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A MECHANISTIC MODEL FOR Sr AND Ba  
RELEASE FROM SEVERELY DAMAGED FUEL\*

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RELEASE FROM SEVERELY DAMAGED FUEL\*

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**ABSTRACT** Among radionuclides associated with fission product release during severe accidents, the primary ones with health consequences are the volatile species of I, Te, and Cs, and the next most important are Sr, Ba, and Ru. Considerable progress has been made in the mechanistic understanding of I, Cs, Te, and noble gas release; however, no capability presently exists for estimating the release of Sr, Ba, and Ru. This paper presents a description of the primary physical/chemical models recently incorporated into the FASTGRASS-VFP (volatile fission product) code for the estimation of Sr and Ba release. FASTGRASS-VFP release predictions are compared with two data sets: (1) data from out-of-reactor induction-heating experiments on declad low-burnup (1000 and 4000 MWd/t) pellets, and (2) data from the more recent in-reactor PBF Severe Fuel Damage Tests, in which one-meter-long, trace-irradiated (89 MWd/t) and normally irradiated (~35000 MWd/t) fuel rods were tested under accident conditions.

## I. INTRODUCTION

Among radionuclides associated with fission product release during severe accidents, the primary ones with health consequences are the volatile species of I, Te, and Cs, and the next most important are Sr, Ba, and Ru. Considerable progress has been made in the mechanistic understanding of I, Cs, Te, and noble gas release; however, no capability presently exists for estimating the release of Sr, Ba, and Ru. This paper presents a description of the primary physical/chemical models recently incorporated into the FASTGRASS-VFP (volatile fission product) code<sup>1,2</sup> for the estimation of Sr and Ba release.

In the FASTGRASS-VFP model, fission product release from fuel is assessed by predicting the migration of fission product atoms and microbubbles from the grain interior first to the grain faces (via diffusion, grain-growth/grain-boundary-sweeping, etc.) and then to the grain edges, where, nominally, release occurs through a network of interconnected tunnels of fission-gas-induced and fabricated porosity. (Release can occur directly through intergranular microcracks if these are predicted to form.) Models must also be developed to describe chemical sequestering effects on the distribution of fission products within the fuel grain structure and on the amount released.

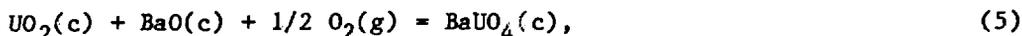
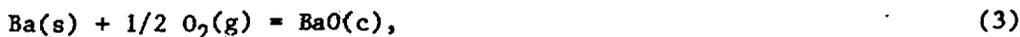
## II. THEORY

In view of the thermochemical conditions in fissioned  $UO_2$  fuel,<sup>3</sup> the following reactions appear to dominate Sr and Ba sequestering effects within the  $UO_2$  matrix:



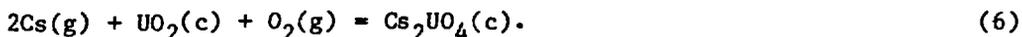
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where s stands for atoms in solution, and c and g stand for crystalline and gas phases, respectively.

In addition, Cs sequestering by the fuel affects the oxygen partial pressure, and thus the Sr and Ba reactions:



There is currently some uncertainty over the importance of reaction (5) for Ba chemistry within the fuel matrix. Kleykamp<sup>4</sup> has suggested that the reaction<sup>5</sup>



and not reaction (5), dominates Ba sequestering within  $\text{UO}_2$ .

In what follows, the inclusion of reaction (5) and/or reaction (7) is neglected and postponed for a subsequent analysis.

For the Sr and Ba reactions, the concentration of seven chemical species (Sr,  $\text{SrO}(c)$ ,  $\text{SrO}(g)$ ,  $\text{O}_2$ , Ba,  $\text{BaO}(c)$ , and  $\text{BaO}(g)$ ) must be determined in order to specify the fraction of fission product Sr and Ba that is available for release from the fuel matrix either in atomic form or in the gas phase. From the law of mass balance, the total fractional atom concentration of Sr and Ba equals the sum of their respective fission yields, i.e.,

$$C_{\text{Sr}}^T = C_{\text{Sr}} + C_{\text{SrO}(c)} + C_{\text{SrO}(g)} = 0.0926 \text{ (BU)} \quad (8)$$

$$C_{\text{Ba}}^T = C_{\text{Ba}} + C_{\text{BaO}(c)} + C_{\text{BaO}(g)} = 0.0682 \text{ (BU)} \quad (9)$$

where  $C_i^T$  = total fractional concentration of species i generated as a function of fractional burnup (BU) and  $C_i$  = fractional concentration of the individual chemical forms of species i. The concentration of  $\text{O}_2$  can be assessed from standard models as a function of temperature, O/U ratio, burnup, and fuel density; thus, three of the seven concentrations are known. The four remaining equations can be obtained from the law of mass action. For the reaction  $\text{Sr} + 1/2 \text{O}_2 = \text{SrO}(c)$ , the equilibrium constant ( $K_1$ ) can be expressed in terms of the free energy of formation ( $\Delta G$ ) and the concentration of the reactants and products; i.e.,

$$K_1 = \exp\left(\frac{-\Delta G_1}{RT}\right) = \frac{a_{\text{SrO}(c)}}{C_{\text{Sr}} P_{\text{O}_2}^{1/2}}, \quad (10)$$

where  $\Delta G_1 = -174,079 + 43.44T$  cal/mol for  $T > 1654$  K and  $-142,835 + 24.55T$  cal/mol for  $T < 1654$  K;  $R = 1.987$  cal/mol·K;  $T$  = temperature in K;

$P_{O_2}$  = oxygen partial pressure; and  $a_{SrO(c)}$  is the activity of SrO(c). For the reaction  $Ba + 1/2 O_2 = BaO(c)$ , the equilibrium constant ( $K_3$ ) can be likewise expressed as

$$K_3 = \exp\left(\frac{-\Delta G_3}{RT}\right) = \frac{a_{BaO(c)}}{C_{Ba} P_{O_2}^{1/2}}, \quad (11)$$

where  $\Delta G_3 = -133186 + 24.56T$  cal/mol and  $a_{BaO(c)}$  is the activity of BaO(c).

In this paper we shall focus on an upper bound for the SrO(g) and BaO(g) vapor pressures,  $P_{SrO}$  and  $P_{BaO}$ , and take the activities of BaO(c) and SrO(c) = 1. Using unity for  $a_{SrO(c)}$  and  $a_{BaO(c)}$  in eqs. (2) and (4) results in

$$P_{SrO} = K_2, \quad (12)$$

$$P_{BaO} = K_4, \quad (13)$$

where

$$K_2 = \exp\left(\frac{-\Delta G_2}{RT}\right),$$

$$K_4 = \exp\left(\frac{-\Delta G_4}{RT}\right),$$

$$\Delta G_2 = 135,344 - 36.42T,$$

and

$$\Delta G_4 = 98,138 - 33.21T.$$

Following the analysis of CsI formation in  $UO_2$  by Appelhans et al.,<sup>6</sup> it is assumed that the formation of the reaction products CsI(g), SrO(g), and BaO(g) requires the presence of reaction sites, which are primarily microbubbles containing the noble fission gases Xe and Kr.

From eqs. (12) and (13) and an equation of state of the Van der Waals form,

$$P(V_b - b) = nRT$$

(where  $b$  is the Van der Waals constant,  $V_b$  is the bubble volume, and  $n$  is the number of atoms of SrO(g) or BaO(g) in the bubble in atoms/cm<sup>3</sup>), the quantity of SrO(g) and BaO(g) can be calculated. As the bubble volume,  $V_b$ , is calculated directly in FASTGRASS-VFP, there are no remaining unknowns in the calculation of  $C_{SrO(g)}$  and  $C_{BaO(g)}$ . (The calculation of CsI is handled in an analogous fashion.)

The oxygen partial pressure is calculated according to the analysis of Blackburn and Johnson,<sup>3</sup> and is given by the following expression:

$$P_{O_2}^{1/2} = \frac{(\phi - 2) + [(\phi - 2)^2 + 4B(3 - \phi)(\phi - 1)/A]^{1/2}}{2B(3 - \phi)/\phi}, \quad (14)$$

where

$$A = \exp(78300/T - 13.6),$$

$$B = \exp(16500/T - 5.1),$$

and

$$\phi = O/U.$$

The value of  $\phi$  can be calculated by taking into account the fissioning of  $^{235}\text{U}$  and the formation of the oxides and uranates given in eqs. (1-4) and eq. (6), i.e.,

$$\phi = \phi_0 + \frac{\dot{F}t}{N_m^0} (\phi_0 - \alpha) - \alpha, \quad (15)$$

where

$$\alpha = C_{\text{SrO}(c)} + C_{\text{SrO}(g)} + C_{\text{BaO}(c)} + C_{\text{BaO}(g)} + C_{\text{Cs}_2\text{UO}_4},$$

and  $\dot{F}$  is the fission rate in fissions/cm<sup>3</sup>/s,  $N_m^0$  is the initial number of heavy metal atoms,  $t$  is the irradiation time, and  $\phi_0$  is the starting O/U ratio. In general, as  $\dot{F}$  and  $T$  are functions of time, eq. (15) is phrased in differential form and integrated over time.

Simultaneous solution of this coupled system of equations yields the equilibrium concentrations as a function of fuel burnup and temperature. (These equations are solved for fission products within the fuel grains and on the grain faces and edges.) The amount of Sr and Ba that is predicted to be retained in the fuel in atomic form or in the vapor phase in microbubbles is assumed available for release, whereas all other species are assumed to be immobilized within the fuel microstructure.

Once the fractions of atomic Sr and Ba are known, their mobility through the fuel microstructure is then assessed. The diffusivity of atomic Sr and Ba is assumed to be identical with that of Xe. BaO(g) and SrO(g) are assumed to migrate within fission gas bubbles.

### III. COMPARISON BETWEEN THEORY AND DATA

The predicted results have been compared with two data sets: (1) the data obtained by Parker and Barton<sup>7</sup> in out-of-reactor induction-heating experiments on dekad, crushed low-burnup (1000 and 4000 MWd/t) pellets; and (2) data from the more recent in-reactor PBF Severe Fuel Damage (SFD) Tests,<sup>8</sup> in which one-meter-long, trace-irradiated (89 MWd/t) and normally irradiated (~35000 MWd/t) fuel rods were tested under accident conditions.

#### III.A Comparison with Out-of-Reactor Data

In Table I, the data of Parker and Barton are compared with FASTGRASS-VFP predictions of Xe, Ba, and Sr release for three values of fuel temperature and two values of fuel burnup. Parker and Barton heated irradiated UO<sub>2</sub> specimens for ~5.5 h in an inert environment. Because fuel fragments having unknown values of open pore-solid surface area were used in the majority of the tests, a quantitative comparison between theory and experiment is difficult. However, as is evident from Table I, the FASTGRASS-VFP predictions follow the trend of observed Xe, Sr, and Ba release as a function of temperature and burnup. For low-burnup irradiations, most of the Ba and Sr is predicted to be

Table I.  
Xe, Ba, and Sr Release Data<sup>a</sup> of Parker and Barton (Ref. 7),  
Compared with FASTGRASS-VFP Predictions

Temperature	Burnup (Mwd/t)	Percent Released					
		Xe		Ba		Sr	
		Data	Theory	Data	Theory	Data	Theory
1400°C (2552°F)	1000	0.5	0	2	0	0.06	0
	4000	6	0.5	0.5	0	0.08	0
1780°C (3236°F)	1000	14	4	21	4	4	4
	4000	42	42	18	28	6	6
1980°C (3596°F)	1000	49	21	51	21	15	21
	4000	71	54	60	54	33	54

<sup>a</sup>Fragments of irradiated fuel, weighing 0.1-0.2 g, were held at the indicated temperatures for 5.5 h.

in atomic form rather than in a sequestered state, and thus available for diffusional release. During the rather long time at temperature ( $\approx 5.5$  h), FASTGRASS-VFP predicts significant release. This prediction is borne out by the data; for example, in the case of the 1000-Mwd/t fuel fragments, the measured Ba release was  $\approx 20\%$  at 1780°C and  $\approx 50\%$  at 1980°C. The corresponding FASTGRASS-VFP-predicted values follow the trend of these data.

Information on the predicted mechanisms of release for these fission products during the Parker and Barton experiments is presented in Table II, which shows

Table II.  
Predicted Intragranular Migration of Xe and Ba in 4000-Mwd/t Fuel  
Fragments during the Parker and Barton Tests (Ref. 7)

(°C)	Product	Percent Released to Grain Boundary by	
		Diffusion	Grain Boundary Sweeping
1400	Xe	59	41
	Ba	8	92
1780	Xe	13	87
	Ba	11	89
1980	Xe	14	86
	Ba	14	85

the calculated fraction of Xe and Ba (results for Sr are similar to those of Ba) released to the grain boundaries of the 4000 MWd/t fuel fragments by random diffusion of gas atoms (and/or bubbles) and by grain boundary sweeping. The majority of intragranular release during these tests is predicted to occur by a grain-growth/grain-boundary-sweeping mechanism. These results for grain-growth/grain-boundary-sweeping effects in low-burnup fuel follow the trend of other reported results.<sup>2</sup> Grain-growth/grain-boundary-sweeping effects are expected to be less important in higher burnup fuels because of the increased presence of fission products on the grain boundaries, which retard boundary movement.

The Ba and Sr species migrating in the fuel are predicted to be primarily in atomic form. Very little BaO(g) and SrO(g) is calculated to exist in bubbles, owing to the relatively low vapor pressure (e.g., as compared to the noble gases) and the limited available bubble volume. Including the formation of Ba uranate(s) will result in even lower vapor pressures and even smaller concentrations of BaO(g) in fission gas bubbles. These calculations indicate that if BaO(g) or SrO(g) exists outside of the fuel, the molecules were formed for the most part either in the fuel open porosity or at the fuel surface, and not within fission gas bubbles. (This conclusion is also valid for CsI.)

### III.B Comparison with In-Reactor Data

The PBF SFD test series<sup>8</sup> was performed to obtain a variety of data on fission-product release under severely-degraded-core conditions similar to those experienced at TMI-2. The tests were performed in the PBF reactor on 32-rod bundles of fresh or irradiated fuel enclosed in an insulated shroud. Each bundle was preconditioned and calibrated prior to the high-temperature transient, which included a heat-up to ~2400 K with resultant clad melting, fuel liquefaction/dissolution, and fuel fragmentation. The test bundle temperature, power, fission product generation and release, and hydrogen generation and release were monitored by a variety of instruments.

The SFD 1-1 transient consisted of a slow heat-up of trace-irradiated (89 MWd/t) fuel to ~1600 K, followed by a rapid heating driven by cladding oxidation in the upper regions of the fuel bundle. The peak fuel temperatures in most of the fuel rods were >2400 K. A significant amount of liquefaction/dissolution occurred in SFD 1-1. In the SFD 1-3 test,<sup>9</sup> the transient closely matched that of SFD 1-1, but normally irradiated (~35,000 MWd/t) fuel rods were used in the test bundles. These irradiated fuel rods had been in the PBF reactor for ~1-1/2 years, with a subsequent storage period of ~4 years.

Table III shows a comparison of release fractions measured during these tests and the FASTGRASS-VFP-calculated release fractions. This comparison shows that FASTGRASS-VFP predictions for the SFD 1-1 and 1-3 tests are in reasonable agreement with the reported results. However, as the SFD 1-1 and 1-3 temperature and liquefaction/dissolution scenarios are somewhat uncertain, these results should again be considered more qualitative than quantitative.

For the trace-irradiated fuel of the PBF SFD 1-1 experiment, low release is predicted. Approximately 5% of the Ba and Sr is predicted to migrate to grain boundaries and to be trapped there during solid-phase fuel heat-up. During fuel liquefaction/dissolution, this inventory of Ba and Sr is predicted to be released. This prediction agrees well with the test data (<1% measured release). For the higher burnup fuel of SFD 1-3, a lower release percentage

Table III.  
 Percentage Fission-Product Release Measured During Two PBF SFD Tests  
 (Refs. 8 and 9), Compared with FASTGRASS-VFP Predictions

Species	SFD 1-1			SFD 1-3		
	Data	Theory		Data <sup>a</sup>	Theory	
		Total	Liquefaction Release on Cooldown		Total	Liquefaction Release on Cooldown
Noble Gas	2.5-9.3	8.4	8	9-22	7.9	5.4
I	12	7.7	7	11	5	3.4
Cs	9.2	7.2	7	10	7	5
Te	0.3	0.15	0.15	<0.5	0.3	0.2
Ba	0.5	6	6	1.5	0.4	0.27
Sr	--	5	5	--	0.2	0.14

<sup>a</sup>Excluding irreversible deposition and filter content.

is predicted (~0.5%). The calculations indicate that chemical sequestering results in the retention of the majority of Ba and Sr in the fuel matrix, primarily as BaO(c) and SrO(c).

Again, the majority of intragranular release occurring during the SFD 1-1 test on trace-irradiated fuel is due to grain growth/grain-boundary-sweeping effects, and the majority of Sr and Ba is predicted to migrate within the UO<sub>2</sub> in atomic form rather than as vapor in fission gas bubbles.

Also shown in Table III is the quantity of fission products predicted to be released through the liquefied regions<sup>10</sup> of the fuel after fuel heat-up and during fuel cooldown. For the SFD 1-1 test, essentially all of the fission products are predicted to be released during this cooldown period. The reason for this result is that in trace-irradiated fuel, very little open porosity is calculated to exist on the grain boundaries. Thus, fuel liquefaction provides release paths for the entrapped fission products.

In the higher burnup fuel of the SFD 1-3 test, fission product release is partitioned between liquefaction release and release through networks of open porosity. The higher degree of open porosity in the normally irradiated fuel is due to much higher concentrations of fission gas on the grain boundaries, and thus more extensive interlinkage to the fuel surface.

Since the release/retention behavior of Ba and Sr in UO<sub>2</sub> fuel is found to be strongly tied to burnup-related chemical and morphological conditions, release correlations that are dependent only on temperature, as presently used, may be inappropriate in predicting the release of fission-product Ba and Sr over a

wide range of severe accident conditions. The fact that the mechanistic approach recently incorporated into the FASTGRASS-VFP model predicts data trends reasonably well is encouraging.

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