

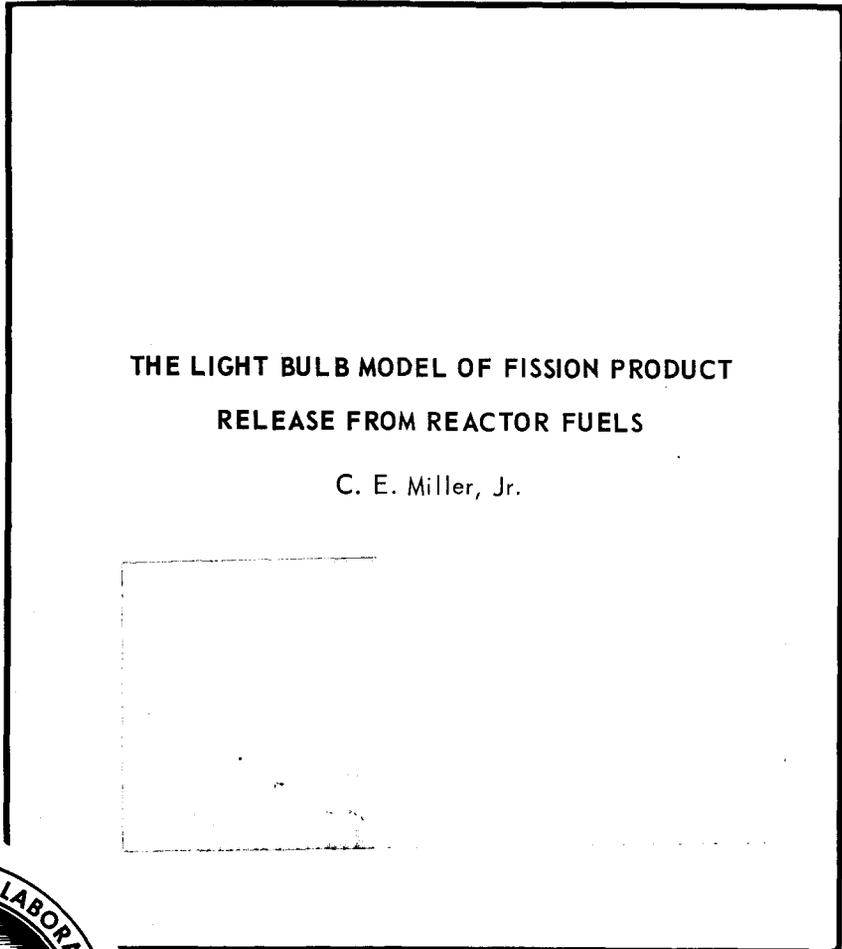


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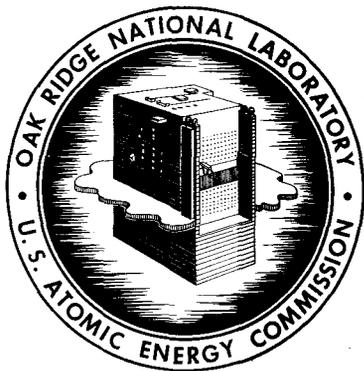
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ORNL-4060
UC-80 - Reactor Technology



THE LIGHT BULB MODEL OF FISSION PRODUCT
RELEASE FROM REACTOR FUELS

C. E. Miller, Jr.



OAK RIDGE NATIONAL LABORATORY

operated by

UNION CARBIDE CORPORATION

for the

U.S. ATOMIC ENERGY COMMISSION

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REACTOR CHEMISTRY DIVISION

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C. E. Miller, Jr.

APRIL 1967

OAK RIDGE NATIONAL LABORATORY
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THE LIGHT BULB MODEL OF FISSION PRODUCT RELEASE FROM REACTOR FUELS

C. E. Miller, Jr.

ABSTRACT

Studies of fission product behavior and characteristics are directed toward the development of mathematical models with which the extent of fission product release can be predicted for a specific set of conditions. One such model has been developed which predicts the release of some fission products from molten reactor fuels.

The model is based on the work of Fonda,¹ who, while working on the development of the gas-filled tungsten filament lamp, observed that the rate of loss in weight of the filament as a function of temperature was lower in the presence of a nonreacting gas than in a vacuum. He explained this by relating to the Langmuir² theory of heat loss from incandescent wires in gases, in which Langmuir conceived that the filament is surrounded by a stationary film of gas through which the heat is carried purely by conduction. Fonda then proposed that evaporation from a filament in the presence of a nonreactive gas is controlled by diffusion through the stationary gas layer on the filament surface. The theories of Langmuir and Fonda can be applied to the release of fission products from reactor fuel if one assumes that in the presence of a cover gas a boundary layer around the fuel does exist and that diffusion through the boundary layer is the rate-controlling step in the release of fission products.

The model relates several variables to the amount of fission product released. These are the composition and pressure of the cover gas, the temperature, surface area, and amount of the molten fuel, the time molten, and the chemical form of the fission product. The model has been tested with data from several sources and satisfactorily explains the observed behavior of fission products and fuel.

INTRODUCTION

A most important area of research in the USAEC Nuclear Safety Program is the study of the maximum credible accident. The consequences of this accident, although the accident itself is highly improbable, are the controlling factors in decisions regarding the siting of large nuclear power reactors in or near populated areas. In water-cooled reactors, the type which includes most U.S.A. power reactors, the loss-of-coolant accident is considered to be the most likely maximum credible accident. Loss of coolant to a reactor core leads eventually to fission product release from the reactor fuel. Many experiments have been performed to measure fission product release both in-pile and out-of-pile. These experiments are intended to provide both empirical and analytical information which can be used to predict the consequence of fission product release for conditions other than those tested, so that the consequence of a maximum credible accident can be realistically evaluated in relation to the siting of reactors near populated areas.

A wealth of data on fission product behavior has been accumulated in previous in-pile and out-of-pile experiments under conditions which simulate reactor accidents. The interpretations of these data have been empirical. The intent of the experimenter has been to recognize the effect of important variables and ultimately to derive mathematical expressions to describe fission product behavior. In an attempt to partially accomplish this intent, the light bulb model of fission product release has been derived.

DEVELOPMENT OF THE MODEL

Fonda,¹ working on the development of the gas-filled tungsten filament lamp, observed that the rate of loss in weight of the filament as a function of temperature was lower in the presence of a nonreacting gas than in a vacuum. He explained this by relating to the Langmuir² theory of heat loss from incandescent wires in gases, in which Langmuir conceived that the filament is surrounded by a stationary film of gas through which the heat is carried purely by conduction. Fonda then proposed that evaporation from a filament in the presence of a non-reactive gas is controlled by diffusion through the stationary gas layer surrounding the filament. The theories of Langmuir and Fonda can be applied to the release of fission products from reactor fuels if one assumes that in the presence of a cover gas a boundary layer around the fuel does exist and that diffusion through the boundary layer is the rate-controlling step in the release of fission products.

The model was derived from the following expression, in which the rate of evaporation of species *A* is controlled by its diffusion through a boundary layer of species *B* (Fick's law of diffusion):

$$J_A = -D_{AB} \frac{dc_A}{dz}, \quad (1)$$

where

- J_A = molar diffusion flux (moles $\text{cm}^{-2} \text{sec}^{-1}$),
- D_{AB} = binary diffusion coefficient in which subscripts *A* and *B* denote the two diffusing species (cm^2/sec),
- c = concentration (moles/ cm^3),
- z = distance (cm).

The assumption of a linear concentration gradient leads to

$$J_A = -D_{AB} \frac{(c_A)_\delta - (c_A)_0}{\delta}, \quad (2)$$

where

- $(c_A)_\delta$ = concentration of species *A* at distance δ from the surface of the melt (moles/ cm^3),
- $(c_A)_0$ = concentration of species *A* in the gas phase in equilibrium with the surface of the melt (moles/ cm^3),
- δ = thickness of film of stagnant gas (cm).

Since a sweep gas is carrying away the evaporating species, $(c_A)_\delta = 0$ and

$$J_A = D_{AB} \frac{(c_A)_0}{\delta}. \quad (3)$$

A fission product species in molten fuel is a dilute solute in a solvent and its concentration $(c_A)_0$ can be obtained from Henry's law as follows:

$$p_A = k_A x_A, \quad (4)$$

where

- p_A = partial pressure of solute (atm),
- k_A = Henry's law constant (atm),
- x_A = mole fraction of solute in solvent.

Henry's law constant k may be expressed as a function of the vapor pressure of the pure component such that

$$p_A = k'_A p_A^0 x_A, \quad (5)$$

where

- k'_A = temperature-independent component of Henry's law constant,
- p_A^0 = vapor pressure of pure solute – temperature-dependent component of Henry's law constant (atm).

The concentration of solute in the gas above the melt may be obtained from the partial pressure assuming the ideal gas law:

$$(c_A)_0 = \frac{k'_A p_A^0 x_A}{RT}, \quad (6)$$

where

- R = gas constant ($\text{cm}^3 \text{ atm mole}^{-1} \text{ deg}^{-1}$),
- T = absolute temperature (deg).

When Eq. (6) is substituted into Eq. (3), one obtains

$$J_A = \frac{D_{AB} k'_A p_A^0 x_A}{\delta RT}. \quad (7)$$

The binary diffusion coefficient is a function of temperature, pressure, and composition. The function for molecules assumed to be rigid spheres is given by classical kinetic theory³ as

$$D_{AB} = 1.858 \times 10^{-3} \frac{[(1/M_A) + (1/M_B)]^{1/2} T^{3/2}}{p[(\sigma_A + \sigma_B)/2]^2}, \quad (8)$$

where

M = molecular weight (g/mole),

p = total pressure (atm),

σ = collision diameter (A).

Substitution of Eq. (8) for the binary diffusion coefficient into Eq. (7) gives the temperature, pressure, and composition dependence of the molar flux:

$$J_A = \frac{2.264 \times 10^{-5} [(1/M_A) + (1/M_B)]^{1/2} T^{1/2} k'_A p_A^0 x_A}{p[(\sigma_A + \sigma_B)/2]^2 \delta} \quad (9)$$

The rate of evaporation must equal the rate of loss from the liquid. Therefore,

$$-u \frac{dx_A}{dt} = AJ, \quad (10)$$

where

u = moles of solution,

t = time (sec),

A = surface area (cm²).

Substitution of Eq. (9) into Eq. (10) with some rearrangement gives:

$$\int_{(x_A)_0}^{x_A} \frac{dx_A}{x_A} = - \int_0^t \frac{2.264 \times 10^{-5} [(1/M_A) + (1/M_B)]^{1/2} A T^{1/2} k'_A p_A^0 dt}{p[(\sigma_A + \sigma_B)/2]^2 \delta u} \quad (11)$$

After integrating, one obtains an expression for the fraction of species A remaining in the melt:

$$\frac{x_A}{(x_A)_0} = \exp \left\{ -2.264 \times 10^{-5} \frac{[(1/M_A) + (1/M_B)]^{1/2} A T^{1/2} k'_A p_A^0 t}{p[(\sigma_A + \sigma_B)/2]^2 \delta u} \right\}, \quad (12)$$

and the fraction of fission products released (fr) from the molten melt is given by

$$\text{fr} = 1 - \exp \left\{ -2.264 \times 10^{-5} \frac{[(1/M_A) + (1/M_B)]^{1/2} A T^{1/2} k'_A p_A^0 t}{p[(\sigma_A + \sigma_B)/2]^2 \delta u} \right\}. \quad (13)$$

The equation relates several variables to the amount of fission product released. These variables are the composition and pressure of the cover gas, the temperature, surface area, and amount of the molten fuel, the time molten, and the chemical form of the fission product.

Equation (13) has been tested with data on fission product release obtained in controlled laboratory experiments.

APPLICATION OF THE MODEL TO FISSION PRODUCT RELEASE

Effects of Temperature of the Molten Fuel

The temperature dependence of the model has been tested using data of Parker on the release of cesium from uranium-aluminum alloy at several different temperatures.⁴ All values needed to solve Eq. (13) can be found except Henry's law coefficient k' and the film thickness δ . However, if an experimental measurement at one temperature is used to determine the ratio of k'/δ , the fraction released at other temperatures can be predicted. A comparison between calculated values of release using Eq. (13) and the experimental values measured by Parker is given in Table 1. A single value of k'/δ was obtained using the 13% release value for cesium in helium at 800°C.

The values used in the calculation are as follows:

$$f_r = 0.13,$$

$$M_A - (\text{neglect } 1/M_A),$$

$$M_B = 4,$$

$$p^0 = 3.12 \text{ atm at } 800^\circ\text{C for elemental cesium,}^5$$

$$T = 1073^\circ\text{K},$$

$$t = 120 \text{ sec},$$

$$A = 0.495 \text{ cm}^2,$$

$$\sigma_A = 4.7 \text{ A,}^6$$

$$\sigma_B = 2.6 \text{ A,}^6$$

$$p = 1 \text{ atm},$$

$$u = 0.00737 \text{ mole.}$$

The value of k'/δ is then calculated to be 0.201 cm^{-1} .

The agreement between calculated and experimental results indicates that the temperature dependence is approximately correct and also that the chemical form of the evaporating species probably is elemental cesium.

Table 1. Calculated vs Measured Release of Cesium from Uranium-Aluminum Alloy in Helium:^a Effects of Temperature

Temperature (°C)	Cesium Release (%)	
	Calculated	Measured
800	13	13
900	25	21
1000	42	48
1105	61	69

^aExperimental data taken from ref. 4.

Effects of Composition of the Cover Gas

Parker⁴ has reported data on the release of cesium from uranium-aluminum alloy in steam-air mixtures and in air as well as in helium. If it is assumed that the apparatus was essentially the same and that the value of k'/δ does not vary significantly with composition of the inert gas, then Eq. (13) should also predict the effects of changing the composition of the cover gas. Table 2 shows the comparison of calculated and experimental values for these different cover gases including the helium data previously shown in Table 1. The same k'/δ value of 0.201 cm^{-1} was used.

Table 2. Calculated vs Measured Release of Cesium from Uranium-Aluminum Alloy:^a Effect of Composition of the Cover Gas

Temperature (°C)	Cesium Release (%)					
	Helium		Steam-Air		Air	
	Calculated	Experimental	Calculated	Experimental	Calculated	Experimental
700			1.4	0.62	1.4	3.1
800	13	13	3.2	1.1	3.3	3.8
900	26	21	6.5	6.5	6.6	6.2
1000	42	48	11.8	11.0	12.0	8.8
1085			17.9	30.5		
1090					18.7	12.4
1105	61	69				
1145					23.6	18.6

^aExperimental data taken from ref. 4.

The conclusion which may be reached from the comparison in Table 2 concerning the equation is that it adequately describes the release of cesium from molten uranium-aluminum alloy in the presence of helium, steam-air mixtures, and air. Conclusions which may be reached concerning the experimental data are: (1) the variations in the release of cesium in helium, steam-air mixtures, and air, such as 69% release at 1105°C in helium vs 19% release at 1145°C in air, are primarily due to the composition of the cover gas; and (2) the chemical form of cesium as it is released from the fuel is the same in all three atmospheres, elemental cesium.

Effect of Heating Time

The time dependence of the model has been tested using data of Creek⁷ on the release of cesium from disks of APPR-type fuel (a UO_2 dispersion in stainless steel). Again the first point was used to calculate the ratio k'/δ of Henry's law coefficient and the film thickness.

The values used in the calculation are as follows:

$$f_r = 0.157,$$

$$M_A - \text{neglect } (1/M_A),$$

$$M_B = 4,$$

$$p^0 = 109.6 \text{ atm at } 1650^\circ\text{C for elemental cesium,}^5$$

$$T = 1923^\circ\text{K},$$

$$A = 0.495 \text{ cm}^2,$$

$$\sigma_A = 4.7 \text{ A,}^6$$

$$\sigma_B = 2.6 \text{ A,}^6$$

$$p = 1 \text{ atm},$$

$$u = 0.005515 \text{ mole},$$

$$t = 6 \text{ sec.}$$

The value of k'/δ as a result of the calculation is 0.0776 cm^{-1} . This value was then used to calculate the release of cesium at other time values. The comparison between the calculated values of release using Eq. (13) and the experimental values given by Creek is shown in Table 3 and plotted in Fig. 1.

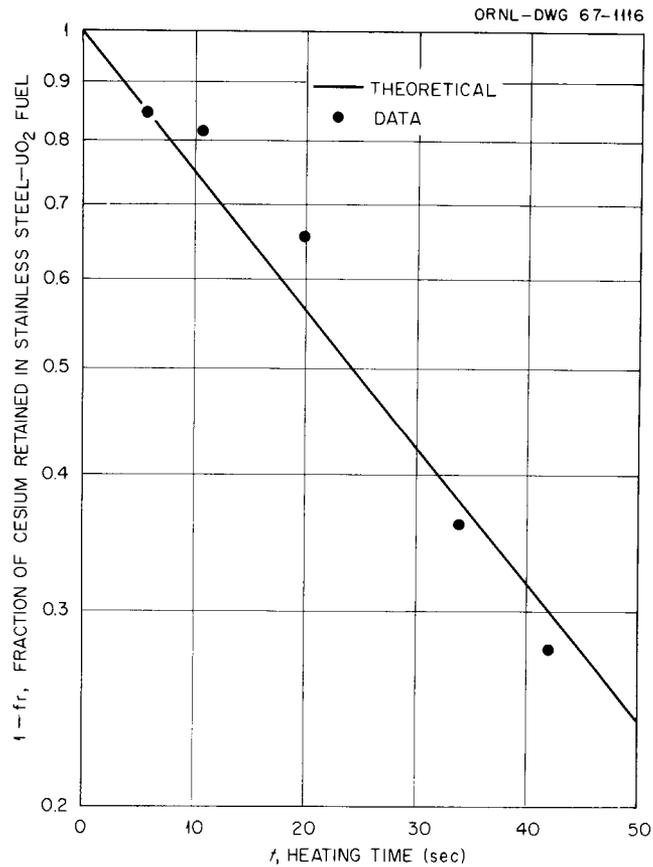


Fig. 1. Fraction of Fission Product Retained in Fuel as a Function of Heating Time. Data taken from ref. 7.

Table 3. Calculated vs Measured Release of Cesium
from APPR Fuel Disks in Helium:^a Effect of Heating Time

Sample	Time (sec)	Cesium Release (%)	
		Calculated	Measured
1	6	15.7	15.7
2	11	27.0	18.7
3	20	43.4	34.5
4	34	62.0	64.0
5	42	69.8	72.2

^aExperimental data taken from ref. 7.

Effects of Surface Area to Volume Ratio

Castleman has performed experiments on the release of iodine from molten uranium at various liquid depths and has shown that the fraction of release is dependent on the surface area to volume ratio.⁸ This dependence can be explained by the light bulb model.

Equation (13) can be written as

$$fr = 1 - \exp\left(-k''\frac{At}{u}\right), \quad (14)$$

where

$$k'' = \frac{(2.264 \times 10^{-5}) [(1/M_A) + (1/M_B)]^{1/2} T^{1/2} k' p^0}{p[(\sigma_A + \sigma_B)/2]^2 \delta}. \quad (15)$$

The ratio A/u is the ratio of the surface area to the amount of fuel. The amount of the fuel can be expressed as the volume of fuel by

$$u = \frac{\rho V}{M}, \quad (16)$$

where

- ρ = density of fuel (g/cm³),
- M = molecular weight of fuel (g/mole),
- V = volume of fuel (cm³).

The ratio A/u then becomes

$$\frac{A}{u} = \frac{MA}{\rho V} = \frac{M}{\rho h}, \quad (17)$$

where

h = liquid depth (cm).

Equation (14), expressed as a function of time and liquid depth, becomes

$$fr = 1 - \exp\left(-k'' \frac{M t}{\rho h}\right). \quad (18)$$

Castleman's data, obtained by reading the values from the plot shown in Fig. 2, are plotted in Fig. 3 as

$$\log Y = -k'' \frac{M t}{\rho h}, \quad (19)$$

where

Y = the fraction of fission product retained in the fuel.

The plot should show a straight line with slope of $(-k''M/\rho)$. There is a slight curvature in the line indicating that some parameter, perhaps the film thickness δ , is changing slightly during the course of the experiment. There is not sufficient information to evaluate k'' . However, the assembly of all points into a common line in Fig. 3 indicates that the fraction released does depend upon the liquid depth, as Castleman has said, and that this dependency can be explained by the light bulb model.

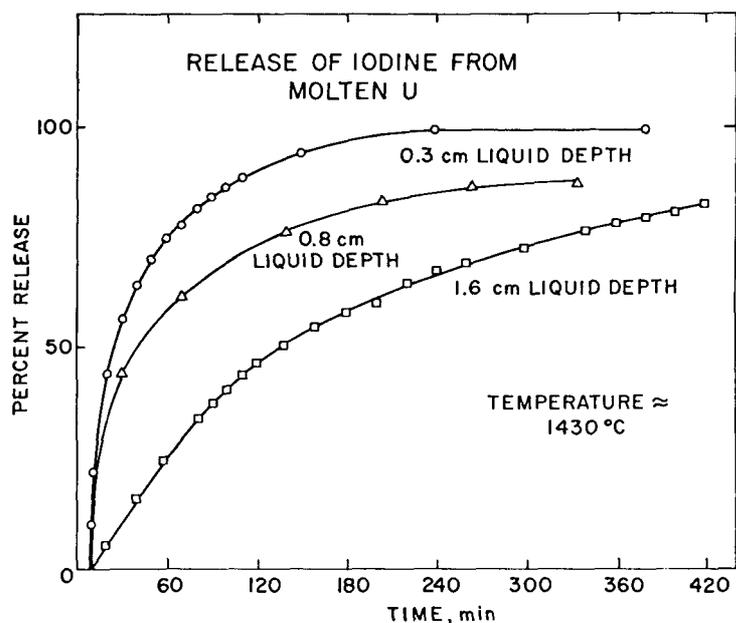


Fig. 2. Release of Iodine from Molten Uranium as a Function of Time and Liquid Depth. (Figure courtesy of A. W. Castleman, Jr., Brookhaven National Laboratory.)

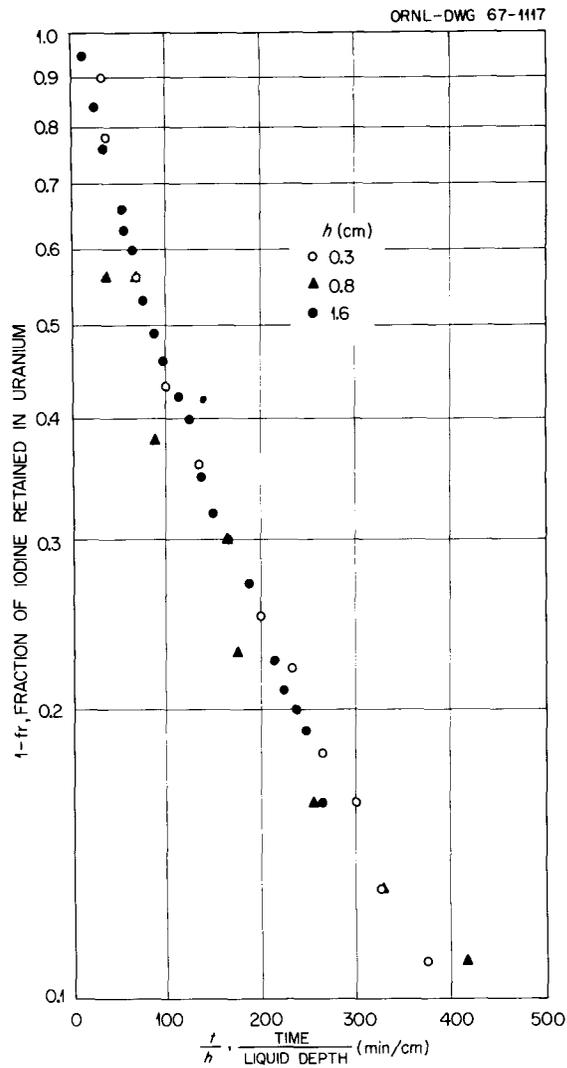


Fig. 3. Fraction of Iodine Retained in Uranium as a Function of Time and Liquid Depth (Light Bulb Model). Data taken from Fig. 2.

APPLICATION OF THE MODEL TO FUEL VAPORIZATION

The fuel (solvent) may also vaporize under the particular conditions of time and temperature for which fission product release is being studied. Therefore, it may be necessary to correct the u term in Eq. (13) for the number of moles of solvent that have vaporized so that it becomes a function of time and temperature. The need for this correction leads to the derivation of the expression describing fuel vaporization.

Equations (1-3) describing the boundary layer diffusion apply to the solvent as well as the solute.

Equation (3) for the solvent is given as

$$J_s = D_{SB} \frac{(c_s)_0}{\delta}, \quad (20)$$

where S denotes the solvent and $(c_s)_0$ denotes the concentration of solvent in the gas phase. The value $(c_s)_0$ is obtained from Raoult's law and the ideal gas law:

$$(c_s)_0 = \frac{p_s}{RT} = \frac{p_s^0 x_s}{RT}. \quad (21)$$

From Eqs. (21) and (20), assuming the mole fraction to be unity, one obtains

$$J_s = D_{sB} \frac{p^0}{\delta RT}. \quad (22)$$

Substitution of Eq. (8) into Eq. (22) gives the flux of solvent molecules as:

$$J_s = \frac{2.264 \times 10^{-5} [(1/M_s) + (1/M_B)]^{1/2} T^{1/2} p_s^0}{p[(\sigma_s + \sigma_B)/2]^2 \delta}. \quad (23)$$

Again as in Eq. (10) a material balance shows that

$$-(du/dt) = AJ_s. \quad (24)$$

The value J_s in Eq. (23) is substituted into Eq. (24), and terms are rearranged to obtain

$$\int_{u_0}^u du = - \int_0^t 2.264 \times 10^{-5} \left(\frac{1}{M_s} + \frac{1}{M_B} \right)^{1/2} \frac{AT^{1/2} p_s^0 dt}{p[(\sigma_s + \sigma_B)/2]^2 \delta}. \quad (25)$$

After integrating Eq. (25), an expression is obtained for the amount of fuel vaporizing rather than the fraction. The fraction is obtained by dividing by the total amount of fuel originally present.

$$(fr)_s = \frac{u_0 - u}{u_0} = 2.264 \times 10^{-5} \left(\frac{1}{M_s} + \frac{1}{M_B} \right)^{1/2} \frac{AT^{1/2} p_s^0 t}{p[(\sigma_s + \sigma_B)/2]^2 \delta u_0}. \quad (26)$$

Note that the fraction of solvent released is a linear function, while the fraction of the fission product released [Eq. (13)] is an exponential.

Equation (26) has also been tested with data from the literature. One such set of data was taken from Parker,⁹ in which the release of fuel was given as a variation of time at the melting temperature of the fuel. The only quantity not experimentally available in the case of fuel vaporization is the film thickness δ , since no Henry's law coefficient is involved. So again, one experimental value of $(fr)_s$ is used to calculate the film thickness; then that thickness is used in the remainder of the calculations for other time periods. The comparison between calculated and measured values is shown in Table 4 and in Fig. 4.

In cases where both solvent and solute release have been measured in the same experiment, the film thickness δ can be found from the solvent release and then substituted into the k'/δ ratio for each solute fission product. A determination of the k' values for important fission products in reactor fuel should be made in order to predict the consequences of a loss-of-coolant accident for conditions which have not been previously studied.

Table 4. Comparison of Calculated vs Measured Vaporization of UO_2

Time (sec)	Percent Released	
	Calculated	Experimental ^a
60	0.098	0.097
90	0.148	0.157
120	0.196	0.156
150	0.246	0.246 ^b

^aExperimental data taken from ref. 9.

^bValues of δ calculated from this point, $\delta = 0.094$ cm.

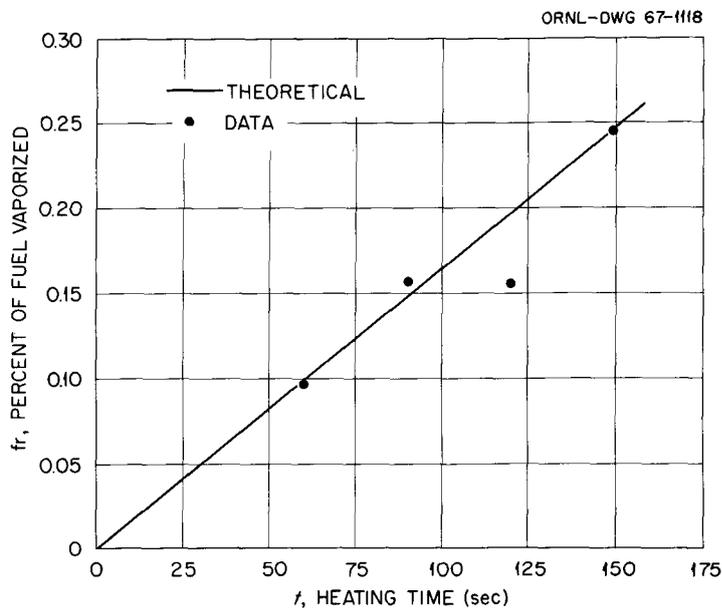


Fig. 4. Percent of Fuel Vaporized as a Function of Heating Time. Data taken from ref. 9.

APPLICATION OF THE MODEL TO RELEASE BELOW THE MELTING POINT OF UO_2

Davies, Long, and Stanaway¹⁰ have presented data on the release of volatile fission products from uranium dioxide. Their work included several experiments to study the emission of fission products on postirradiation heating of UO_2 in the range of maximum temperature from 2000 to 2200°C. The data are given in Table 5. Table 6 gives additional data concerning the conditions of time and temperature with which the data in Table 5 were acquired.

In testing the applicability of the light bulb model to these data, the release of UO_2 was first calculated as a function of time and temperature for the several experiments. Equation (26) was

used with the following values for run D/66 to calculate the film thickness δ :

$$\begin{aligned} fr &= 0.45, \\ M_S &= (\text{neglect } 1/M_S), \\ M_B &= 2 \text{ (hydrogen)}, \\ A &= 0.35 \text{ cm}^2, \\ p &= 1 \text{ atm}, \\ \sigma_B &= 2.9 \text{ A},^6 \\ \sigma_S &= 5 \text{ A},^6 \\ u_0 &= 0.05/270 = 1.85 \times 10^{-4} \text{ mole}, \\ p^0 &= 7.55 \times 10^{-5} \text{ atm},^{11} \\ t &= 300 \text{ sec}, \\ T &= 2428^\circ\text{K (average of 2100 and 2210}^\circ\text{C)}. \end{aligned}$$

The film thickness is then calculated to be 0.29 cm. The calculated value of δ (0.29 cm) was then used to calculate the fraction of UO_2 released at the other times and temperatures. A step function was used for each run, in which the fraction remaining $(1 - fr)$ was calculated for each step and used as the original amount of UO_2 present for the next step. A typical time-temperature profile is shown in Fig. 5. The fraction of UO_2 released in the final heating step is

$$(fr)_S = 1 - (1 - fr_1)(1 - fr_2)(1 - fr_3), \quad (27)$$

where the numerical subscripts refer to the heating steps.

The releases of the fission products cerium, ruthenium, barium, strontium, cesium, and tellurium were calculated in the same manner except, of course, that Eq. (13) was used rather than Eq. (26) to calculate the fr values. Equation (27) was used in the same manner.

Table 5. Fission Product and UO_2 Emission from UO_2 During Grain Growth^a

Sample No. S/13, Surface Area $7 \text{ cm}^2/\text{g}$, Density 10.7 g/cm^3

Run No.	Temperature ($^\circ\text{C}$) ($\pm 50^\circ\text{C}$)	Time (hr)	Fraction Released of -								
			^{133}Xe	^{131}I	^{132}Te	^{137}Cs	^{89}Sr	^{140}Ba	^{106}Ru	^{144}Ce	U
D/94	2000	2.1	0.05	0.14	0.18	0.11	0.09	0.05	0.01	0.02	
D/64	2000	4.5	0.34		0.59	0.12	0.14	0.17	0.12	0.05	0.04
D/88	2050	1.5	0.23		0.66	0.21	0.19	0.20	0.22	0.08	0.10
D/95	2150	1.5	0.16	0.19	0.39	0.06	0.15	0.15	0.15	0.06	
D/65	2200	1.5 ^b	0.72		0.68	0.11	0.52	0.54	0.63	0.25	0.26
D/66	2200	5.0	0.99		0.94	0.33	0.83	0.74	0.78	0.47	0.45

^aThis table is taken from ref. 10.

^bThis number should be 2.0 (see Table 6, Run D/65).

Table 6. Time and Temperature Conditions for Fission Product Release Data of Table 5^a

Nominal Temp.	2000°C		2000°C		2050°C		2150°C		2200°C		2200°C	
Nominal Time	2.1 hr		5.6 hr		1.5 hr		1.5 hr		1.5 hr		5.0 hr	
Run No.	D/95		D/64		D/88		D/95		D/65		D/66	
Experimental Sequence	Temp. (°C)	Time (min)	Temp. (°C)	Time (min)	Temp. (°C)	Time (min)						
	1600	30	1600	90	1600	90	1600	90	1600	90	2100	300
	1800	90	1800	90	1800	90	1800	90	2100	118	2210 at hottest point	
	2000	135	2000	270	2050	90	2110	90	2250 at hottest point			
	1900	45			2000	40	2000	30	Filament burnt out			
	1800	45			1900	40	1900	30				
	1700	25			1800	30	1800	30				
					1700	40	1700	60				
					1600	30						

^aThis table was taken from ref. 12.

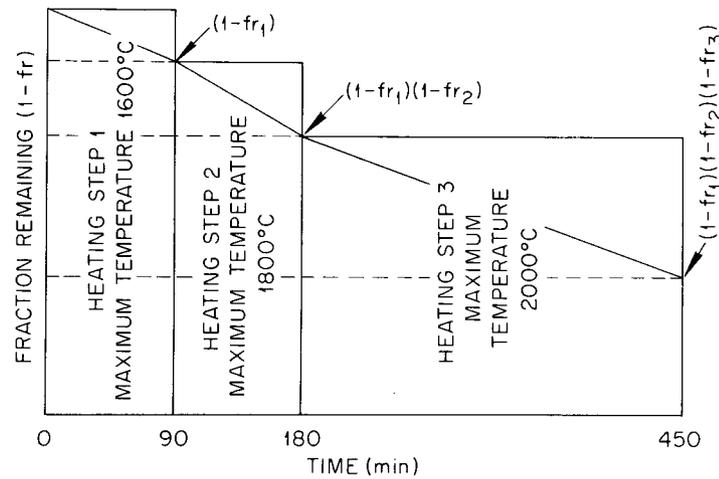


Fig. 5. Typical Time-Temperature Profile for Davies, Long, and Stanaway Experiments Showing Mathematical Relationship for the Amount of Fuel Remaining at the Beginning of Each Heating Step. Data taken from ref. 12.

Table 7 shows the calculated values and the values measured by Davies, Long, and Stanaway, also shown in Table 5. Notice that the fission product headings for the calculated values in Table 7 are the chemical forms of the fission product which give the best fit to the data. The chemical form is important in the choice of the expression for the vapor pressure, p^0 . No calculations were made for iodine because of a lack of experimental data. No fit was found for xenon, probably because the vapor pressure expression was not suitable.

The light bulb model appears to explain the data of Davies, Long, and Stanaway. Therefore, one can conclude that boundary layer diffusion is the rate-limiting step in the emission of fission products in the temperature range 2000 to 2200°C for this type of postirradiation annealing experiment. Uranium dioxide is solid in that temperature range. It is not surprising that the vaporization of UO_2 can be explained by boundary layer diffusion. The filament in Fonda's light bulb was solid in the temperature range in which he found boundary layer diffusion applicable. The fact that the fission product vaporization can also be explained by this mechanism, however, is surprising. Apparently in the region of grain growth, the solid-state diffusion of fission products in the UO_2 is not important. They are essentially free to be released.

Other investigators have found that some mechanism other than solid-state diffusion is important in the grain-growth region. Toner and Scott¹³ reported that above 1600°C the rate of release of fission gases is higher than one would predict on the basis of the equivalent sphere diffusion model alone. They say that for design purposes it is best to assume that all of the fission gas will be released from those portions of the UO_2 that are above 1600°C. Table 6 shows that this is the temperature range in which Davies, Long, and Stanaway worked, and so one would conclude that the release of fission products and the vaporization of fuel can be explained and predicted not only for molten fuels but also in the case of UO_2 for solid fuel above 1600°C.

Table 7. Comparison of Calculated and Measured Release of Fission Products from UO₂ During Grain Growth^a

Run No.	Temperature (°C) (±50°C)	Time (hr)	Fraction Released													
			Calc. TeO ₂	Meas. ¹³² Te	Calc. Cs	Meas. ¹³⁷ Cs	Calc. SrO	Meas. ⁸⁹ Sr	Calc. BaO	Meas. ¹⁴⁰ Ba	Calc. Ru	Meas. ¹⁰⁶ Ru	Calc. CeO	Meas. ¹⁴⁴ Ce	Calc. UO ₂	Meas. U
D/94	2000	2.1	0.37	0.18	0.11 ^b	0.11	0.09 ^b	0.09	0.09	0.05	0.04	0.01	0.02	0.02	0.03	
D/64	2000	4.5	0.50	0.59	0.14	0.12	0.16	0.14	0.16	0.17	0.08	0.12	0.04	0.05	0.05	0.04
D/88	2050	1.5	0.41	0.66	0.12	0.21	0.13	0.19	0.12	0.20	0.07	0.22	0.03	0.08	0.04	0.10
D/95	2150	1.5	0.46	0.39	0.12	0.06	0.21	0.15	0.18	0.15	0.15	0.15	0.06	0.06	0.08	
D/65	2200	2.0	0.59	0.68	0.10	0.11	0.49	0.52	0.36	0.54	0.58	0.63	0.21	0.25	0.23	0.26
D/66	2200	5.0	0.94 ^b	0.94	0.26	0.33	0.85	0.83	0.74 ^b	0.74	0.78 ^b	0.78	0.47 ^b	0.47	0.45 ^b	0.45

^aThe measured values in this table are taken from ref. 10.

^bThese values were used to calculate δ or k'/δ .

DISCUSSION OF THE MODEL – LIMITS OF RELEASE

The data from small-scale experiments have been interpreted by the use of a boundary layer diffusion model in which the rate-limiting step in release of fission products and fuel is diffusion through a gas film. Since the presence of the gas film retards the release of fission products and fuel, conditions which reduce the film thickness cause an increase in release, and conditions which cause an increase in film thickness cause a decrease in release. This leads to the conclusion that maximum release would occur if there were no film, that is, in a vacuum. The maximum release then can be described by a modification of the Langmuir equation for evaporation in a vacuum:¹⁴

$$fr = 1 - \exp \left[\frac{-0.0583 k' p^0 A t}{(MT)^{1/2} u} \right]. \quad (28)$$

This expression has been tested in the study of the release of plutonium from uranium by McKenzie.¹⁵ The minimum release can be described by Eq. (1) if the concentration gradient dc/dz is expressed as a function of time. In the case of no flow through the cooling channels of a large reactor core, for example, the evaporating material may saturate the gas space, resulting in a zero concentration gradient – with no further release until conditions change.

Thus, by the identification of the rate-controlling mechanism governing release in small-scale experiments, one can deduce the extent of maximum release in a reactor accident and identify factors which affect the extent of release.

SUMMARY AND CONCLUSIONS

A model has been developed which is based on boundary layer diffusion to describe the release of fission products from reactor fuel. The model is also applicable to the vaporization of fuel materials. The assumptions of the model are:

1. A boundary layer of blanket gas of thickness δ cm is over the melt.
2. The partial pressure of a component over the melt is given by Henry's law ($p_A = k'_A p_A^0 x_A$) for fission products and by Raoult's law ($p_S = p_S^0 x_S$) for the fuel.
3. The rate-determining step of the release is diffusion through the boundary layer.
4. The concentration of released fission products in the atmosphere outside the boundary layer is zero.
5. There is a linear concentration gradient of fission products or fuel material through the boundary layer.

The model has been tested with data from several sources and satisfactorily explains the observed behavior of fission products and fuel. The model describes the dependence of the fraction released on the atmosphere, that is, its composition and pressure; the solvent, that is, its surface and amount; the chemical form of the fission products; the temperature; and time at temperature.

The success of the model in predicting correctly the dependence of fission product release rate on identity of cover gas is especially significant, since other theoretical release models do not predict such a dependence.

Application of the model to the emission of fission products below the melting point of UO_2 indicated that in postirradiating annealing experiments above 1600°C , the rate-limiting step in the release of fission products and the vaporization of UO_2 is boundary layer diffusion. The model shows that the vaporization of fuel contributes substantially to the release of the fission products and must be considered in an explanation of fission product behavior.

The model indicates that maximum possible release of fission products and fuel would occur in a vacuum and that the release could then be expressed by a modified Langmuir equation for vaporization. It is most likely, however, that at large scale the gas film will be present and that a concentration gradient will exist. It is further likely that the small-scale experimental data may indicate greater release than would actually be experienced at large scale, since the actual concentration gradient may be less than that postulated for the light bulb model, in which the concentration outside the gas boundary was assumed to be zero. This possibility points out the need for larger-scale fission product release experiments to investigate the effects of size on the release mechanism. The subject of scale-up as it pertains to the U.S. Nuclear Safety Program has been discussed further elsewhere.^{16,17}

If one can assume at this point that the model and the small-scale experimental data are applicable at large scale, then further studies are indicated to make the data more useful. For example, Henry's law constants are needed. An independent research program should investigate the solubility of fission products in various chemical forms in reactor fuels and determine the Henry's law constants. The program should determine the effects of different O/U ratios, different fabrication techniques, and burnup on the solubility with the intent of determining whether or not the Henry's law constant can be predicted for specific applications. In addition, further investigations of the variables affecting the boundary layer thickness δ are needed to determine if the thickness, too, can be predicted.

The model indicates that in order to make the fullest use of the data from small-scale experiments, certain information should be reported. This includes the amount of fuel vaporized so that the film thickness can be calculated, the surface area to volume ratio, the complete temperature history, and the composition of the cover gas.

The use of simulated fuel is important to certain large-scale experiments. The model indicates that two points are important concerning the fission product-fuel relationship: (1) the chemical form of the fission product in the fuel and (2) the solubility of the fission product in the fuel. These can be determined by measuring the Henry's law constant for the simulated fuel and comparing it with similar measurements made on irradiated fuel. The simulant fuel should be a valid substitute for irradiated fuel if the proper fission product solubility is achieved.

This process of modeling simulated reactor accident events will continue. As the program of scale-up in experiments on fission product behavior develops, models such as the light bulb would be refined and developed, so that the consequences of a maximum credible accident can realistically be evaluated in relation to the siting of reactors near populated areas.

NOMENCLATURE

- A = surface area (cm^2)
 c = concentration (moles/ cm^3)
 $(c_i)_\delta$ = concentration of species i at distance δ from the surface of the melt (moles/ cm^3)
 $(c_i)_0$ = concentration of species i in the gas phase in equilibrium with the surface of the melt (moles/ cm^3)
 D_{ij} = binary diffusion coefficient (cm^2/sec)
 fr = fraction released
 h = liquid depth (cm)
 J_i = molar diffusion flux (moles $\text{cm}^{-2} \text{sec}^{-1}$)
 k = Henry's law constant (atm)
 k' = temperature-independent component of Henry's law constant
 M_i = molecular weight (g/mole)
 p = total pressure (atm)
 p_i = partial pressure of solute (atm)
 p_i^0 = vapor pressure of pure solute - temperature-dependent component (atm)
 R = gas constant ($\text{cm}^3 \text{ atm mole}^{-1} \text{ deg}^{-1}$)
 Subscripts i or j are A for fission product, B for cover gas, and S for fuel
 T = absolute temperature (deg)
 t = time (sec)
 u = moles of solution
 V = volume (cm^3)
 x = mole fraction of solute in solvent
 Y = fraction of fission product retained in the fuel
 z = distance (cm)
 δ = thickness of film of stagnant gas (cm)
 ρ = density (g/cm^3)
 σ_i = collision diameter (A)

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