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Steam oxidation of fuel in defective LWR rods

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Abstract

Oxidation of UO_2 by pure steam at pressures of 7 and 70 atm and 500°C and 600°C was measured in a thermogravimetric apparatus. The kinetics are linear, vary as the square root of the steam pressure, and are consistent with initial rates extrapolated from higher-temperature experiments in 1-atm steam. At temperatures characteristic of normal operation of defective fuel rods, the rate of hydrogen production by thermal oxidation of the fuel in steam is small compared with that due to cladding corrosion. The presence of H_2 in the steam has a much greater retarding influence on fuel oxidation than on cladding oxidation. Other potential sources of fuel chemical reactivity in steam, including reaction in cracks in the hot pellet interior and radiolysis of steam by recoiling fission fragments, do not result in significant fuel oxidation. During the incubation stage of fuel-rod degradation, the bulk of the evidence indicates that fuel oxidation is not a major source of the hydrogen in the fuel–cladding gap that eventually may cause secondary-hydriding failure of the rod. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Occasionally a fuel rod develops a small leak during operation. Subsequent damage to the rod develops in two stages. In the first or incubation stage, water rapidly enters the primary defect and replaces the inert gases in the fuel–cladding gap with superheated steam. Because of corrosion of the cladding inner wall by steam, hydrogen is produced and with time replaces steam. If the stress and hydrogen content in the cladding are high, the second or deterioration phase ensues. The secondary defect usually forms far from the primary defect, at locations where the gas is richest in H_2. Massive hydriding of the cladding may cause opening of a long axial split that admits coolant directly into the rod. The dissolved O_2 in the coolant causes the fuel to oxidize, which results in contamination of the primary coolant circuit.

It is widely believed that steam in the gas space of the rod in the incubation stage also causes oxidation of the fuel [1,2]. There are several mechanisms by which oxidation can occur, but in all cases the overall reaction is

$$UO_2 + xH_2O \rightarrow UO_{2+x} + xH_2. \qquad (1)$$

Were oxidation to take place, not only would fuel properties such as thermal conductivity and fission-product retention be degraded, but the fuel would become an additional source of hydrogen, thus promoting the onset of the deterioration phase.

Steam–hydrogen mixtures rather than pure steam are expected to be present in the fuel–cladding gap during the incubation stage. There is no direct evidence of fuel oxidation during the incubation phase. On the one hand, urania and steam thermochemistry favor oxidation; at 500–600°C in pure steam, the equilibrium oxide is U_3O_8 [3]. On the other hand, the much lower oxygen pressures in steam–hydrogen mixtures barely move stoichiometric UO_2 into the UO_{2+x} solid–solution phase field. For example, in steam containing 10 mol% H_2 at 525°C, the equilibrium fuel stoichiometry is $UO_{2.000001}$ [3]. This poses a thermodynamic limitation on the extent of fuel oxidation irrespective of the kinetics of the process.

The purpose of the present paper is twofold: the first is to measure the oxidation kinetics of UO_2 in high-

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pressure steam at temperatures in the 500–600°C range, where no data are available; the second is to combine these data with other information to estimate the extent of fuel oxidation during the incubation phase of the degradation process in a defective fuel rod.

The kinetics of UO_2 oxidation in steam has been studied at temperatures >800°C, but only at 1 atm pressure [4–6]. These investigations were primarily aimed at characterizing severe-accident performance of the fuel. They showed conclusively that the rate is controlled by the surface reaction in which water molecules are decomposed to produce oxygen atoms that enter the solid and H_2 that returns to the gas. Extrapolating these results to 525°C gives an initial rate of oxygen absorption (or H_2 production) in pure steam at 1 atm of $\sim 2 \times 10^{-12}$ mol /cm^2 s. Anticipating the experimental results of Section 2, the fuel oxidation rate in 70-atm pure steam in the 500–600°C temperature range is approximately three times higher than the extrapolated rates based on the high-temperature 1-atm experiments. Therefore, at 70 atm at 525°C, the initial fuel oxidation rate is $\sim 5 \times 10^{-12}$ mol O/cm^2 s. At this rate, oxidation of a pellet of UO_2 to $UO_{2.01}$ would require nearly 8 months, assuming that only the geometric surface area of the pellet was exposed to the steam in the gap. Oxidation of the cladding (sponge Zr at 350°C [7]), which occurs simultaneously, produces H_2 at a rate ~ 10 times larger than that due to fuel oxidation.

On the other hand, post-irradiation examination (PIE) of failed fuel rods often show significantly greater fuel oxidation than suggested by the kinetics described above and the thermodynamic restrictions due to H_2 in the gas in the gap. Une et al. [1] measured the O/U ratio of a failed BWR fuel rod that exhibited a small primary defect near the midplane and a larger secondary-hydriding perforation near the bottom. The rod had been left in the reactor for a few months after detection of the opening of the primary defect. The radially averaged fuel O/U ratio near the opened secondary hydriding blister was ~ 2.06; near the primary defect, the fuel O/U ratio was ~ 2.04. These sizable extents of oxidation are expected due to contact of fuel near the cladding defects with liquid coolant. If water has >3 ppm of dissolved oxygen, U_4O_9 can form. However, the fuel in the intact upper portion of the rod more than 1 m away from the primary defect showed an O/U ratio of ~ 2.02. It is unlikely that liquid water penetrated the gap this far away from the primary defect during operation, so the upper end of the fuel stack must have been exposed to a steam–hydrogen mixture.

Similar observations were reported by Yagnik et al. [8] for two failed but nondegraded BWR fuel rods. After removal from the reactor, the rods remained in pool storage for about two years before PIE. The cladding of both rods suffered a defect due to pellet-cladding interaction and a small through-wall crack at a heavily hydrided region. At locations at least 30 cm from either of the two failures, the radially average fuel O/M ratio was ~ 2.010 in one of the rods and 2.004–2.016 in the other. Although these hyperstoichiometries are less than those reported by Une et al. [1], they are still significantly greater than expected on thermodynamic grounds for fuel exposed to steam–hydrogen at temperatures of an operating defective BWR rod.

These PIE observations of fuel oxidation do not correlate with fuel burnup. This suggests that any changes in internal rod chemistry that may occur during prolonged irradiation do not significantly affect the fuel's propensity towards oxidation in steam. Two independent laboratory observations support this conclusion. First, Matzke's [9] measurement of the oxygen potential of fuel irradiated to burnups from 28 to 150 GWd/tU showed no significant oxidation. The highest possible degree of hyperstoichiometry (as determined by the measured oxygen potential) corresponded to $UO_{2.001}$. The sink for oxygen produced by fission is most likely to be the inner surface of the cladding, where thin (few micron) oxide layers are commonly observed in post-irradiation examination of intact rods.

Second, Imamura and Une [4] compared the rates of steam oxidation at 1000°C of fresh fuel and fuel irradiated to 27 GWd/tU. The latter oxidized 2.6 times faster than the unirradiated specimens. This increase was ascribed to an increase in the fuel surface area accessible to steam in the irradiated material. However, the basic rate constant of the surface reaction that decomposes steam appeared to be independent of burnup of the fuel.

There are several possible explanations for the observations hyperstoichiometry in fuel exposed to steam during the incubation stage of degradation. The first three assume the phenomenon to be real and offer explanations. The last explanation raises the possibility that the observation of hyperstoichiometry is an artifact.

First, the steam oxidation kinetics extrapolated from experiments conducted at 1 atm pressure and high temperature may have missed an oxidation mechanism that appears at low temperatures and high steam pressures. However, the thermodynamic limitation on the O/U ratio of fuel in low-temperature steam–hydrogen gases also appears to have been violated.

A second possibility, adopted by Lewis et al. [10], is that the gas in the gap penetrates cracks in the pellet and reacts with fuel at temperatures much higher than the fuel surface temperature. However, even with access of the gas to the fuel interior, temperatures above 1100°C are required to give a thermodynamic limit of $O/U = 2.01$ in a gas that is 99% steam and 1% H_2. This mechanism is analyzed in Section 3.

A third possibility is radiolysis of steam in the fuel–cladding gap. This hypothesis appears to have originated with Markowitz [11] and continues to be invoked

[10]. Fission fragments recoiling through a steam-filled gap deposit energy at a rate of ~10^{19} eV/cm^3 s [12] and decompose water molecules into H_2O_2, O_2 and H_2. Hydrogen peroxide and molecular oxygen, being much more potent oxidizing agents than water, may react with the fuel despite the presence of H_2. The yield of H_2 in irradiation of pure saturated steam at 70 atm pressure is ~7 molecules/100 eV of deposited energy [13], and each radiolytically produced H_2 is accompanied by an equal number of H_2O_2 molecules. If all H_2O_2 produced in the steam filling a 25-μm thick gap reacted with the fuel, the initial rate of H_2 production from this source would be ~50 times greater than that due to corrosion of a sponge-Zr liner on the cladding inner wall at 350°C. The initial rate of fuel oxidation that must accompany this rate of hydrogen production would be 0.06 O/U units per day.

The above three possibilities are addressed in this paper; the first by experiments; the second by calculation; and the third by recourse to independent data. A fourth possibility is that the oxidized fuel often observed during post-irradiation examination of defective rods, even those which experienced only a small primary flaw but no secondary degradation, is produced after reactor shutdown. Because the reactor is cooled down before the pressure is reduced, at shutdown the fuel–cladding gap becomes flooded with liquid water which contains some oxygen. Fuel temperatures during pool storage are in excess of 100°C, so oxidation over periods of years is likely. In addition, gamma-ray radiolysis of water in the rod, may enhance oxidation of the fuel.

2. UO_2 oxidation by steam at normal operating temperatures

2.1. Experimental

Oxidation of UO_2 was measured at 500°C and 600°C at steam pressures of 70 and 7 atm. Experiments were conducted in a high-pressure thermobalance of the type described in Ref. [14]. The apparatus shown in Fig. 1 is a variant of the earlier design described in Ref. [14]. In the original version, H_2 (or He) flowed through the thermobalance chamber and mixed with injected steam before moving down to the reaction section housing the UO_2 specimen (disks ~1-mm thick and 10-mm diameter) suspended from the balance by a gold chain. The purpose of flowing helium through the upper chamber is to protect the microbalance from the corrosive effects of steam. In the present work, this version was used for the H_2O–H_2 gas mixture experiments.

To study oxidation in pure steam, water is injected at the bottom of the apparatus, as shown in Fig. 1. This modification differs from the original version only by exchange of the locations of water injection and gas-mixture withdrawal. The modified design permits operation in pure steam at temperatures up to 600°C. It maintains helium in the upper chamber to protect the microbalance at the same time permitting a pure steam atmosphere to be established in the reaction zone. Helium flowing downward from the top does not penetrate the reaction chamber steam by molecular diffusion because of the slow upflow of the steam, nor by natural convection currents because its mass density is less than that of the steam below it. In effect, a He/H_2O 'interface' exists at the outlet port. The helium basically acts as a piston pressurizing the steam beneath it.

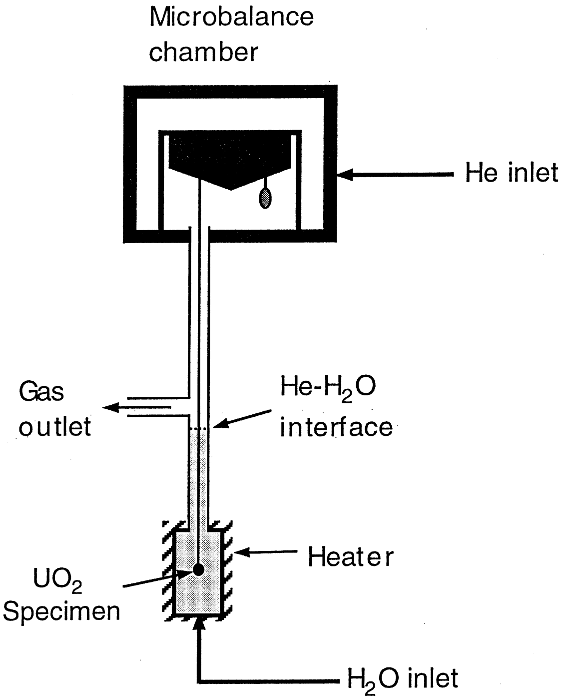

Fig. 1. Modified microbalance for use in high pressure pure steam up to 600°C.

During experiments lasting up to two weeks, the specimen weight, reaction chamber temperature, gas and water flow rates, and system pressure were continuously monitored. The overall weight gain recorded by the thermobalance was checked against before-and-after weight measurements on an external microbalance. To check for the presence of higher uranium oxide phases, the reacted specimens were examined microscopically.

2.2. Results

Only one test was conducted in a mixed H_2/H_2O gas using the original version of the TGA. As expected from the thermodynamic limit to the stoichiometry, no weight gain was observed after one week in 4 mol% H_2 in steam at 70 atm total pressure and 600°C. To allow significant oxidation (i.e., to an O/U approaching the upper phase boundary of the fluorite phase), the H_2 concentration would have to be reduced to a few parts per million at 500–600°C. This low H_2 content in steam is nearly impossible to achieve experimentally, and in addition, this condition is not characteristic of the gas in the gap of a defective fuel rod.

Although not germane to the degradation process in a defective fuel rod, tests in pure steam were conducted for two reasons: First, to see how low-temperature oxidation kinetics compare with the plentiful data at higher temperatures. Second, to determine if the steam pressure affects oxidation kinetics, a point that has not been possible to clarify in the high-temperature experiments.

All tests in pure steam showed a constant rate of weight gain, indicating linear kinetics. In experiments of up to two weeks duration, the maximum observed weight gain corresponded to oxidation of initially stoichiometric specimens to $UO_{2.02}$. This O/U ratio is very far from the equilibrium O/U (~2.7) and is well below the upper phase boundary of the UO_{2+x} phase at these temperatures (>2.1). Therefore, all data represent initial oxidation rates that are unaffected by the ultimate thermodynamic limit. Not surprisingly, examination of the reacted specimens by optical microscopy and by scanning electron microscopy showed the microstructure to be essentially identical to that of the fresh UO_2 [15].

The measured weight gain rates were converted to oxidation rates per unit area (moles O/cm^2 s) to permit comparison with the high-temperature data from the literature. Since the present data represent initial rates unencumbered by equilibrium restrictions, they are compared to the analogous initial rates from the high-temperature data, which are obtained directly from the weight–gain plots or the derived rate constants reported in Refs. [4–6].

Fig. 2 compares the present data with the initial oxidation rates from Refs. [4–6] extrapolated to the present temperature regime. Although the high-temperature tests were conducted in 1-atm steam, their extrapolations represented by the dashed lines in Fig. 2 agree with the present data at 600°C in 7-atm steam.

The results of the experiments in 70-atm steam are shown as the solid triangles in Fig. 2. Like the tests in 7-atm steam, the reproducibility of the measured oxidation rates is quite good. The 70-atm data at the two temperatures exhibit an activation energy (~21 kcal/mol) that is very close to that measured in the high-temperature tests reported in Refs. [4–6]. The 70-atm data, however, lie distinctly above the extrapolations of the high-temperature data, indicating a measurable steam-pressure effect on the oxidation kinetics. The effect of steam pressure on the oxidation rate is shown in Fig. 3. The rates at 70 and 7 atm differ by a factor of ~3, which confirms the root-*p* relation proposed in Ref. [6].

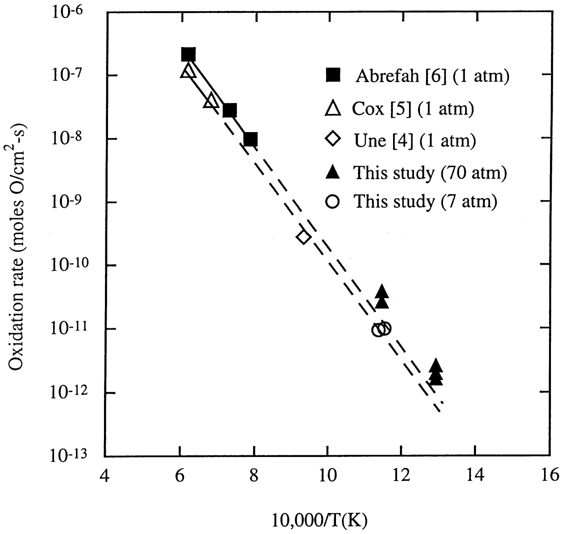

Fig. 2. Initial oxidation rates of UO_2 in pure steam. The dashed lines are extrapolations of the high temperature data.

The relation

$$\text{rate} \propto \sqrt{p} \tag{2a}$$

is shown as the solid curve in Fig. 3. However, the Langmuir-type pressure dependence suggested by Dobrov et al. [16],

$$\text{rate} \propto \frac{Ap}{1+Ap}, \tag{2b}$$

cannot be ruled out on the basis of two experimental points. The dashed curve in Fig. 3 represents Eq. (2b) with $A = 0.042$ atm^{-1}. Unfortunately, distinguishing between these two pressure dependencies was not pos-

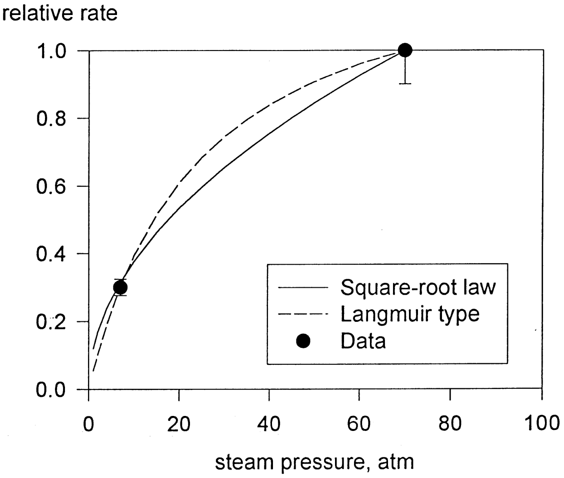

Fig. 3. Steam-pressure effect on UO_2 oxidation at 600°C.

sible with the present apparatus. A test at an intermediate pressure of ∼20 atm would not have had sufficient precision to distinguish between the two curves. At 1 atm steam pressure, the two curves in Fig. 3 differ by a factor of about 2, but the oxidation rate proved to be too low to reliably measure.

3. Effect of gas penetration into cracks in the fuel

The basic reason that essentially no fuel oxidation occurs at the pellet periphery is that the temperature here is too low (< ∼600°C). At these temperatures, not only are the oxidation kinetics in pure steam slow, but the presence of even a small amount of H_2 in the gas places a thermodynamic limit on the O/U ratio that is very near 2.00. However, during normal operation, the fuel is interlaced with a network of cracks caused by thermal stresses generated by the radial temperature gradient in the pellet. These cracks are chiefly radially and axially oriented, thereby providing a communication path between the cold periphery and the hot center.

In a defective fuel rod, the steam–hydrogen mixture fills the crack network as well as the gap. Both fuel oxidation kinetics and (for a fixed H_2O/H_2 ratio in the gas) the equilibrium O/U ratio of the oxide increase with temperature. Consequently, fuel oxidation can occur in the hot central portion of the pellet while the periphery remains essentially stoichiometric. However, the buildup of the O/U ratio in the center of the fuel generates an oxygen concentration gradient in the solid which transports oxygen back to the pellet periphery. Here, because of the hydrogen in the gas and the thermodynamic dictate at this temperature, reduction back to stoichiometric UO_2 takes place. Two experimental observations suggest that the equilibrium O/U ratio very close to 2.00 is maintained at the pellet surface. First, in high-temperature experiments, reduction by hydrogen was found to be very much more rapid than oxidation by steam [6]. Second, Lay's measurement of the chemical diffusion coefficient of oxygen in UO_{2+x} was based on the assumption that a stoichiometry of $UO_{2.00}$ was maintained at the H_2–solid interface [17]. In Lay's experiments, temperatures as low as 600°C were investigated.

Based on the above information, a steady-state cyclical oxidation–reduction is proposed. Steam supplied by a specified H_2O/H_2 gas mixture in the gap diffuses radially inward through the crack network to the center of the pellet where kinetically limited oxidation of the fuel occurs. The reaction products, H_2 in the gas in the cracks and interstitial oxygen ions in the solid, are transported by diffusion in their respective phases to the pellet periphery where the O/U ratio is maintained at 2.00 by efficient hydrogen reduction. The cracked solid is simulated as a radially uniform random population of radial and axial cracks. Circumferential cracks are ignored, so solid state diffusion of oxygen is not impeded by the microstructure. Gas diffusion, however, follows a tortuous path characteristic of porous bodies. The temperature distribution is assumed to be parabolic, with the centerline and surface temperatures specified.

Rather than attempt to solve the gas and solid-state radial diffusion equations coupled by a reaction rate law at the crack surface, the simpler representation shown in Fig. 4 is used. Because the activation energy for fuel oxidation by steam is 50% greater than that of oxygen diffusion in the solid, and because the thermodynamic limit to oxidation is less restrictive at high temperatures, most of the fuel oxidation occurs at the pellet center. In the cylindrical region in Fig. 4 labeled RXN zone, the reaction given by Eq. (1) takes place and the concentrations in both the gas and in the solid are considered to be uniform. The surrounding annular region is reserved for transport only; concentration gradients of H_2 in the gas and of O in the solid generate fluxes of these species shown by the arrows in Fig. 4. Steam moves radially inward in equimolar counterdiffusion with H_2. The boundary between the two zones is set at a fractional radius η_0, which is an adjustable parameter of the model.

The quantitative aspects of the model are given in Appendix A. The model was applied to the following conditions, which are representative of those in a steam-filled defective BWR fuel rod:

- fuel surface and centerline temperatures, 500°C and 1300°C, respectively;
- pellet radius, 0.5 cm;
- pellet fractional open porosity due to cracks, 0.02;
- width of cracks, 2 μm;
- tortuosity of crack path in fractured fuel, 10;
- total pressure, 70 atm.
- During the incubation phase of the development of a degraded fuel element, the H_2 mole fraction of the

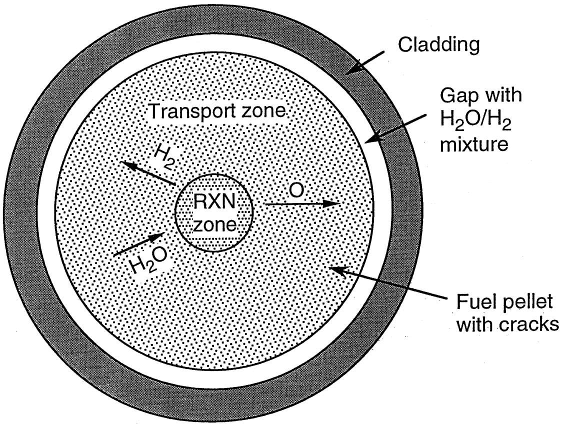

Fig. 4. Two-zone transport/reaction model for steam penetrating cracked UO_2 pellets.

gas in the fuel–cladding gap varies from zero immediately after the primary defect opens to nearly unity, the condition needed for massive hydriding of the cladding. For the present calculation, a mole fraction of H_2 in the gap equal to 0.1 was conservatively selected.

- Radial location of the boundary between the reaction and transport zones: 0.15. The results are not significantly affected if the parameter η_0 is increased from 0.15 to 0.25.

Fig. 5 shows the distribution of the H_2 mole fraction in the cracks and the stoichiometry deviation of the fuel in the pellet after steady state has been attained. The H_2 mole fraction profile is virtually flat because the diffusivity of H_2 in the gas in the cracks is many orders of magnitude larger than the diffusivity of oxygen in UO_{2+x}. Since the latter is thermally activated, the gradient of the excess oxygen concentration becomes progressively steeper as the cool fuel surface is approached.

The volume-averaged stoichiometry of the fuel is 2.005. No reasonable alteration of the parameters of the model produces a significant increase in this result. Fuel oxidation by steam permeating cracks does not appear to be an important process in defective fuel rods.

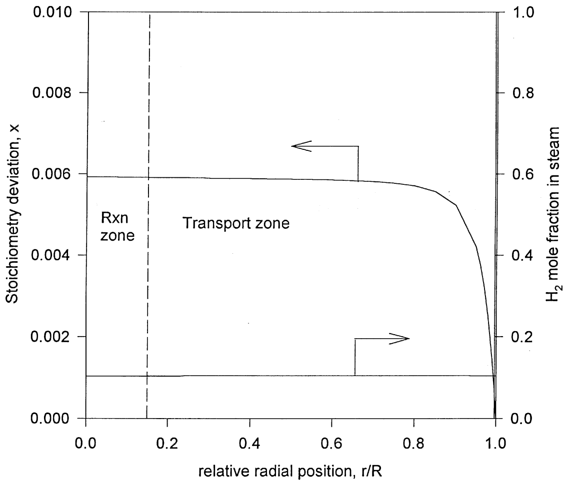

Fig. 5. Concentration profiles calculated from the two-zone oxidation model.

4. Effect of steam radiolysis

The calculation presented in Section 1 showing a potentially significant effect of steam radiolysis on fuel oxidation ignored two crucial mitigating factors. The large fuel oxidation and associated H_2 production rates calculated in Section 1 do indeed prevail at the moment that steam first floods the rod interior following opening of the primary flaw in the cladding wall. However, these rates rapidly decrease because of the effect of hydrogen on the radiolysis process and the limited availability of steam to the rod interior.

4.1. Effect of H_2 on steam radiolysis

In laboratory experiments using alpha particle irradiation of pure steam, the initial radiolytic yields (*G* values) of H_2, and by element conservation, of O_2 and/or H_2O_2 as well, vary from 3 to 10 molecules/100 eV as the saturated-steam temperature increases from 250°C to 300°C [13]. However, in a closed system, the buildup of radiolysis products, including H_2, causes the yields of H_2 to decrease by a factor of ~2 in 20 h. The yields continue to decrease with time until the gas composition reaches a state of radiation equilibrium. At this point, steam decomposition ceases.

In the batch irradiation experiments reported in Ref. [13], the yield of H_2O_2 could not be measured, but radiation-produced O_2 was detectable. On adding H_2 to the steam, the *G*-value for O_2 decreased sharply; for 8.5 mol.% H_2 in the steam at 70 atm, the O_2 yield was a factor of 25 lower than the value in pure steam. The loss of O_2 could have resulted from reaction of this species with the excess H_2 to produce hydrogen peroxide. However, none of this product was detected. It appears that the relatively small concentration of added H_2 essentially stops net water decomposition by efficiently converting O_2 and H_2O_2 back to H_2O. Since substantial H_2 concentrations develop in the fuel–cladding gap of a defective fuel rod by water reaction with the internal cladding surface in a matter of days, steam radiolysis should effectively terminate shortly after opening of the primary flaw [18].

4.2. In-reactor tests

The laboratory experiments described above were intended to measure G values in irradiated steam; the dose rate was insufficient to detect UO_2 oxidation even if it occurred. For the latter purpose, sealed capsules containing water and UO_2, along with structural metals such as stainless steel, Zircaloy, and copper, were irradiated for 25 days in the Halden reactor [19]. The irradiation temperature was approximately 290°C. The objective of these in-reactor tests was to create conditions as favorable as possible for steam radiolysis and UO_2 oxidation. The fuel specimens were coated with highly enriched uranium to increase the fission fragment flux in the steam phase over that delivered by fuel of normal reactor-grade enrichment. Each capsule contained a reservoir of liquid water in order to maintain a fixed steam pressure of ~70 atm. The gap between the fuel surface and the metal heat-sink surface was ~500 μm in order to provide as thick a steam layer for radiolysis as feasible.

The fission fragment energy deposition rate in the steam in the Halden tests was larger than that experienced by the steam in the gap of a defective fuel rod, and was 4–5 orders of magnitude greater than that in the laboratory tests described in the previous section. In the laboratory experiments, wall reactions were suppressed by gold-coating interior metal surfaces of the irradiation chamber. In the Halden tests, on the other hand, the irradiated steam was in direct contact with structural alloys which could compete with the fuel specimens for reactive oxidizing species produced from steam decomposition. This feature was intended to simulate the environment of the steam in the fuel–cladding gap of a defective fuel rod.

Two methods were used for determining fuel oxidation in the Halden test specimens. The first was their weight gain. Following removal from the test rig after irradiation and opening the capsules in the hot cell, the specimens were found to be cracked or chipped and visibly discolored (they had turned from black to brown). The small weight gains that were measured corresponded to O/U increases from 2.00 to as large as 2.04. At the time that these results were published [19], chemical O/U measurements (by oxidation to U_3O_8) had not yet been performed. These have since become available. Five UO_2 samples from five separate capsules showed practically no oxidation. The three specimens reported in Ref. [19] to have gained weight yielded post-irradiation O/U ratios of 2.005, 2.006 and 2.004, respectively. Two other UO_2 specimens, taken from capsules that also contained Zircaloy plates, both showed O/U ratios of 2.008. Since the capsules were assembled at the Halden reactor in air, some O_2 was contained in the initial fill gas. Based on the mass of fuel and the free volume in the capsule, this source of oxygen could have contributed an O/U increase of $\sim$0.007 if all O_2 were absorbed by the fuel specimens and none by the metal internal structures.

The direct O/U measurements by firing to U_3O_8 are judged to be more accurate than the hot-cell measurements of the weight changes before and after irradiation. The former are not affected by mechanical degradation of the specimen and by chemical interaction with and particulate pickup from the metallic components of the capsule. Therefore, the tentative conclusion offered in Ref. [19] that steam radiolysis had induced fuel oxidation needs revision. In view of the direct O/U determinations, there is now no evidence that closed-system irradiation of steam produces oxidation of adjacent fuel. The discoloration of the surface of the specimens in the in-reactor test is indicative of a chemical reaction, probably oxidation. However, this reaction must have been restricted to a very thin layer of the surface because the overall O/U ratio of the specimens was not affected.

Since the capsules were closed systems, any H_2 produced by steam corrosion of the metallic structures would have remained in the 70-atm steam. The null result of the capsule irradiation tests is consistent with the observations from the laboratory alpha-particle experiments of a very significant effect of relatively small H_2 concentrations in suppressing steam decomposition by ionizing radiation [13]. This effect could have been eliminated by using a refreshing-autoclave design for the in-reactor tests, However, this condition would not be representative of that found in a defective fuel rod, where steam access to the fuel during the incubation period of deterioration is highly restricted and significant H_2 concentrations are a certainty.

5. Transport limitations to fuel oxidation

5.1. *Diffusional resistances*

The laboratory experiments and the in-reactor tests described above were of the 'unlimited-steam' type. In both cases, a reservoir of liquid water communicated with the irradiation zone and insured that the steam partial pressure here remained at the saturation value ($\sim$70 atm). In a defective fuel rod, on the other hand, the water reservoir is the coolant outside the fuel rod. It communicates with the fuel via the series transport resistances offered by the small primary defect and the long fuel–cladding gap. The gap is probably closed over most of its length by swollen pellets, but cracks in the fuel periphery provide an equivalent gap for gas transport that is a few tens of microns thick.

Assessment of water vapor transport in this geometry is the object of the DEFECT code [18], but a simple approximate analysis can reveal the extent of the difficulty in supplying the rod interior with steam. The analysis will show that even if all water entering the rod oxidizes the fuel, the extent of oxidation is small. To move into the rod, water vapor diffuses through the primary flaw in the cladding in equimolar counterflow with escaping H_2. The steam then diffuses along the fuel–cladding gap to react with the fuel. To simplify the analysis of the second transport step, diffusion only is permitted for a specified distance along the rod on either side of the primary defect. At the end of the diffusion distance, reaction with fuel reduces the steam mole fraction to zero. The flux of steam into the rod, J, under these restrictions is given by

$$\begin{aligned} J &= \pi r_{\text{flaw}}^2 D_g C_g (1 - y_i)/\delta_{\text{clad}} \\ &= 2 \times 2\pi R_f b D_g C_g (y_i - 0)/L, \end{aligned} \tag{3}$$

where $r_f = 0.5$ cm is the fuel pellet radius, $r_{\text{flaw}} = 15$ μm the equivalent radius of the primary defect, $b = 25$ μm the equivalent thickness of the fuel–cladding gap, $\delta_{\text{clad}} = 0.9$ mm the cladding thickness, $L = 1$ m the diffusion-only distance on either side of the primary defect, $D_g = 0.05$ cm^2/s the diffusion coefficient of H_2O in gap,

C_g the total gas concentration in the gap (assumed ideal), y_i the steam mole fraction in the gap at the location of the primary defect. Eliminating y_i, in the second equality of (3) yields

$$J = \frac{4\pi R_f b D_g C_g}{L(1+\beta)}, \tag{4}$$

where

$$\beta = \frac{4R_f b \delta_{clad}}{r_{clad}^2 L}. \tag{5}$$

With the numerical values given above, $\beta = 2$ and $J = 3 \times 10^{-9}$ mol/s. This water flux is assumed to be consumed completely by a 3-m high fuel stack, which contains ~20 mol of uranium. The time rate of change of the O/U ratio of $\sim 3 \times 10^{-9}/20 = 1.5 \times 10^{-10}$ s^{-1} or $\sim 5 \times 10^{-3}$ yr^{-1}. In one year of operation in the defective state, the 3-m length of fuel would experience an average O/U increase from 2.000 to ~2.005. This result indicates that even if the steam–UO_2 reaction dominated the interior chemistry of a defective rod, the rate of oxidation would be severely restricted by the rate at which steam from the external coolant can be supplied to the fuel inside the rod. Moreover, the calculation is conservative because water consumption by cladding oxidation has been neglected.

5.2. The 'Open System' model

In order to explain the high O/U ratios observed in PIE of defective BWR fuel rods, Une et al. [20] propose that hydrogen starvation conditions are established in the gap. This notion is diametrically opposed to the DEFECT model [8,18], which requires steam-starved conditions for hydriding of Zircaloy to occur. The degree of steam starvation needed to induce rapid hydrogen absorption by sponge-Zr and Zircaloy has been determined experimentally [21]. The open system model proposed by Une et al. [20] does not involve chemical thermodynamic restrictions on fuel oxidation, nor does it allow for either the kinetics of fuel oxidation as discussed in Sections 1 and 2 of this paper, or for the type of transport limitations discussed in Section 5.1. The open system model simply posits that all of the water reaching a particular elevation in the rod following transport in the gap reacts with the fuel. The hydrogen liberated by this reaction (which is given by Eq. (1) above) is then assumed to be immediately absorbed by the adjacent Zircaloy. Since both elements in water are immobilized (in the model), the ensuing pressure reduction draws more water into the rod through the cladding defect. In effect, the combination of Zircaloy at ~350°C and UO_2 at 500–800°C is assumed to be a perfectly efficient water getter.

While this model cannot be totally ruled out, it suffers from a seemingly insurmountable inconsistency: In order to oxidize fuel, the gas in the gap must be rich in water and depleted in hydrogen. On the other hand, in order to hydride the cladding, the gas must be rich in hydrogen and contain very little water. Obviously, the gas cannot possess both attributes simultaneously. Une et al. [20] assume that the former condition prevails but do not explain how Zircaloy can absorb hydrogen from a steam-rich gas.

6. Discussion and conclusions

Several lines of evidence were examined to determine whether steam oxidation of the fuel occurs during the incubation phase of degradation of a defective fuel element. Neither thermal oxidation, reaction in the interior of cracked pellets, nor steam radiolysis can drive the O/U ratio of the oxide above ~2.008. The chief source of the chemical stability of the fuel in irradiated steam appears to be the presence in the gas of a modest (<~10 mol%) concentration of hydrogen. This species is produced by steam corrosion of exposed metals, and at temperatures where fuel in a defective rod operates, strongly inhibits the ability of H_2O to oxidize UO_2. The inhibiting effect of H_2 is due both to its thermochemical influence on fuel stoichiometry and to the resistance it provides for steam transport in a defective rod.

The significant extents of fuel oxidation frequently reported in PIE of defective elements invariably involve massive cladding failure. In these cases, liquid coolant directly contacts the fuel and dissolved O_2 can produce highly hyperstoichiometric uranium oxides. However, this observation does not prove that fuel oxidation occurred during the incubation period following opening of the small primary flaw but before massive cladding failure. During this phase, only superheated steam fills the rod void volumes.

The second possible source of the observed oxidation of fuel removed from cladding that had suffered a split or flaw is reaction during pool storage by liquid water that entered the rod interior during the final reactor shutdown.

In summary, despite PIE observations of oxidized fuel, there is no conclusive evidence that this reaction occurred with steam during the incubation stage following initial cladding perforation. All theoretical arguments, laboratory experiments, and an in-reactor test indicate that UO_2 is resistant to oxidation by irradiated steam as long as a even a minor percentage of hydrogen in present.

The sequence of events following opening of a primary flaw in the cladding are clear. The original fill of pure steam is converted, over a period of days or weeks, to dry H_2. When the H_2/H_2O ratio exceeds a critical value of $\sim 10^3$, rapid absorption of hydrogen by the cladding occurs [21] and may lead to massive failure.

The main uncertainty in the course of this process is whether the fuel or the cladding is primarily responsible for the reaction with steam that produces the H_2. The kinetics of steam oxidation of sponge-Zr or Zircaloy is well known. This reaction persists even in mixed gases containing as little as a few percent H_2O in H_2. The evidence presented in this paper suggests that UO_2, even under irradiation, is not as powerful a reducing agent for steam as is zirconium or Zircaloy. Consequently the fuel is an inert substance during the incubation stage of the degradation process in failed cladding.

Appendix A. Cyclical model of the oxidation of cracked fuel by steam–hydrogen gases

As shown in Fig. 4, the fuel pellet is divided into a hot central reaction zone surrounded by an annular region where diffusional transport occurs. The transport zone is in the range $\eta_0 < \eta < 1$, where η is the radial position relative to the pellet radius. Here, H_2 conservation in the gas in the cracks is expressed by

$$\frac{d}{d\eta}\left(\eta\frac{dq}{d\eta}\right) = 0, \tag{A.1}$$

where q is the H_2 mole fraction in the gas at radial position η. The first integral of Eq. (A.1) is

$$\frac{dq}{d\eta} = -\frac{C_1}{\eta}, \tag{A.2}$$

where C_1 is the integration constant. Using the boundary condition $q(\eta = 1) = q_1$, the specified H_2 mole fraction in the gas in the gap, the second integral is

$$q = -C_1 \ln \eta + q_1. \tag{A.3}$$

The above analysis has neglected the temperature dependence of the gas-phase diffusion coefficient. This property is evaluated at the arithmetic mean temperature of the fuel at the periphery (T_1) and on the centerline (T_0).

The diffusion coefficient of oxygen in UO_{2+x}, on the other hand, has too strong a temperature dependence to ignore. According to Lay [17], it is

$$D_0 = A_0 e^{-E_0/T}, \tag{A.4}$$

where $A_0 = 0.5$ cm^2/s and $E_0 = 14\,350$ K.

Oxygen conservation in the solid portion of the annular transport region is expressed by

$$\frac{d}{d\eta}\left(\eta e^{-E_0/T}\frac{dx}{d\eta}\right) = 0, \tag{A.5}$$

where x is the oxygen excess at fractional radius η. The first integral of Eq. (A.5) is

$$\frac{dx}{d\eta} = -\frac{B_1}{\eta e^{-E_0/T}} \tag{A.6}$$

and the second integral is

$$x = B_1 \int_{\eta}^{1} e^{E_0/T}\frac{d\eta'}{\eta'} + x_1. \tag{A.7}$$

According to the assumption of gas–solid equilibrium at the fuel periphery x_1 is the oxygen excess at temperature T_1 in steam of H_2 mole fraction q_1; x_1 is essentially zero.

A parabolic temperature distribution in the fuel is assumed:

$$T = T_1 + (T_0 - T_1)(1 - \eta^2). \tag{A.8}$$

For the inner reaction zone in Fig. 4, oxidation of the fuel takes place at the volume-average temperature:

$$T_{RXN} = \frac{2}{\eta_0^2}\int_0^{\eta_0} \eta T(\eta)\, d\eta. \tag{A.9}$$

The rate of reaction of UO_{2+x} with steam containing water vapor and hydrogen at partial pressures of p_{H_2O} and p_{H_2}, respectively, is taken from the equation proposed by Dobrov et al. [16]. This equation fits the high-temperature data of Refs. [5,6] quite well. Dobrov's equation, as applied to the reaction zone of Fig. 4, is

$$R_{RXN} = \rho_U k_0 \exp\left(-\frac{E_{RXN}}{T_{RXN}}\right) \frac{A(1-q_0)P_{tot}}{1 + A(1-q_0)P_{tot}}\left[1 - \frac{a_0(T_{RXN}, x_0)}{(1-q_0)/q_0}\right], \tag{A.10}$$

where R_{RXN} is the reaction rate, moles O (or H_2) per cm^2 s, $\rho_U = 0.041$ mol/cm^3 the molar density of uranium in UO_2, $k_0 = 2.2$ cm/s the pre-exponential factor of surface reaction rate constant, $E_{RXN} = 21\,250$ K the activation energy of the surface reaction rate constant, $A = 2.5$ atm^{-1} the steam–pressure effect parameter, $P_{tot} = 70$ atm the total pressure, q_0 the mole fraction of H_2 in the cracks in the reaction zone, x_0 the oxygen excess in the oxide in the reaction zone.

$a_0(T_{RXN}, x_0)$ is the steam-to-hydrogen ratio that would be in equilibrium with UO_{2+x_0} at temperature T_{RXN}. This quantity is a form of the oxygen activity of the solid oxide, and it is calculated from the free energy of formation of water vapor coupled with the thermochemical model of UO_{2+x} developed by Blackburn [22]. The last term in the brackets in Eq. (A.10) gives the extent of disequilibrium between the gas and solid phases in the reaction zone.

The fluxes of H_2(g) and O(s) leaving the reaction zone and entering the transport zone are given by

$$J_{H_2} = -\frac{\varepsilon D_g C_g}{R_f \tau}\left(\frac{dq}{d\eta}\right)_{\eta=\eta_0} \quad \frac{\text{moles } H_2}{\text{cm}^2\ \text{s}}, \tag{A.11}$$

where ε is the porosity of cracked solid, τ the tortuosity of diffusion path in cracked solid, D_g the diffusivity of H_2/H_2O binary gas (cm^2/s) (Ref. [22], Appendix A), C_g the molar concentration of gas (assumed ideal) (mol/cm^3), R_f the radius of fuel pellet (cm) and

$$J_0 = -\frac{\rho_U A_0 \exp\left(-E_0/T(\eta_0)\right)}{R_f}\left(\frac{dx}{d\eta}\right)_{\eta=\eta_0} \quad \frac{\text{moles O}}{\text{cm}^2\ \text{s}}. \tag{A.12}$$

The concentrations x_0 and q_0 are determined by H_2 and oxygen balances on the reaction zone. Each mole of H_2 produced by the reaction of Eq. (1) generates one mole of interstitial oxygen. Both of these must leave the reaction zone at equal rates, or

$$J_{H_2} = J_0. \tag{A.13}$$

With the gradients at η_0 expressed by Eqs. (A.2) and (A.6), substitution of Eqs. (A.11) and (A.12) into Eq. (A.13) yields the constant of proportionality relating the integration constants B_1 and C_1

$$B_1 = \left(\frac{\varepsilon D_g C_g}{\rho_U \tau A_0}\right) C_1. \tag{A.14}$$

The product $D_g C_g$ varies as $\sim T^{0.68}$ [22], and for the purposes of the present analysis, is taken to be a constant evaluated at the mean fuel temperature.

A second condition satisfies the stoichiometry of Eq. (1): for each mole of steam reacted, one mole of H_2 is produced and leaves the reaction zone. This yields the relation

$$J_{H_2} = \frac{1}{2}\eta_0 R_f \sigma R_{RXN}, \tag{A.15}$$

where σ is the surface area (due to cracks) per unit fuel volume. The mean width of the cracks is $2\epsilon/\sigma$. Substituting Eqs. (A.10) and (A.11) (with the gradient in the latter replaced by Eq. (A.2)) gives

$$C_1 = \left(\frac{\sigma\tau R_f^2 \eta_0^2 \rho_U k_0}{2\varepsilon D_g C_g}\right) \exp\left(-\frac{E_{RXN}}{T_{RXN}}\right) \frac{A(1-q_0)P_{tot}}{1 + A(1-q_0)P_{tot}}\left[1 - \frac{a_0(T_{RXN}, x_0)}{(1-q_0)/q_0}\right]. \tag{A.16}$$

The solution algorithm is as follows:

1. A value of C_1 is guessed.
2. q_0 is obtained from Eq. (A.3) at $\eta = \eta_0$.
3. B_1 is computed from Eq. (A.14).
4. x_0 is obtained from Eq. (A.7) at $\eta = \eta_0$.
5. C_1 is computed from Eq. (A.16). If this value agrees with the guess in step 1, the solution has been achieved.

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