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BEHAVIOR OF FISSION PRODUCTS IN LWR FUEL RODS UNDER ACCIDENT CONDITIONS

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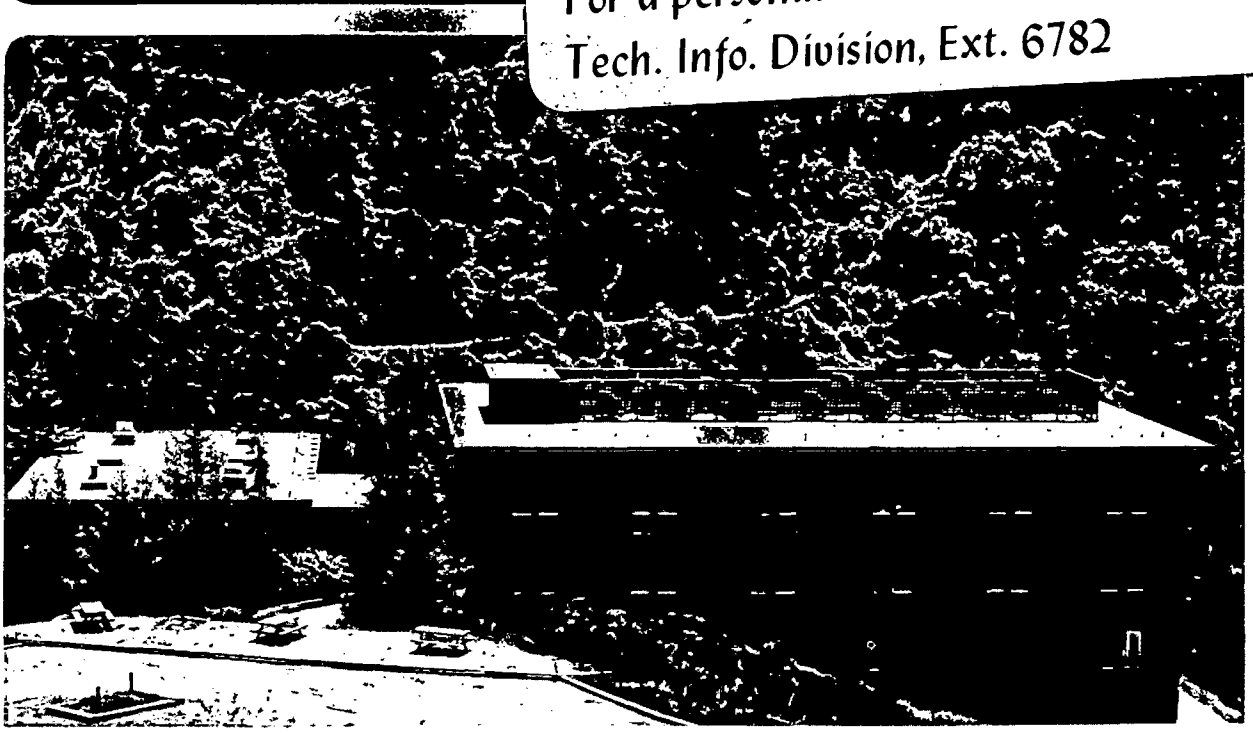

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Extended Abstract

From the standpoint of LWR safety an area of prime concern is the release of radioactivity to the environment. In the event of a loss of coolant, there is a rapid rise in temperature of the fuel rods which could fail by cladding rupture. Steam can then react with the fuel and fission products, and with the zircaloy cladding liberating hydrogen. And if the primary pressure system is breached, air could also be present. This means that the ruptured fuel rods will be exposed to a steam-hydrogen-air environment, depending on the nature of the accident.

The chemical states of the fission products are set by the immediate environment which is generally oxidizing. This means that one needs to consider the oxygen potentials [$\Delta\overline{G}(O_2) = RT\ln P_{O_2}$] of the environment in order to predict the stable fission product species that will be released from the hot fuel. When water vapor is present at high temperatures many elements form stable gaseous hydroxides. And release of fission products occurs as volatile compounds. Hence, modeling of the behavior of the fission products involves predicting the chemically stable volatile species that will be released from the fuel during reactor accidents.

Of the fission products released during irradiation, the emphasis in this paper will be on the chemistry of the elements which are radiotoxic (I, Cs, Te, Sb, Ru, Sr, Ba), or have high fission yields (Cs, Sr, Ba, Ru, Mo), or are volatile, or form volatile chemical compounds (Cs, Rb, I, Br, Te, Se, Sr, Ba, Mo, Ru). Using available thermochemical information [1,2], equilibrium calculations have been performed for the

reactions of these fission products for the oxygen potentials prevailing in various accident situations. The partial pressures are calculated for a low (1000 K) and a high fuel temperature (2000 K) for each scenario, although temperatures as high as 3000 K may be achieved:

I. Breached Fuel Rods in Water-Steam Environment Containing Hydrogen: The oxygen potentials in this situation are set by the H_2O/H_2 ratio, which was assumed equal to unity for the present calculations. In addition to the oxidizing environment, the presence of steam permits the formation of volatile hydroxide species. Under these conditions, the calculated partial pressures of the predominant species for each of the fission products are shown in Table 1. Clearly, CsOH, RbOH, CSI, RbI, Cs_2MoO_4, Rb_2MoO_4, Te_2, and Se_6 will be the major equilibrium species released from the fuel, although at high temperatures release of Cs, Rb, Cs_2O, Rb_2O, Sb, $Ba(OH)_2$, and $TeO(OH)_2$ will also become important. These species plate out on cooler solid surfaces, depending on their vapor pressures.

II. Breached Fuel Rods in Steam-Air Environment: In this case, the oxygen potentials are set by the steam-air mixture and may be as high as in air. This environment is obviously more oxidizing than in situation I. For these conditions, Table 1 lists the partial pressures of the stable fission product species. CsOH, RbOH, CsI, RbI, Cs_2MoO_4, Rb_2MoO_4, $TeO(OH)_2$, Se_6, and Sb still predominate, but now release of RuO_3, MoO_3, and $Ba(OH)_2$ must also be considered. The contribution of elemental iodine is small since the ratio of (CsI + RbI) to ($I + I_2$) is estimated to be 10^3 to 10^4 over the entire temperature range. The released fission products will plate out on cooler regions of the fuel or the cladding. On the other hand, release of steam and water through the containment

rupture could carry away part of the fission products as aerosols.

III. Breached Fuel Rods in Air: The fuel rods are exposed to air in this case and fuel temperatures will be very high (up to 2500 K) due to the absence of any effective cooling. The oxygen potentials are assumed to be -3 to -27 kcal/mol for which the partial pressures of the fission product species released from the hot fuel are also given in Table 1. The predominant species are essentially the same as in situation II, except for the absence of any hydroxides. In addition, SeO_2, TeO_2, and Sb_4O_6 dominate for these elements, and significant partial pressures of elemental iodine also develop. However, CsI + RbI partial pressures are still calculated to be several orders of magnitude larger than elemental iodine. The released fission products should condense at the cooler regions of the fuel or of the cladding.

The model predictions described here necessarily suffer from a lack of reliable thermodynamic data, notably for the gaseous hydroxides. In addition, a more comprehensive assessment of the chemical of the fission products behavior must consider the formation of nitrogen and carbon-bearing species, such as nitrates and nitrites, and metal carbonyls.

Obviously, the above analysis is limited in scope. The actual release of the fission product species to the environment is a complex function of the abundance and the chemical state of the generic fission product, the release rate from the hot fuel, the vapor pressure, the migration behavior in the fuel rod, and the conditions of the particular accident (concurrent release of volatile fission products and ingress of steam/air). These effects will be considered in detail later.

References

1. I. Barin, O. Knacke, and O. Kubaschewski, Thermochemical Properties of Inorganic Substances, Springer-Verlag, Berlin and New York (1973 and 1977).
2. D. R. Stull and H. Prophet, JANAF Thermochemical Tables 2nd Edition, NSRDS-NBS 37, National Bureau of Standards, Washington, D. C. (1971); also 1974, 1975, and 1978 JANAF Supplements.

Table 1. Calculated Vapor Pressures of the Predominant Volatile Fission Product Species for the Three Accident Scenarios

Fission Product	Temp. K	Scenario I[a]		Scenario II[a]		Scenario III[a]	
		Species	Pressure Range, atm	Species	Pressure Range, atm	Species	Pressure Range, atm
Cs,Rb[b]	1000	M,MOH	10^{-2}-10^{-5}	MOH,M	10^{-4},10^{-11}	M,M_2O	10^{-15},<10^{-20}
	2000	M_2O,M,MOH	1-20	M_2O,M,MOH	10^{-3}-8	M,M_2O	10^{-3},10^{-5}
Cs,Rb[c]	1000	MOH	10^{-5}	M,MOH,M_2MoO_4	<10^{-5}	M,M_2MoO_4	10^{-19},10^{-7}
	2000	M_2MoO_4,M,MOH	1-8	M,MOH,M_2MoO_4	10^{-3}-1	M,M_2MoO_4	10^{-4},1
Te	1000	Te_2,$TeO(OH)_2$	0.1,10^{-4}	$TeO(OH)_2$	10^{-4}	TeO_2	10^{-4}
	2000	Te_2,$TeO(OH)_2$	10^2,1	$TeO(OH)_2$	1	TeO_2	10^2
Se	1000	Se_6	0.5	Se_6	0.5	SeO_2	10^{-5}
	2000	Se_6	10^2	Se_6	10^2	SeO_2	1
I[d]	1000	MI,I	10^{-3},10^{-10}	MI,I	10^{-3},10^{-3}	MI,I	10^{-3},0.1
	2000	MI,I	8,10^{-6}	MI,I	8,10^{-2}	MI,I	8,2
Mo	1000	Mo	10^{-27}	MoO_2,MoO_3	10^{-20},10^{-8}	MoO_2,MoO_3	10^{-20},10^{-7}
	2000	Mo	10^{-10}	MoO_2,MoO_3	10^{-6},10^{-2}	MoO_2,MoO_3	10^{-6},0.1
Ru	1000	Ru	10^{-26}	RuO_3,RuO_4	10^{-9},10^{-10}	RuO_3,RuO_4	10^{-7},10^{-5}
	2000	Ru	10^{-8}	RuO_3,RuO_4	0.1,10^{-4}	RuO_3,RuO_4	10^{-2},10^{-3}
Sb	1000	Sb	10^{-3}	Sb	10^{-3}	Sb_4O_6	10^{-2}
	2000	Sb	1	Sb	1	Sb_4O_6	4
Sr	1000	$Sr(OH)_2$	10^{-9}	$Sr(OH)_2$	10^{-9}	SrO	10^{-19}
	2000	$Sr(OH)_2$	10^{-4}	$Sr(OH)_2$	10^{-4}	SrO	10^{-6}
Ba	1000	$Ba(OH)_2$	10^{-7}	$Ba(OH)_2$	10^{-7}	BaO	10^{-15}
	2000	$Ba(OH)_2$	10^{-2}	$Ba(OH)_2$	10^{-2}	BaO	10^{-4}

a. $\Delta\overline{G}$ (O_2), kcal/mol: Scenario I = -90 to -65; Scenario II = -20; Scenario III = -3 to -27

b. Cs_2UO_4/Rb_2UO_4 is assumed to be the stable solid phase

c. Cs_2MoO_4/Rb_2MoO_4 is assumed to be the stable solid phase

d. Similar pressures have been calculated for elemental bromine and the bromides

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