experiments. Once confirmed, these or similar relations may be used to predict release from coated-particle fuel elements under reactor conditions.

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APPENDIX

Development of Working Equations

1. Steady-State Fractional Release by Recoil

Consider release from a spherical fuel particle of radius a. It is assumed that fission products are emitted from the point of fission in random directions and travel a distance, R, in the fuel. From Fig. 5, it may be seen that the probability, P_E, that a fission product will escape is equal to the fraction of the surface of the sphere of radius, R, with center at the fission point, which lies outside the fuel particle. The fission point lies a distance, ξ, from the center of the fuel particle.

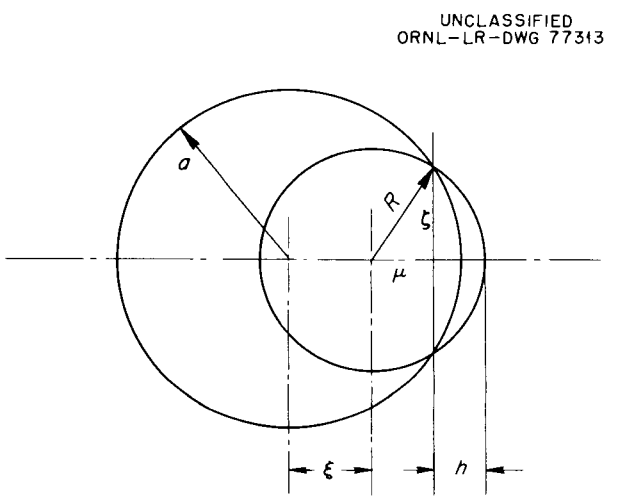

Fig. 5. Recoil from Spherical Fuel Particle.

From Fig. 5 it can be seen that P_E is given by $(2\pi rh)/(4\pi R^2)$ or simply $(R-\mu)/2R$. From Fig. 5

$$\mu^2 = R^2 - \zeta^2 = R^2 - [a^2 - (\xi + \mu)^2]$$

$$\mu^2 = R^2 - a^2 + \xi^2 + 2\xi\mu + \mu^2$$

$$\mu = \frac{a^2 - R^2 - \xi^2}{2\xi}$$

hence

$$P_E = \begin{cases} 1/2 - \dfrac{a^2 - R^2 - \xi^2}{4\xi R} & \text{for } \begin{cases} R < 2a \text{ and} \\ (a-R) \leq \xi \leq a \end{cases} \\ 0 & \text{for } \begin{cases} R < 2a \text{ and} \\ \xi < a-R \end{cases} \\ 1 & \text{for } \begin{cases} R > 2a \end{cases} \end{cases} \tag{28}$$

The rate of escape of a given fission product by recoil per unit volume of fuel, R_o, is equal to the product, $P_E B_o$. Hence, the total release rate from a fuel particle will be

$$R_R = \int_{a-R}^{a} R_o \, 4\pi\xi^2 d\xi$$

the fractional release by recoil, f_R, is defined as $R_R/(\frac{4}{3}\pi a^3 B_o)$ so that

$$f_R = \frac{3}{a^3}\int_{a-R}^{a} P_E \, \xi^2 d\xi \quad . \tag{29}$$

Substitution of P_E from Eq. (28) into this integral yields

$$f_R = \frac{3}{a^3}\int_{a-R}^{a} \left[\frac{1}{2} - \frac{a^2-R^2}{4\xi R} + \frac{\xi}{4R}\right] \xi^2 d\xi \ .$$

The result of integration and evaluation at the limits is[26]

$$f_R = \frac{3}{4}\left(\frac{R}{a}\right) - \frac{1}{16}\left(\frac{R}{a}\right)^3 \tag{1}$$

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[26]D. W. White, A. P. Beard, and A. H. Willis, "Irradiation Behavior of Dispersion Fuels," USAEC Report KAPL-P-1849, Knolls Atomic Power Laboratory, Nov. 18, 1957, p. 15.

2. Steady-State Fractional Release by Diffusion with Internal Generation

The diffusion and decay of a fission product in a spherical fuel particle or fuel element with homogeneous internal generation can be described by a differential equation based on Fick's law and conservation of mass[27]

$$\frac{\partial c}{\partial t} = D\left(\frac{\partial^2 c}{\partial r^2} + \frac{2}{r}\frac{\partial c}{\partial r}\right) + B_o - \lambda c \ , \tag{30}$$

where

B_o = production rate density of a given fission product $\frac{(\text{moles})}{(\text{volume})(\text{time})}$,

$c\ (r,t)$ = concentration of a given fission product in fuel $\frac{(\text{moles})}{(\text{volume})}$,

r = radial coordinate in sphere (length).

At steady state, the time derivative vanishes, and Eq. (30) becomes

$$\frac{d^2c}{dr^2} + \frac{2}{r}\frac{dc}{dr} - \frac{\lambda}{D}c = \frac{B_o}{D} \ . \tag{31}$$

Since the solubility of the fission-product gases will be extremely low in the fuel, and the gas should be removed rapidly from the outside of a fuel element, the boundary conditions will be taken as:

$$c\ (a) = 0;\ c\ (0) \text{ remains finite} \ . \tag{32}$$

The solution to Eq. (31) satisfying conditions of Eq. (32) is:

$$c(r) = \frac{B_o}{\lambda}\left[1 - \frac{a}{r}\,\frac{\sinh\left(r\sqrt{\frac{\lambda}{D}}\right)}{\sinh\left(a\sqrt{\frac{\lambda}{D}}\right)}\right] \ . \tag{33}$$

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[27]W. B. Cottrell, H. N. Culver, J. L. Scott, and M. M. Yarosh, "Fission-Product Release from UO_2," USAEC Report ORNL-2935, Oak Ridge National Laboratory, Sept. 13, 1960.

The rate of release from the fuel by diffusion, R_D, can be found as:

$$R_D = -4\pi a^2 D \left.\frac{dc}{dr}\right|_{r=a} . \tag{34}$$

From Eq. (33)

$$\left.\frac{dc}{dr}\right|_{r=a} = -\frac{B_o}{\lambda a}\,[\phi \text{ ctnh } \phi - 1] \quad , \tag{35}$$

where

$$\phi = \sqrt{\frac{\lambda a^2}{D}} .$$

The fraction of a given species released by diffusion, f_D, is given by $R_D/(4/3\ \pi a^3 B_o)$, so that

$$f_D = \frac{3}{\phi^2}\,[\phi \text{ ctnh } \phi - 1] . \tag{2}$$

Equation (15) follows directly by use of appropriate symbols for the fuel element in the preceding development.

3. Release of Parent-Daughter Pair by Diffusion with Internal Generation

Where a parent substance, A, is generated in the fuel at a uniform rate, diffuses out of the fuel, and simultaneously decays to form a mobile daughter, B, which also diffuses out of the fuel, the differential equations governing the process at steady state follow from Eq. (30).

$$\frac{d^2c_A}{dr^2} + \frac{2}{r}\frac{dc_A}{dr} - \frac{\lambda_A}{D_A}c_A = \frac{B_o}{D_A} , \tag{36}$$

$$\frac{d^2c_B}{dr^2} + \frac{2}{r}\frac{dc_B}{dr} - \frac{\lambda_B}{D_B}c_B = \frac{\lambda_A}{D_B}c_A , \tag{37}$$

where

subscript A refers to parent,

subscript B refers to daughter.

Boundary conditions are:

$$c_A(a) = c_B(a) = 0$$

$$c_A(0) \text{ and } c_B(0) \text{ remain finite .} \tag{38}$$

The solution for $c_A(r)$ is identical with Eq. (33). This expression may be then substituted into Eq. (37) to yield a differential equation for c_B alone, whose solution satisfying Eq. (38) is:

$$c_B(r) = \frac{B_o}{\lambda_B}\left[1 - \left(\frac{a}{r}\right)\left(\frac{\eta^2}{\eta^2-1}\right)\frac{\sinh\frac{r}{a}\phi_B}{\sinh\phi_B} + \left(\frac{a}{r}\right)\left(\frac{1}{\eta^2-1}\right)\frac{\sinh\frac{r}{a}\phi_A}{\sinh\phi_A}\right], \tag{39}$$

where

$$\phi_A = \sqrt{\frac{\lambda_A a^2}{D_A}}$$

$$\phi_B = \sqrt{\frac{\lambda_B a^2}{D_B}}$$

$$\eta = \frac{\phi_A}{\phi_B} = \sqrt{\frac{\lambda_A D_B}{\lambda_B D_A}} \quad .$$

Calculation of the release rates for each species by Eq. (34) leads to expressions for the fractions of each species released by diffusion, based on the generation rate of A; that is

$$f_{DA} = \frac{R_{DA}}{4/3\ \pi a^3 B_o}$$

$$f_{DB} = \frac{R_{DB}}{4/3\ \pi a^3 B_o} \quad . \tag{40}$$

These results are

$$f_{DA} = \frac{3}{\phi_A^2}\left[\phi_A \operatorname{ctnh}\phi_A - 1\right] \tag{4}$$

$$f_{DB} = \frac{3}{\phi_B^2}\left[\left(\frac{\eta^2}{\eta^2-1}\right)\phi_B \operatorname{ctnh}\phi_B - \left(\frac{\eta}{\eta^2-1}\right)\phi_B \operatorname{ctnh}\eta\phi_B - 1\right] . \tag{5}$$

Reduction to Eqs. (6) and (7) is direct when ϕ_A and ϕ_B are both large.

4. Steady-State Diffusion and Decay Through a Particle Coating or Outer Layer of a Fuel Element

Consider now a spherical shell, of inner radius a and outer radius b, enclosing a free volume, V_f, to which fission gas is released at a rate, R_F moles/time. No material is generated in the shell, and transport of gas occurs by Knudsen flow, with flux of a given species proportional to the gradient of its partial pressure (or concentration). The differential equation describing the process is quite similar to Eq. (33).

$$\frac{d^2c}{dr^2} + \frac{2}{r}\frac{dc}{dr} - \frac{\lambda\epsilon}{K}\, c = 0 \quad . \tag{41}$$

The boundary conditions are taken as:

$$c(a) = c_a;\ c(b) = 0 \ . \tag{42}$$

The solution of Eq. (41) satisfying Eq. (42) is

$$c = c_a \left(\frac{a}{r}\right) \frac{\sinh\left(\frac{b-r}{b-a}\,\psi\right)}{\sinh\psi} \quad , \tag{43}$$

where

$$\psi = \sqrt{\frac{\lambda\epsilon(b-a)^2}{K}} \ .$$

The rate at which gas enters the inner surface, R_a moles/time is given by

$$R_a = -4\pi a^2 K \left.\frac{dc}{dr}\right|_{r=a} = 4\pi a K c_a \left[1 + \frac{a}{b-a}\,\psi\ \mathrm{ctnh}\ \psi\right] , \tag{44}$$

and the rate at which it leaves the outer surface, R_b, is

$$R_b = -4\pi b^2 K \left.\frac{dc}{dr}\right|_{r=b} = \frac{4\pi abK\ c_a\sqrt{\frac{\lambda\epsilon}{K}}}{\sinh\psi} \quad . \tag{45}$$

To find c_a, one makes a material balance on the internal free volume, V_f, assuming that c_a is uniform throughout.

$$R_F - \lambda c_a\ V_f - R_a = 0 \ . \tag{46}$$

Equations (44) and (46) may be combined to yield an expression for c_a

$$c_a = \frac{R_F}{V_f\lambda + 4\pi aK\left(1 + \frac{a}{b-a}\,\psi\,\mathrm{ctnh}\,\psi\right)} \quad . \tag{47}$$

This is then substituted into Eq. (45) to obtain the rate of release from the outer surface

$$R_b = \frac{R_F}{\sinh\psi\left[\frac{V_f\lambda}{4\pi abK}\sqrt{\frac{K}{\lambda\epsilon}} + \frac{1}{b}\sqrt{\frac{K}{\lambda\epsilon}}\left(1 + \frac{a}{b-a}\,\psi\,\mathrm{ctnh}\,\psi\right)\right]} \quad , \tag{48}$$

which can be slightly simplified to

$$R_b = \frac{R_F}{\frac{a}{b}\sinh\psi\left[\frac{V_f\psi}{4\pi a^2(b-a)\epsilon} + \frac{b-a}{a\psi} + \mathrm{ctnh}\,\psi\right]} \quad . \tag{49}$$

For application of Eq. (49) to a single particle coating, one may take $V_f \approx 4\pi a^2\delta\epsilon_s$. The fractional release from the coating, f_C, defined as R_b/R_F, is then

$$f_C = \frac{1}{\frac{a}{b}\sinh\psi\left[\frac{\delta}{b-a}\left(\frac{\epsilon_s}{\epsilon}\right)\psi + \frac{b-a}{a\psi} + \mathrm{ctnh}\,\psi\right]} \quad . \tag{9}$$

For diffusion across a low-permeability shell surrounding a fuel element, the inner and outer dimensions are taken as A and B, respectively, $V_f \approx \frac{4}{3}\pi A^3\epsilon_E$, and the fractional release from the shell, f_E, is

$$f_E = \frac{1}{\frac{A}{B}\sinh\Psi\left[\frac{\Psi}{3}\left(\frac{A}{B-A}\right)\frac{\epsilon_E}{\epsilon_L} + \frac{B-A}{A\Psi} + \mathrm{ctnh}\,\Psi\right]} \quad , \tag{14}$$

where

$$\Psi = \sqrt{\frac{\lambda\epsilon_L(B-A)^2}{K_L}} \quad .$$

5. Maximum Severity of Pressure Buildup in Coatings

The relation between the internal absolute pressure P necessary to cause rupture of a particle coating and the yield stress, Y, of the coating is given as[28]

$$P = P_o + \frac{2}{3} Y \left[1 - \left(\frac{a}{b}\right)^3 \right] . \tag{12}$$

The pressure may also be related to the burnup of fuel in the coated particle through application of the gas law to the internal free volume, V_f. The relationship which applies is

$$P = \frac{Zn_T R^* T}{V_f} . \tag{50}$$

If one neglects differential thermal expansion of the particle and coating, $V_f \approx 4\pi a^2 \delta \epsilon_s$ as indicated previously. The number of moles of gas within the free volume at any time, neglecting any release or decay, is given by the relation

$$n_T = \frac{4}{3}\pi a^3 n' Bu\ f_F , \tag{51}$$

n' is given by

$$n' = \frac{\rho_F x_u \gamma_T}{100\ M_F} . \tag{52}$$

Equations (50) and (51) may be combined to yield the relation between pressure and percentage burnup

$$P = \frac{a n' Bu\ f_F Z R^* T}{3 \delta \epsilon_s} . \tag{53}$$

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[28]Rodney Hill, The Mathematical Theory of Plasticity, p. 98, Oxford University Press, London, 1950.

Elimination of pressure between Eqs. (53) and (12) produces an expression for the burnup necessary to cause coating rupture in terms of coated-particle properties and system conditions,

$$Bu = \frac{2\delta\epsilon_s Y\left[1 - \left(\frac{a}{b}\right)^3\right]}{af_F n' ZR^*T}\left\{1 + \frac{P_o}{\frac{2}{3}Y\left[1 - \left(\frac{a}{b}\right)^3\right]}\right\} . \tag{11}$$

6. Relation Between Release Rate from Specimen and Composition at Sampling Point for Steady-State, In-Pile-Release Experiments

The continuous, in-pile, fission-gas-release experiments may be represented schematically as in Fig. 6.

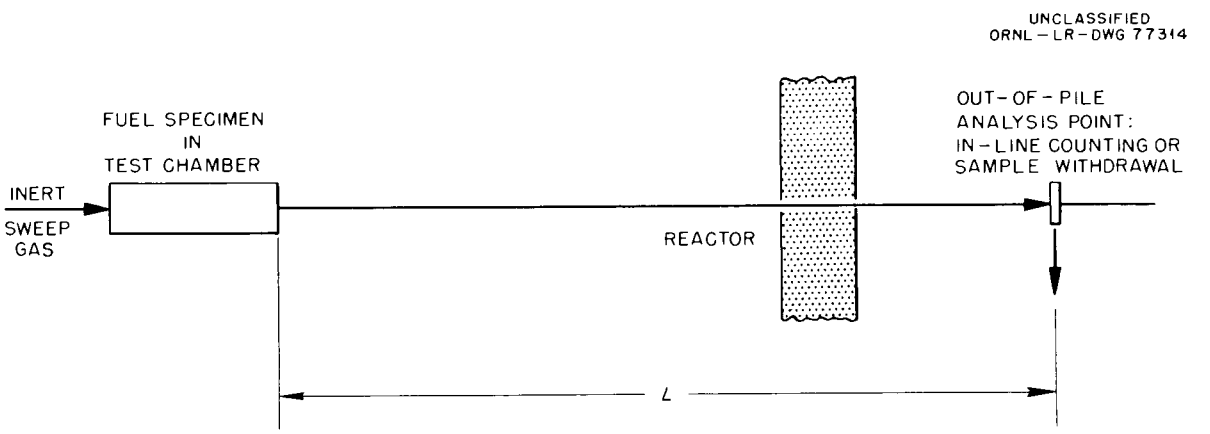

Fig. 6. Continuous In-Pile-Release Experiment Schematic.

If the test chamber volume is V_C, pure sweep gas enters at the rate of Q volume/time, and the gas around the fuel is assumed to contain a small, spatially uniform concentration of the fission product of interest, C_o, a steady-state material balance on the gas chamber yields,

$$V_c \frac{dC_o}{dt} = R_T - QC_o - \lambda C_o V_C = 0 \tag{54}$$

or

$$C_o = \frac{R_T}{Q + \lambda V_C} . \tag{55}$$

If the sweep gas flows from the test chamber to the sampling point in turbulent flow, so that the velocity profile in the gas is reasonably

flat and radial concentration gradients can be neglected, the differential equation describing steady-state transport of fission gas in the sweep line is

$$\frac{dC}{dz} - \frac{\lambda}{u} C = 0 \quad , \tag{56}$$

where

z = distance from fuel specimen chamber (length),

u = linear velocity of sweep gas in line $\frac{(\text{length})}{(\text{time})}$,

$C(z)$ = average concentration of fission product in sweep gas at distance z from fuel specimen $\frac{(\text{moles})}{(\text{volume})}$.

The boundary condition is

$$C(0) = C_o \ . \tag{57}$$

The solution for $C(z)$ is

$$C(z) = C_o e^{-\frac{\lambda z}{u}} \ . \tag{58}$$

The concentration at the sample point, $z = L$, can be calculated from Eq. (58) and C_o eliminated between Eqs. (58) and (55) to yield the relation between the actual release rate at the fuel specimen and the downstream fission-gas concentration

$$R_T = (Q + \lambda V_C)\, e^{\frac{\lambda V_L}{Q}}\, C \ . \tag{16}$$

In comparing Eqs. (16) and (58), note that the ratios L/u and V_L/Q are the same.

When flow in the sweep line is laminar, as is often the case, a question arises as to the validity of Eqs. (56), (57), and (58) since in laminar flow the velocity and concentration in the line will vary with radial position. The differential equation describing laminar flow, diffusion, and decay in the sweep line is derived from a material balance on a small ring of fluid, symmetric about the pipe axis, under the assumption of the usual parabolic laminar velocity profile.

$$\frac{\partial^2 c}{\partial r^2} + \frac{1}{r}\frac{\partial c}{\partial r} - \frac{2u}{D_G}\left[1 - \left(\frac{r}{r_o}\right)^2\right]\frac{\partial c}{\partial z} - \frac{\lambda}{D_G}\, c = 0 \ , \tag{59}$$

where

$c(r,z)$ = concentration of fission product in sweep gas $\frac{(\text{moles})}{(\text{volume})}$,

r = radial distance from center of tube (length),

r_o = inner tube wall radius (length),

z = longitudinal distance along tube from fuel specimen (length),

D_G = diffusivity of given component in the flowing gas $\frac{(\text{length})^2}{(\text{time})}$,

u = mean velocity of flowing gas = $\frac{Q}{\pi r_o^2}\,\frac{(\text{length})}{(\text{time})}$.

The boundary conditions on Eq. (59) are

$$\begin{aligned} &c(r,0) = c_o \\ &c(0,z) \text{ remains finite} \\ &\frac{\partial c}{\partial r}(r_o,z) = 0 \ . \end{aligned} \tag{60}$$

This problem has been treated by Lauwerier,[29] who obtained an analytical solution for $c(r,z)$. Calculations from the general solution are difficult since the solution is given as an infinite series of functions which must, themselves, be evaluated from infinite series. However, an approximate solution, valid for points in the tube removed from the entrance and for small values of the parameter group $\left(\frac{\lambda r_o^2}{4D_G}\right)$ is given as follows:

$$c(y,\Omega) = C_o\left(1 + \frac{\alpha}{4}\right)\left[1 - \alpha y^2\left(1 - \frac{y^2}{2}\right)\right] e^{-2\alpha\Omega} \ , \tag{61}$$

where

$$y = \frac{r}{r_o}$$

$$\Omega = \left(\frac{2D_G}{r_o^2 u}\right) z$$

$$\alpha = \left(\frac{\lambda r_o^2}{4D_G}\right) \ .$$

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[29] H. A. Lauwerier, "A Diffusion Problem with Chemical Reaction," Appl. Sci. Res., Sect. A, 8: 366–76 (1959).

This solution should be valid for all but the shortest sweep lines (say for $z \geq 2$ ft) since α is of the order of 10^{-4} or less for all fission gases of interest.

The mean fission-product concentration at a given cross section, $C(z)$, is related to the point concentration, $c(r,z)$ by

$$\pi r_o^2 \, u \, C(z) = \int_0^{r_o} c(r,z) \; 2u \left[1 - \left(\frac{r}{r_o}\right)^2\right] 2\pi r dr$$

or in terms of the variables of Eq. (56)

$$C(\Omega) = 4 \int_0^1 c(y,\Omega)(y - y^3) \, dy \; . \tag{62}$$

Upon integration, one obtains

$$C(\Omega) = \left(1 - \frac{\alpha^2}{16}\right) e^{-2\alpha\Omega} \tag{63}$$

which, from substitution of the appropriate quantities for α and Ω, becomes

$$C(z) = \left[1 - \frac{1}{16}\left(\frac{\lambda r_o^2}{4D_G}\right)^2\right] e^{-\frac{\lambda z}{u}} \; . \tag{64}$$

Since the quantity $\frac{1}{16}\left(\frac{\lambda r_o^2}{4D_G}\right)^2 \ll 1$, Eq. (64) reduces exactly to Eq. (58), and the use of Eq. (16) is justified either for laminar or turbulent flow in the sweep line.

7. Release Fractions as a Function of Time for Neutron-Activation Experiments

Since specimen irradiation is carried out prior to the start of a neutron-activation experiment, there is no generation of fission products within the specimen during the experiment, and internal fission-gas concentrations and release rates decrease with time. The differential equation describing unsteady-state diffusion and decay in a spherical fuel particle follows directly from Eq. (30) with $B_o = 0$

$$\frac{\partial c}{\partial t} = D\left(\frac{\partial^2 c}{\partial r^2} + \frac{2}{r}\frac{\partial c}{\partial r}\right) - \lambda c \; . \tag{65}$$

The boundary conditions are

$$c(r,0) = c_o$$

$$c(a,t) = 0$$

$$c(0,t) \text{ remains finite .} \tag{66}$$

Equations (65) and (66) may be transformed into a simpler system by introduction of a new variable, $c^*(r,t) = c(r,t)e^{\lambda t}$ where c^* is the concentration that would have existed at a point in time and space if decay had not occurred. Substitution of c^* into Eqs. (65) and (66) yields

$$\frac{\partial c^*}{\partial t} = D\left(\frac{\partial^2 c^*}{\partial r^2} + \frac{2}{r}\frac{\partial c^*}{\partial r}\right) \tag{67}$$

and

$$c^*(r,0) = c_o$$

$$c^*(a,t) = 0$$

$$c^*(0,t) \text{ remains finite .} \tag{68}$$

These equations describe diffusion without decay in a sphere and solutions for this system are presented in standard references[30] as

$$c^*(r,t) = \frac{2ac_o}{\pi r}\sum_{k=1}^{\infty} \frac{(-1)^{k+1}}{k} \sin\left(\frac{k\pi r}{a}\right) e^{\frac{-Dk^2\pi^2 t}{a^2}} . \tag{69}$$

The corresponding value of $c(r,t)$ is given by multiplying the value of c^* by $e^{-\lambda t}$.

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[30]H. S. Carslaw and J. C. Jaeger, Conduction of Heat in Solids, 1st ed., p. 200, Oxford University Press, London, 1947.

The rate of release from the outer surface of the sphere is given by

$$R_a = -4\pi a^2 D \left.\frac{\partial c}{\partial r}\right|_{r=a} \tag{70}$$

where R_a = release rate of a given fission product from fuel $\frac{(\text{moles})}{(\text{time})}$ upon differentiation of Eq. (69) and substitution in Eq. (70), one obtains

$$R_a = 8\pi a D c_o e^{-\lambda t} \sum_{k=1}^{\infty} e^{-\frac{Dk^2\pi^2 t}{a^2}} . \tag{71}$$

The fractional release for the transient case is defined as the ratio of the moles of gas which have escaped up to time, t, and not yet decayed, divided by the moles of gas which would have remained in the specimen at t if no release had occurred.[31] For diffusional release, this fraction is

$$f_S = \frac{n(t)}{\frac{4}{3}\pi a^3 c_o e^{-\lambda t}} . \tag{72}$$

One may obtain an expression for n(t) by a material balance on all gas external to the sphere

$$\frac{dn}{dt} = R_a - \lambda n \tag{73}$$

with n(0) = 0.

The solution is obtained in the form

$$n(t) = e^{-\lambda t} \int_0^t e^{\lambda \bar{t}} R_a(\bar{t}) d\bar{t} \tag{74}$$

where $\bar{t}$ = dummy time variable of integration.

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[31]W. B. Cottrell, H. N. Culver, J. L. Scott, and M. M. Yarosh, "Fission-Product Release from UO_2," USAEC Report ORNL-2935, Oak Ridge National Laboratory, Sept. 13, 1960.

If $R_a(t)$ is substituted from Eq. (71) and the integral evaluated,

$$n = \frac{4}{3}\pi a^3 c_o e^{-\lambda t}\left[1 - \frac{6}{\pi^2}\sum_{k=1}^{\infty}\frac{1}{k^2}\, e^{\frac{-Dk^2\pi^2 t}{a^2}}\right] . \tag{75}$$

The fractional release by diffusion is then, from Eq. (72)

$$f_S(t) = \left[1 - \frac{6}{\pi^2}\sum_{k=1}^{\infty}\frac{1}{k^2}\, e^{-\frac{Dk^2\pi^2 t}{a^2}}\right] . \tag{76}$$

For values of $\frac{D\pi^2 t}{a^2}$ less than 0.01, equivalent to values of f_S less than 0.1, the expression in brackets is well approximated by

$$\sqrt{\frac{36Dt}{\pi a^2}} ,$$

and hence

$$f_S(t) = 6\sqrt{\frac{Dt}{\pi a^2}} \tag{24}$$

for values of f_S less than 0.1.
The often observed linear dependence of $f_S(t)$ on $\sqrt{t}$ is thereby predicted. As previously mentioned, Eqs. (76) and (24) are often applied to nonspherical geometries, taking a as the radius of an "equivalent sphere" with the same surface-to-volume ratio as the actual specimen. For low release fractions where Eq. (24) holds, this should be a good approximation, since most of the release is coming from a thin layer near the surface of the specimen and overall geometry is of little importance.

8. Release Fraction–Time Relationship in Neutron-Activation Tests for Step Changes in Operating Temperature

The question arises as to whether or not the f_S vs $\sqrt{t}$ relation will hold if the operating temperature (and hence diffusion coefficient) is changed during a run. This problem can be treated as a simple extension of the case for constant diffusion coefficient, if the diffusion coefficient is taken as a function of time only.

Define a new "time" variable, t', by the relation

$$t' = \int_0^t D(\bar{t})d\bar{t} \tag{77}$$

where $\bar{t}$ = dummy time variable of integration.

Since

$$\frac{\partial c^*}{\partial t} = \frac{\partial c^*}{\partial t'}\frac{\partial t'}{\partial t} = D(t)\frac{\partial c^*}{\partial t'} . \tag{78}$$

Equation (68) may be written in terms of t' as

$$\frac{\partial c^*}{\partial t'} = \frac{\partial^2 c^*}{\partial r^2} + \frac{2}{r}\frac{\partial c^*}{\partial r} \tag{79}$$

and the boundary conditions are unchanged. The solution will be identical with Eq. (69) except that t' will replace the product Dt. (Note that $t' = Dt$ if D is a constant.) The expression for instantaneous release rate, analogous to Eq. (71) is

$$R_a = 8\pi a D(t) c_o e^{-\lambda t} \sum_{k=1}^{\infty} e^{\frac{-k^2\pi^2 t'}{a^2}} \tag{80}$$

which, when substituted into Eq. (74) yields

$$n = 8\pi a c_o e^{-\lambda t} \int_0^t D(\bar{t}) \sum_{k=1}^{\infty} e^{\frac{-k^2\pi^2 t'}{a^2}} d\bar{t} . \tag{81}$$

The indicated integration may be simply performed if one notes that $D(t)dt = dt'$, to yield

$$n = \frac{4}{3}\pi a^3 c_o e^{-\lambda t} \left[1 - \frac{6}{\pi^2} \sum_{k=1}^{\infty} \frac{1}{k^2} e^{\frac{-k^2\pi^2 t'}{a^2}} \right] . \tag{82}$$

Thus

$$f_S(t') = 1 - \frac{6}{\pi^2} \sum_{k=1}^{\infty} \frac{1}{k^2} e^{\frac{-k^2\pi^2 t'}{a^2}} . \tag{83}$$

To show the actual f_S vs time relation, a specific case will be considered

$$D(t) = \begin{cases} D_1 \text{ for } 0 < t < t_1 \\ D_2 \text{ for } t_1 < t < t_2 \\ D_3 \text{ for } t_2 < t \end{cases} \tag{84}$$

where D_1, D_2, and D_3 are constants. This would correspond to a neutron-activation experiment in which the annealing temperature was changed to new constant values at times t_1 and t_2. From the definition of t',

$$t' = \begin{cases} D_1 t & \text{for } 0 < t < t_1 \\ D_1 t_1 + D_2(t - t_1) & \text{for } t_1 < t < t_2 \\ D_1 t_1 + D_2(t_2 - t_1) + D_3(t - t_2) & \text{for } t > t_2 \end{cases} . \tag{85}$$

In general for stepwise heating, one can show that

$$t' = D_{N+1}(t - t_N) + \sum_{j=1}^{N} D_j(t_j - t_{j-1}) \tag{86}$$

where

N = number of times annealing temperature is changed during activation experiment,

D_j = diffusion coefficient during time interval $t_{j-1} < t < t_j$ $\frac{(\text{length})^2}{(\text{time})}$,

t_j = time at which annealing temperature is changed, $j = 1, 2, \ldots N$. $(t_o = 0)$ (time) .

For small release fractions ($f_S < 0.1$), the simplification of Eq. (24) holds and

$$f_S(t') = 6\sqrt{\frac{t'}{\pi a^2}} \ . \tag{25}$$

In terms of the example above

$$f_S(t) = \begin{cases} \dfrac{6}{\sqrt{\pi a^2}}\sqrt{D_1 t} & \text{for } 0 < t < t_1 \\[2ex] \dfrac{6}{\sqrt{\pi a^2}}\sqrt{D_1 t_1 + D_2(t - t_1)} & \text{for } t_1 < t < t_2 \\[2ex] \dfrac{6}{\sqrt{\pi a^2}}\sqrt{D_1 t_1 + D_2(t_2 - t_1) + D_3(t - t_2)} & \text{for } t > t_2 \ . \end{cases} \tag{26}$$

In the general case, t' can be evaluated from Eq. (86).

NOTATION

Upper Case

A	fuel element radius (length)
B	outer radius of low-permeability shell surrounding fuel element (length)
B_o	production rate density of a given fission product $\frac{(\text{moles})}{(\text{volume})(\text{time})}$
B_T	production rate of a given fission product $\frac{(\text{moles})}{(\text{time})}$
B_u	percent burnup of fuel, $100\ \frac{(\text{fuel atoms fissioned})}{(\text{fuel atoms initially present})}$
C	average concentration of a given fission product in sweep gas $\frac{(\text{moles})}{(\text{volume})}$
C_o	fission-product concentration in gas volume surrounding fuel specimen $\frac{(\text{moles})}{(\text{volume})}$
D	Fick's law diffusion coefficient for a given fission product in fuel $\frac{(\text{length})^2}{(\text{time})}$

Upper Case (continued)

D_A diffusion coefficient of parent in a parent-daughter pair $\frac{(\text{length})^2}{(\text{time})}$

D_B diffusion coefficient of daughter in a parent-daughter pair $\frac{(\text{length})^2}{(\text{time})}$

D_G diffusion coefficient for fission product in sweep gas $\frac{(\text{length})^2}{(\text{time})}$

D_j diffusion coefficient during time interval $(t_{j-1} < t < t_j)$, $j = 1, 2, \ldots N$ $\frac{(\text{length})^2}{(\text{time})}$

D' diffusional release parameter, D/a^2, $(\text{time})^{-1}$

K permeability of particle coating $\frac{(\text{length})^2}{(\text{time})}$

K_E permeability of fuel element matrix $\frac{(\text{length})^2}{(\text{time})}$

K_L permeability of shell surrounding fuel element $\frac{(\text{length})^2}{(\text{time})}$

L length of sweep line from fuel specimen to sample point (length)

M_F atomic weight of fissionable material $\frac{(\text{mass})}{(\text{mass-atom})}$

N number of times annealing temperature is changed during activation experiment

N_f number of particles with failed coatings

$\dot{N}_f$ rate of coating failure $\frac{(\text{particles})}{(\text{time})}$

P pressure in void space between fuel particle and coating $\frac{(\text{force})}{(\text{area})}$

P_E probability that a fission fragment will escape by recoil

P_o pressure outside fuel particle coating $\frac{(\text{force})}{(\text{area})}$

Q volumetric flow rate of sweep gas $\frac{(\text{volume})}{(\text{time})}$

R recoil range of fission product (length)

R_a release rate of a given fission product from fuel $\frac{(\text{moles})}{(\text{time})}$

R_{a_1} release rate from fuel for $t < t_1$ $\frac{(\text{moles})}{(\text{time})}$

R_{a_2} release rate from fuel for $t > t_1$ $\frac{(\text{moles})}{(\text{time})}$

Upper Case (continued)

R_b release rate of a given fission product from particle coating $\frac{(\text{moles})}{(\text{time})}$

R_D release rate of a given fission product from fuel by diffusion $\frac{(\text{moles})}{(\text{time})}$

R_F release rate of a given fission product from fuel $\frac{(\text{moles})}{(\text{time})}$

R_o release rate of a given fission product per unit volume of fuel $\frac{(\text{moles})}{(\text{volume})(\text{time})}$

R_R release rate of a given fission product by recoil $\frac{(\text{moles})}{(\text{time})}$

R_T release rate of a given fission product from test specimen $\frac{(\text{moles})}{(\text{time})}$

R^* universal gas constant $\frac{(\text{pressure})(\text{volume})}{(\text{mole})(\text{degree absolute})}$

T absolute temperature (degrees)

V_C volume of gas surrounding specimen in sweep capsule (volume)

V_F volume of fuel (volume)

V_f free volume between fuel particle and coating (volume)

V_L volume of sweep line between specimen and sample point (volume)

Y yield stress of particle coating $\frac{(\text{force})}{(\text{area})}$

Z gas compressibility factor $\frac{PV}{n_T R^* T}$

Lower Case

a radius of spherical fuel particle or of "equivalent sphere" with same surface-to-volume ratio as fuel particle (length)

b outer radius of particle coating (length)

c concentration of a given fission product $\frac{(\text{moles})}{(\text{volume})}$

c_A concentration of parent in a parent-daughter pair $\frac{(\text{moles})}{(\text{volume})}$

c_a concentration of fission product in free volume between fuel particle and coating $\frac{(\text{moles})}{(\text{volume})}$

Lower Case (continued)

c_B	concentration of daughter in a parent-daughter pair $\frac{(\text{moles})}{(\text{volume})}$
c_o	concentration of fission product in fuel at start of experiment $\frac{(\text{moles})}{(\text{volume})}$
c^*	concentration function, $ce^{\lambda t}$, $\frac{(\text{moles})}{(\text{volume})}$
e	base of natural logarithms, 2.718
f_C	fraction of a fission product released from fuel that escapes from coating
f_D	fraction of a fission produced that escapes from fuel by diffusion
f_{DA}	fraction of a parent fission product produced that escapes from fuel by diffusion <u>as parent</u>
f_{DB}	fraction of parent fission product produced that escapes from fuel by diffusion <u>as daughter</u>
f_E	fraction of a fission product released from coated particles that escapes from fuel element
f_F	fraction of <u>all</u> gaseous fission products produced that is released from fuel particles
f_G	fraction of a fission product released during anneal portion of neutron-activation test
f_H	fraction of a fission product released as "burst" in neutron-activation test
f_I	fraction of a fission product released during low-temperature irradiation
f_P	fraction of a fission product produced that escapes from fuel particles by all mechanisms
f_R	fraction of a fission product produced that escapes from fuel particles by recoil
f_S	fraction of a fission product released during slow rate portion of neutron-activation test
f_T	fraction of a fission product produced that escapes from test specimen (fuel element, coated, or uncoated particle)
h	geometrical distance, Fig. 5, (length)
j	summation index
k	summation index
n	moles of a fission product released during anneal portion of neutron-activation test and not decayed at time, t, (moles)

Lower Case (continued)

n' total moles of fission products produced per percent burnup of fuel (moles)

n_E moles of a fission product external to fuel at start of anneal period (moles)

n_o moles of a given fission product present in fuel specimen at start of anneal period (moles)

n_T total moles of fission gas in free volume between fuel particle and coating

r radial distance from center of fuel particle or sweep line (length)

r_o inside wall radius of sweep line (length)

t time, measured from start of anneal portion of neutron-activation test (time)

$\bar{t}$ dummy time variable of integration (time)

t' variable defined in Eq. (77) $(\text{length})^2$

t_C time between end of irradiation and start of anneal portion of neutron-activation test, "cooling time" (time)

t_j time at which specimen temperature is changed in neutron-activation test ($j = 1, 2, \ldots N$) (time)

u average velocity of sweep gas $\frac{(\text{length})}{(\text{time})}$

x distance from surface of fuel in a direction normal to surface (length)

x_E mass fraction of fissionable isotope in fuel atoms, "enrichment", for example $\frac{(\text{mass of } U^{235})}{(\text{mass of total } U)}$

x_u mass fraction of fuel chemical species in fuel material, for example $\frac{(\text{mass of } U)}{(\text{mass of } UC_2)}$

y reduced tube radius, r/r_o

z distance along sweep line, measured from fuel specimen (length)

Upper Case Greek

Φ decay-diffusion parameter for fuel element, $\sqrt{\frac{\lambda \epsilon_E A^2}{K_E}}$

Ψ decay-diffusion parameter for fuel element, $\sqrt{\frac{\lambda \epsilon_L (B-A)^2}{K_L}}$

Ω dimensionless distance along sweep line, $\frac{2\, D_G\, z}{r_o^2\, u}$

Lower Case Greek

α decay-diffusion parameter for sweep line, $\frac{\lambda r_o^{\,2}}{4\, D_G}$

γ yield of a given fission product, $\frac{\text{(atoms produced)}}{\text{(fission)}}$

γ_T total yield of gaseous fission products $\frac{\text{(atoms produced)}}{\text{(fission)}}$

δ thickness of high-porosity shell between fuel particle and coating (length)

ϵ open porosity of particle coating $\frac{\text{(open pore volume)}}{\text{(total volume)}}$

ϵ_E open porosity of fuel element matrix $\frac{\text{(open pore volume)}}{\text{(total volume)}}$

ϵ_L open porosity of low-permeability layer surrounding fuel element $\frac{\text{(open pore volume)}}{\text{(total volume)}}$

ϵ_s open porosity of high-porosity shell between fuel particle and coating $\frac{\text{(open pore volume)}}{\text{(total volume)}}$

ζ geometrical distance, Fig. 5 (length)

η parent-daughter release parameter, $\sqrt{\frac{D_B \lambda_A}{D_A \lambda_B}}$

λ decay constant $(\text{time})^{-1}$

λ_A decay constant of parent in parent-daughter pair $(\text{time})^{-1}$

λ_B decay constant of daughter in parent-daughter pair $(\text{time})^{-1}$

Lower Case Greek (continued)

μ geometrical distance, Fig. 5 (length)

ξ geometrical distance, Fig. 5 (length)

ρ_F fuel density $\frac{(\text{mass})}{(\text{volume})}$

σ_a neutron-absorption cross section (length^2)

σ_f neutron-fission cross section (length^2)

τ half life, $\frac{0.693}{\lambda}$, (time)

ϕ decay-diffusion parameter for single particle, $\sqrt{\frac{\lambda a^2}{D}}$

ϕ_A decay-diffusion parameter for parent in parent-daughter pair, $\sqrt{\frac{\lambda_A a^2}{D_A}}$

ϕ_B decay-diffusion parameter for daughter in parent-daughter pair, $\sqrt{\frac{\lambda_B a^2}{D_B}}$

ϕ' neutron flux $\frac{(\text{neutrons})}{(\text{area})(\text{time})}$

ψ decay-diffusion parameter for particle coating, $\sqrt{\frac{\lambda\epsilon(b-a)^2}{K}}$

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