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THE CONSERVATION EQUATIONS GOVERNING POROSITY AND ACTINIDE

REDISTRIBUTION IN MIXED OXIDE FUELS

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It has often been stated that the movement of the as-fabricated porosity in a mixed oxide fuel due to the temperature gradient is responsible for actinide redistribution (1-5). The purpose of this note is to assess the accuracy of this assertion.

Conservation statements may be written for the following components of the system consisting of vapor-containing pores and solid heavy metal oxide:

- (a) The number of pores
- (b) Total mass
- (c) Plutonium mass

Conservation statement (a) leads to a description of the evolution of the radial porosity distribution in the fuel element and combination of all three permits assessment of the conditions under which actinide redistribution due to the movement of closed pores can occur.

In order to treat the movement of pores in mixed oxide fuel, the following assumptions are made:

- 1) The pores are closed and migrate only in the radial direction under the influence of the temperature gradient in a cylindrical fuel rod.
- 2) The pore migration velocity is a known function of radial position (via the known temperature and O/M gradients).
- 3) The pores are all of the same size.
- 4) The volume of each pore is independent of radial position and time.

As a result of assumptions 1 and 3, collisions and coalescence between migrating pores do not occur.

Consider a region in the fuel at radial position r at time t . This region contains $N(r,t)$ pores per unit of fuel volume and M_s grams of solid fuel per unit volume of total fuel. If the density of the solid fuel is denoted by ρ_s grams of solid/cm³ (solid) and the volume of each pore by V_p , the fact that only solid and vapor are present is expressed by:

$$V_p N + \frac{M_s}{\rho_s} = 1 \quad (1)$$

where $V_p N$ and M_s/ρ_s are the volume fractions of the vapor and solid phases, respectively.

An observer stationed on a plane perpendicular to the r -direction would observe a flux of pores moving towards the center and a flux of solid oxide moving in the opposite direction. These fluxes are denoted by:

$$J_p = \text{flux of pores in the } +r\text{-direction, pores/cm}^2\text{-sec}$$

(2)

$$J_s = \text{flux of solid oxide in the } +r\text{-direction, grams solid/cm}^2\text{-sec}$$

Since the pores move exclusively in the radial direction under the influence of the thermal gradient, their flux is given by:

$$J_p = -vN \quad (3)$$

where v is the migration velocity of the individual pores, which is known as a function of temperature, temperature gradient and local fuel O/M. Consequently, v may be considered as a specified function of radial position, $v(r)$. The minus sign in Eq (3) appears because the pore velocity is usually considered to be positive when in the $-r$ direction.

(a) Conservation of Pores

The conservation statement applicable to the number of pores in the fuel (in cylindrical coordinates) is:

$$\frac{\partial N}{\partial t} = -\frac{1}{r} \frac{\partial}{\partial r} (rJ_p) \quad (4)$$

Inserting Eq (3) into Eq (4) yields:

$$\frac{\partial N}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} (rvN) \quad (5)$$

The initial condition on Eq (5) is

$$N(r,0) = N_0 \quad (6)$$

where $N_0 = P_0/V_p$ is the initial uniform concentration of pores in the fresh fuel. P_0 is the as-fabricated porosity. The appropriate boundary condition for Eq (5) is:

$$N(\infty, t) = N_0 \quad (7)$$

0 0 0 0 3 9 0 0 0 1 0
 where the outer fuel radius has been replaced by infinity because of the absence of pore motion (due to the low temperature) at all fractional radii greater than about 3/4.

The relative porosity at r and t is given by:

$$\eta(r,t) = \frac{N(r,t)}{N_0} = \frac{P(r,t)}{P_0} \quad (8)$$

where $P(r,t)$ denotes the porosity at r and t . Using Eq (8), the pore conservation equation is:

$$\frac{\partial \eta}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} (rv\eta), \quad r > r_0 \quad (9)$$

and the initial and boundary conditions become:

$$\eta(r,0) = 1 \quad (10)$$

$$\eta(\infty,t) = 1 \quad (11)$$

Eq (9) is valid only over the region $r > r_0$, where r_0 is the radius of the central void developed as a consequence of pore migration. It may be determined by equating the volumes of solid per unit fuel length before and after pore migration (assuming that no axial movement of the fuel occurs). The volume of solid per unit length of fresh fuel is $(1-N_0V_p)\pi R^2$, where R is the fuel radius. When a central void and non-uniform porosity distribution have been developed, the total volume of solid fuel per unit length is:

$$\pi R^2 - V_p \int_{r_0}^R N_2 \pi r dr = \pi r_0^2$$

Equating solid volumes before and after pore redistribution and using $P_o = N_o V_p$ yields:

$$\frac{1}{2} r_o^2 \left(\frac{1-P_o}{P_o} \right) = \int_{r_o}^{\infty} r(1-\eta) dr \quad (12)$$

where the upper limit on the integral has been approximated by infinity.

Given the pore migration velocity $v(r)$, Eqs (9) through (11) can be solved numerically for the relative porosity $\eta(r,t)$. Eq (12) then yields the radius of the central void (at time t).

(b) Total Mass Conservation

A unit volume in the fuel contains M_s grams of the heavy metal oxides and $V_p N$ cm³ of a vapor phase which contains a small quantity of gaseous oxides of U and Pu. The total mass of the heavy metals (as the dioxides) in a unit volume of fuel (solid plus vapor) is $M_s + \rho_v V_p N$, where ρ_v is the mass density of heavy metal oxides in the vapor within the pores. Assuming the perfect gas law to apply to the gaseous actinide oxides, ρ_v is given by:

$$\rho_v = \frac{270 p_{U+Pu}}{RT} \quad (13)$$

where p_{U+Pu} is the actinide oxide vapor pressure at temperature T and R is the gas constant.

The total mass flux of the heavy metals (either as solid or as vapor) past a plane perpendicular to the r -direction is $J_s + \rho_v V_p J_p$ grams/cm²-sec. Conservation of total mass of the heavy metals in the fuel is expressed by:

$$\frac{\partial}{\partial t} \left(\frac{M_s}{\rho_s} + \frac{\rho_v}{\rho_s} V_p N \right) = -\frac{1}{r} \frac{\partial}{\partial r} \left[r \left(\frac{J_s}{\rho_s} + \frac{\rho_v}{\rho_s} V_p J_p \right) \right] \quad (14)$$

where the equation has been divided by the constant solid density ρ_s . At 2400°K, the total vapor pressure of the actinide oxides over typical hypostoichiometric mixed oxide fuels is $\sim 10^{-5}$ atm. Inasmuch as the density of the solid oxide is ~ 11 grams/cm³, the ratio $\rho_v/\rho_s \approx 10^{-8}$. Because this ratio is so small, the second terms in the parentheses of Eq (14) may be neglected compared to the first terms. The total mass conservation equation reduces to:

$$\frac{\partial (M_s/\rho_s)}{\partial t} = -\frac{1}{r} \frac{\partial}{\partial r} (r J_s/\rho_s) \quad (15)$$

Multiplying Eq (4) by the constant V_p and adding the result to Eq (15) gives:

$$\frac{\partial}{\partial t} \left(\frac{M_s}{\rho_s} + V_p N \right) = -\frac{1}{r} \frac{\partial}{\partial r} \left[r \left(\frac{J_s}{\rho_s} + V_p J_p \right) \right]$$

According to Eq (1) the sum $M_s/\rho_s + V_p N$ is unity, so that the left hand side of the above equation is zero. Therefore, the sum $J_s/\rho_s + V_p J_p$ is a constant. Since this sum is zero at $r=R$, the constant is zero and the flux of solid is given by:

$$J_s = -\rho_s V_p J_p \quad (16)$$

(c) Plutonium Conservation

The Pu/(Pu+U) ratios in the solid and in the vapor in the pores are denoted by $q(r,t)$ and $u(r,t)$, respectively (using appropriate thermochemical data, u may be described as a function

of T, O/M, and q). The Pu concentration and flux may be written as:

$$\frac{\text{Mass of Pu}}{\text{unit vol. fuel}} = qM_s + u\rho_v V_p N, \quad \text{grams Pu/cm}^3$$

$$\text{flux of Pu} = qJ_s + u\rho_v V_p J_p, \quad \text{grams Pu/cm}^2\text{-sec}$$

In expressing the flux of plutonium by the above formula, solid state diffusion of plutonium has not been considered. Movement of plutonium in the solid by this mechanism would require addition of the diffusive term $-D_s \rho_s (\partial q / \partial r)$, where D_s is the volume diffusion coefficient of Pu⁴ in the mixed oxide, to the purely convective contribution qJ_s in the plutonium flux expression.

Conservation of plutonium is expressed by:

$$\frac{\partial}{\partial t} \left(q \frac{M_s}{\rho_s} + u \frac{\rho_v}{\rho_s} V_p N \right) = - \frac{1}{r} \frac{\partial}{\partial r} \left[r \left(q \frac{J_s}{\rho_s} + u \frac{\rho_v}{\rho_s} V_p J_p \right) \right] \quad (17)$$

As in the total mass balance, the second terms in the parentheses may be neglected because of the smallness of ρ_v/ρ_s and the above equation reduces to:

$$\frac{\partial}{\partial t} (qM_s) = - \frac{1}{r} \frac{\partial}{\partial r} (rqJ_s) \quad (18)$$

Applying the product differentiation rule to Eq (18) and using Eq (15) yields:

$$M_s \frac{\partial q}{\partial t} = - J_s \frac{\partial q}{\partial r} \quad (19)$$

which is subject to the following conditions:

$$q(r,0) = q_0 \quad (20)$$

where q_0 is the cation fraction of plutonium in the fresh fuel.

A solution to Eqs (19) through (21) is:

$$q(r,t) = q_0 \quad (22)$$

Although there may be other solutions to this partial differential equation and its associated initial and boundary conditions, Eq (22) is probably the only physically acceptable one. Eq (22) states that no actinide redistribution occurs due to the migration of closed pores in mixed oxide fuel.

The problem described above has been considered by Lackey, Homan and Olsen⁽⁵⁾. They write the governing conservation equations in finite difference form to facilitate incorporation into an existing fuel modeling code. Their Eqs (13) and (15) may be transformed to differential equations and compared with the equations obtained above; when so converted, their Eq (13) is identical to our Eq (9).

Converting their Eq (15) to differential form in the same manner yields:

$$(u-q) \frac{1}{r} \frac{\partial}{\partial r} (rJ_s) + M_s \frac{\partial q}{\partial t} = - J_s \frac{\partial u}{\partial r} \quad (23)$$

which is not the same as the analogous differential equation developed in the preceding section (i.e., Eq (19)). Their Eq (15) (or Eq (23) above) is believed to be incorrect for the following reason:

Their symbol MA_i represents the mass of heavy metal added to the radial increment i during the time period. Since the density of heavy metal oxides in the vapor is exceedingly small compared with that in the solid, MA_i is essentially entirely made up of the flux of solid fuel with a negligible contribution from the mass of the

heavy metal contained in the vapor of the pores. Consequently, the Pu fraction by which MA_i is multiplied should be that of the solid, not of the vapor in equilibrium with the solid. Making this correction is equivalent to replacing u by q in Eq (23), which then reduces to Eq (19).

Migration of closed pores cannot contribute to actinide redistribution provided that:

(a) The density of the heavy metal oxides in the vapor contained in the pores is very much smaller than the solid density. If ρ_v were comparable in magnitude to ρ_s (as is the case in true zone refining where the moving second phase is a liquid), then the moving phase would have sufficient capacity to store one component and sweep it along the temperature gradient.

(b) Solid state diffusion of plutonium in the mixed oxide is negligible. Analysis of this effect⁽⁶⁾ suggests that the contribution of solid state diffusion may be of some importance in hyperstoichiometric material (in which D_s is large) but is of no consequence when $O/M \leq 2$.

The close connection between observed pore migration and actinide redistribution^(5,7) does not necessarily mean that the latter is directly responsible for the former. Rather, pore migration probably alters the conditions necessary for actinide redistribution by vapor transport along radial cracks or interconnected porosity⁽⁷⁾. First, densification of the columnar grain region by pore sweeping heals cracks and fissures. Second, the creation of the central void lowers the temperature^{and the oxygen-to-metal ratio} of the central part of the fuel, thereby drastically reducing the vapor pressure of the volatile actinide oxides. Hence, both the driving force and the flow area for transport down cracks are reduced by restructuring, and vapor transport of the actinides becomes immeasurably slow.

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