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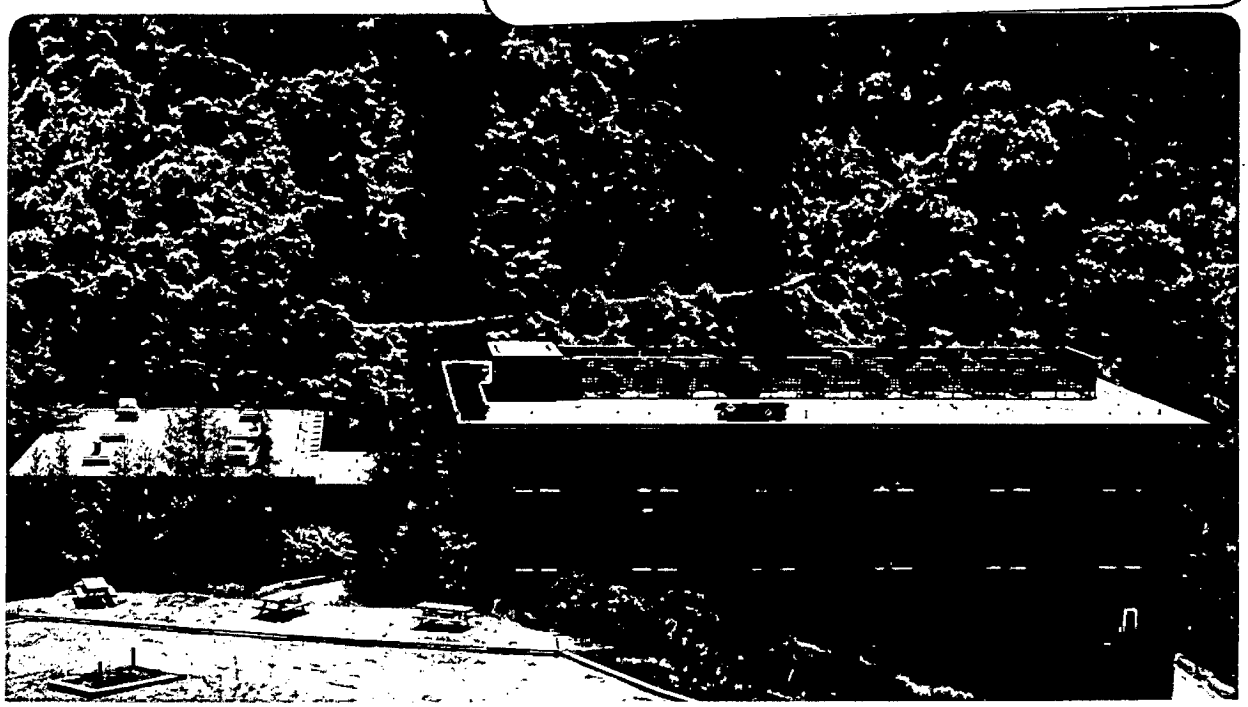

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IS PCI AN IODINE SCC PHENOMENON?

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It is a very common belief that the pellet-cladding interaction (PCI) phenomenon which afflicts the Zircaloy cladding of LWR fuel rods is a manifestation of stress corrosion cracking (SCC) with the responsible chemical agent being elemental iodine(1). On its face, this mechanism is contrary to thermodynamics; since the fission yield of cesium exceeds that of iodine, CsI, not I or I_2, is the overwhelmingly favored species. Cesium iodide, however, does not cause stress corrosion cracking of zircaloy in laboratory tests. It is commonly assumed that the iodine pressure in an intact fuel rod is controlled by the formation of the cesium-fuel compound Cs_2UO_4, which produces a free iodine pressure of $\sim 10^{-19}$ atm(2,3). This iodine pressure, which roughly corresponds to the atom density of intergalactic space, can hardly be expected to drive an earthly process at measureable rates. Radiolysis of CsI has been put forth as a mechanism for generating sufficiently large non-equilibrium concentrations of free iodine to cause Zircaloy SCC, but attempts to verify this hypothesis have been unsuccessful (2,4-6).

Recently, Götzmann(7) has suggested that the formation of the ternary cesium-molybdenum-oxygen compound Cs_2MoO_4, which is thermochemically more stable than the corresponding cesium-uranium-oxygen compound, could increase the free iodine partial pressure to a value large enough to cause Zircaloy SCC. Assuming that cesium molybdate forms according to thermodynamics, which is not at all certain since no such compound has ever been observed in irradiated LWR fuel, the pressure of atomic iodine in equilibrium with fuel with an oxygen potential of -100 kcal/mole is $\sim 4 \times 10^{-16}$ atm at 600K (7). It can be shown that such a small pressure cannot drive a sufficiently large diffusive flux of iodine in a cladding crack to sustain crack propagation in an

SCC process. Consider a crack 100 μm deep and 10 μm wide at its mouth If iodine is transported by molecular diffusion from the mouth to the tip of this crack, the maximum flux is given by:

$$N_I = D(p_I)_1/aRT$$

where D is the diffusion coefficient of atomic iodine in the gas filling the crack, $(p_I)_1$ is the iodine pressure at the crack mouth, a is the crack length, R is the gas constant and T is the temperature. For a typical total pressure of 10 atm in the fuel element, the diffusion coefficent of iodine in helium is estimated to be ~0.2 cm^2/s(8). Using these data in the above formula gives an iodine atom flux in the crack of 10^5 $cm^{-2}s^{-1}$. Or, only 100 iodine atoms/s enter the mouth of the crack per centimeter of length. In obtaining this result, the iodine pressure at the crack tip was assumed to be zero. This is thermodynamically impossible, for there must at least be an iodine pressure corresponding to dissociation of gaseous CsI which presumable fills the crack. If the crack is propagating by stress corrosion cracking, it is more likely that the iodine pressure at the crack tip is at least that needed to maintain the ZrI/Zr two-phase system in equilibrium.

Instead of direct diffusion of elemental iodine, Gotzmann(7) has suggested that the CsI/Cs couple acts to transport iodine from the fuel surface to the crack tip, in a manner analogous to the transport of oxygen in the fuel by the CO_2/CO or H_2O/H_2 couples. The purpose of the present note is to pursue this suggestion quantitatively to determine if it can provide the justification for the role of iodine in Zircaloy SCC.

In the vapor transport model, iodine is transported from the outer fuel surface (designated as location 1) to the tip of a growing crack in the cladding in the form of CsI. At the crack tip (location 2) CsI is

decomposed to deliver iodine to the crack. The liberated cesium gas diffuses back to the fuel-cladding gap to pick up more iodine from the fuel surface. For modeling purposes, a crack of length a and constant width is assumed. No chemical reaction is permitted on the sides of the crack, which are assumed to be covered with a zirconium iodide film whose surface is in equilibrium with the prevailing iodine activity of the gas. However, the crack propagates because of the iodine supply to the tip, and penetration of the crack into the metal continually exposes fresh metal surface which acts as a sink for iodine transported by CsI. Although the fuel surface temperature is somewhat higher than the inner cladding temperature because of the thermal resistance of the fuel-cladding gap, the system is assumed isothermal for the present analysis.

The iodine pressures at the fuel surface and the crack tip are determined by appropriate chemical equilibria. In addition, the following reaction is in equilibrium at both locations:

$$Cs(g) + I(g) = CsI(g) \qquad (1)$$

At the fuel surface the iodine pressure is assumed to be controlled by the equilibrium(7):

$$2CsI(s) + Mo(s) + 2O_2(g) = Cs_2MoO_4(s) + 2I(g) \qquad (2a)$$

or

$$2CsI(s) + MoO_2(s) + O_2(g) = Cs_2MoO_4(s) + 2I(g) \qquad (2b)$$

The equilibrium iodine pressure established by these reactions depends on the activity of molybdenum or its oxide. When this is specified, the temperature at the fuel surface given, and the presence of pure condensed CsI assumed, both $(p_{CsI})_1$ and $(p_I)_1$ are fixed and $(p_{Cs})_1$ is given by:

$$(p_{Cs})_1 = \frac{(p_{CsI})_1}{K_0 (p_I)_1}$$

where K_0 is the equilibrium constant of reaction (1) and the CsI pressure is equal to the vapor pressure.

The iodine potential at the crack tip is assumed to be controlled by the iodine pressure in equilibrium with the Zr(s)/ZrI(s) two-phase solid system:

$$Zr(s) + I(g) = ZrI(s) \tag{3}$$

Hence for the specified temperature, $(p_I)_2$ is fixed by the above reaction and the equilibrium of reaction (1) can be written as:

$$(p_{Cs})_2 = \frac{(p_{CsI})_2}{K_0 (p_I)_2}$$

In the vapor transport model, there is a nonzero net flux of the element iodine from the fuel surface to the crack tip but the net flux of cesium (either as Cs vapor or CsI vapor) must be zero. Thus:

$$N_{CsI} = N_{Cs} \tag{4}$$

where the diffusive fluxes of CsI and Cs are

$$N_{CsI} = \frac{D}{aRT}\left[(p_{CsI})_1 - (p_{CsI})_2\right] \tag{5}$$

$$N_{Cs} = \frac{D}{aRT}\left[(p_{Cs})_2 - (p_{Cs})_1\right] \tag{6}$$

Here D is the diffusion coefficient of Cs or CsI (the two are assumed to be equal) in the inert gas filling the crack. From eqs (4) - (6):

$$(p_{CsI})_1 - (p_{CsI})_2 = (p_{Cs})_2 - (p_{Cs})_1 \tag{7}$$

Eliminating $(p_{Cs})_1$ and $(p_{Cs})_2$ by the equations derived previously yields:

$$(p_{CsI})_2 = \left[\frac{1 + \frac{1}{K_0 (p_I)_1}}{1 + \frac{1}{K_0 (p_I)_2}}\right] (p_{CsI})_1 \tag{8}$$

Substituting Eq(8) into Eq(5) yields:

$$N_{CsI} = \frac{D(p_{CsI})_1}{aK_0\ RT}\left[\frac{1/(p_I)_2 - 1/(p_I)_1}{1 + \frac{1}{K_0(p_I)_2}}\right] \qquad (9)$$

Taking 600K as a typical temperature at the fuel-cladding interface, the thermodynamic quantities in Eq(9) are:

$(p_{CsI})_1 = 1.2 \times 10^{-9}$ atm(ref. 9)

$(p_I)_2 = 6 \times 10^{-16}$ atm (refs. 3 and 7)

$(K_0 = 3 \times 10^{25}$ atm^{-1} (ref. 10)

$$(p_I)_1 = \begin{cases} 2 \times 10^{-14} \text{ atm for } \overline{\Delta G_{O_2}} = -90 \text{ kcal/mole} \\ 4 \times 10^{-16} \text{ atm for } \overline{\Delta G_{O_2}} = -100 \text{ kcal/mole} \end{cases} \text{(Fig. 6 of ref. 7)}$$

Using these values in Eq(9), the CsI flux for $\overline{\Delta G_{O_2}} \approx -100$ kcal/mole is zero because the iodine activity (i.e., p_I) is the same at the fuel surface and at the crack tip. However, for $\overline{\Delta G_{O_2}} > -100$ kcal/mole, $(p_I)_1 \gg (p_I)_2$ and Eq(9) simplifies to:

$$N_{CsI} = \frac{D(p_{CsI})_1}{aRTK_0(p_I)_2} \qquad (10)$$

The diffusion coefficient of cesium or cesium iodide in helium at pressures ranging from 5 atm (typical of a BWR fuel rod) to 20 atm (for a prepressurized PWR fuel rod) is ~ 0.2 cm^2/s(8). For a typical stress corrosion crack length of 100 μm, Eq(10) gives a cesium iodide flux down the 10 μm wide crack of less than 0.02 molecules/s per centimeter length.

Thus, the CsI/Cs vapor transport mechanism does not appear to be any more likely to cause stress corrosion cracking than does a process based on transport of elemental iodine inside the crack. In both cases the enormous stability of cesium iodide prevents attainment of iodine activities sufficiently high to approach those found necessary for stress corrosion cracking of zircaloy in laboratory experiments utilizing free iodine ($\sim 10^{-6}$ atm, ref. 6). There does not appear to be any way of justifying on fundamental grounds the role of iodine in PCI failures of light water reactor fuel pins.

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