

# MECHANISM OF THE LOCAL CORROSION OF FUEL ELEMENT CLADDING DUE TO DECOMPOSITION OF HYDROGEN SOLUTION IN THE NEIGHBORHOOD OF THE COOLANT SATURATION TEMPERATURE

A.S. IVANOV, P.A. KALASHNIKOVA, A.A. KOVALISHIN, M.D. TARAN

NRC "Kurchatov Institute", Academician Kurchatov Square, 1, 123182, Moscow, Russia

Email contact of corresponding author A.S. Ivanov: asi.kiae@gmail.com

## Abstract

A detailed study of the process of hydrogen release into gas-vapor bubbles in the neighborhood of the coolant saturation temperature was performed. The processes of dissolution and diffusion were taken into account. It was found that the decrease in the concentration of hydrogen in the liquid phase occurs until the flow of hydrogen into the bubbles is comparable to the production of hydrogen due to radiolysis. In this case, a jump in the hydrogen concentration leads to a sharp restructuring of the entire picture of the time dependences of the components concentrations. This is especially true for the behavior of the  $O_2$  and  $H_2O_2$  concentrations, i.e. main oxidants of zirconium cladding of fuel elements. It has been shown that the hydrogen concentration in the coolant may decrease by orders of magnitude in a short time. In this case the efficiency of radiolytic oxygen suppression reduces drastically, and concentration of the radiolytic oxygen and hydrogen peroxide in the coolant may increase considerably, thus promoting local oxidation of fuel element claddings.

## 1. INTRODUCTION

Despite the absence of deviations of monitored quality parameters of the primary circuit coolant from the allowed value ranges, essentially deeper corrosion of fuel element claddings is observed for operation at the thermal power level of up to 104% of  $N_{nom}$  and when implementing the 18-month fuel cycle, compared to the operation according to the previously used operating procedure [1]. This may point to involvement of new corrosion mechanisms when increasing the reactor power, and may necessitate making corrections to the requirements for the water-chemistry regime (WCR) of the primary coolant for operation at the elevated power level. The point is that the conclusion about the absence of water chemistry upsets pertains to integral parameters of the coolant quality, but the coolant water chemistry may change locally, only in a certain area, while integrally remaining within the specified requirements throughout the entire circuit. The radiolysis suppression conditions may also change locally in this case.

End (stable) products of radiolysis include the following three substances: hydrogen  $H_2$ , oxygen  $O_2$ , and hydrogen peroxide  $H_2O_2$ . It should be emphasized that  $O_2$  and  $H_2O_2$  are most important in terms of the corrosion problems. The initial concentration of  $H_2$  in the coolant determines equilibrium concentrations of hydrogen itself and of  $H_2O_2$  and  $O_2$ , i.e. the ratio of equilibrium concentrations of all three radiolysis products.

As a result of presaturation of the circuit water by hydrogen, equilibrium concentrations of  $H_2O_2$  and  $O_2$  tend to zero after the reactor has reached full capacity. This is precisely the phenomenon called "radiolysis suppression". Therefore, it is hydrogen content that plays the role of one of the key factors influencing the corrosion processes.

The hydrogen concentration reduction value depends on the gas phase nucleation and growth kinetics, and on the kinetics of hydrogen release to bubbles formed in the neighborhood of the

saturation temperature. The concentration and sizes of the gas phase nuclei play an essential role here [2, 3].

The sharp local decrease in the hydrogen concentration and the corresponding increase in the radiolytic oxygen content may be due to two phase transitions in the reactor coolant at successive temperatures. First of all, this is decomposition of hydrogen solution in the coolant in the neighborhood of the boiling point, followed by the liquid-vapor phase transformation. Thus, behavior of solubility of hydrogen in the coolant under operating conditions, especially near the saturation temperature, is one of the basic elements controlling the WCR stability.

## 2. DIFFUSION OF DISSOLVED HYDROGEN INTO FORMED BUBBLES IN THE NEIGHBORHOOD OF THE SATURATION POINT

We consider the problem of gas diffusion into a bubble with a moving phase boundary in a bounded spherical domain of radius  $S$  (see Fig. 1). The initial domain radius  $S_0$  is defined by the concentration of bubbles in the liquid phase, with the initial bubble radius  $R_0$ .

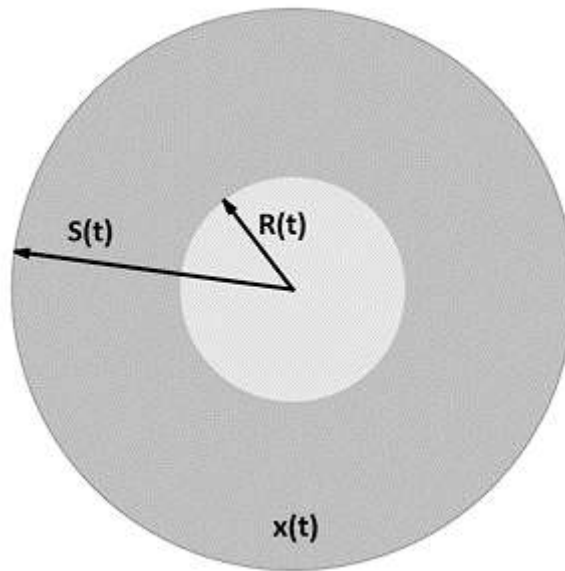


FIG. 1. Schematic representation of the liquid–bubble system at time  $t$ .

Denote the number of the dissolved gas molecules per unit volume as a function of distance  $r$  from the bubble center at time  $t$  by  $n(r, t)$ . For the diffusion mode, the bubble growth dynamics can be described by the following differential equation [2]:

$$\frac{\partial n(r, t)}{\partial t} = D\Delta n(r, t) - \text{div} [n(r, t)\vec{v}(\vec{r}, t)], \quad (1)$$

$\vec{v}(\vec{r}, t)$  is the velocity field, and  $D$  is the diffusion coefficient of hydrogen in water.

In the spherical coordinate system with the origin at the bubble center the liquid velocity is characterized only by the radial component  $v_r(r, t)$ :

$$v_r(r, t) = \frac{R^2(t)}{r^2} \frac{dR(t)}{dt}, \quad (2)$$

where  $R(t)$  is the bubble radius.

Initial condition:

$$(r, 0) = n_0, r \in [R_0, S_0]. \quad (3)$$

Symmetry condition on the moving outer boundary of the domain:

$$\left(\frac{dn}{dr}\right)_{r=S} = 0; t \geq 0. \quad (4)$$

The condition on the bubble surface is written for two temperature ranges.  $T < T^*$  and  $T > T^*$ ,  $T^*$  - decomposition temperature of the hydrogen solution.

When there is solubility ( $T < T^*$ ), this is the Henry's law:

$$\begin{aligned} x(R, t) &= \frac{P_{H_2}}{k_H}; t \geq 0, \\ P_{H_2} &= n_{H_2} kT, \end{aligned} \quad (5)$$

where  $x(R, t)$  is the mole fraction of hydrogen on the bubble surface, and  $n_{H_2}$  is the concentration of hydrogen molecules in the bubble.

When there is no solubility ( $T > T^*$ ):

$$x(R, t) = 0. \quad (6)$$

The partial pressure of hydrogen in the bubble  $P_{H_2} = P - P_{H_2O} + 2\sigma/R$ , where  $\sigma$  is the water surface tension coefficient. The increase in the amount of hydrogen in a bubble increases its radius. At the initial instant the mole fraction of hydrogen in the liquid phase is taken as  $x_0$ . Gas diffuses from the liquid to the bubble until the equilibrium concentration  $x_F$  is reached. The equation for the bubble radius can be found from the equilibrium condition of hydrogen molecules:

$$\frac{d}{dt} \left( \frac{4}{3} \pi R^3 n_{H_2} \right) = 4\pi R^2 D \left[ \frac{\partial n(r, t)}{\partial r} \right]_{r=R(t)}; t \geq 0. \quad (7)$$

This relationship corresponds to the diffusion flow of hydrogen molecules through the surface of radius  $R(t)$ . System of equations (1-7) was solved numerically. Results of numerical calculations were obtained for parameters corresponding to the reactor conditions.

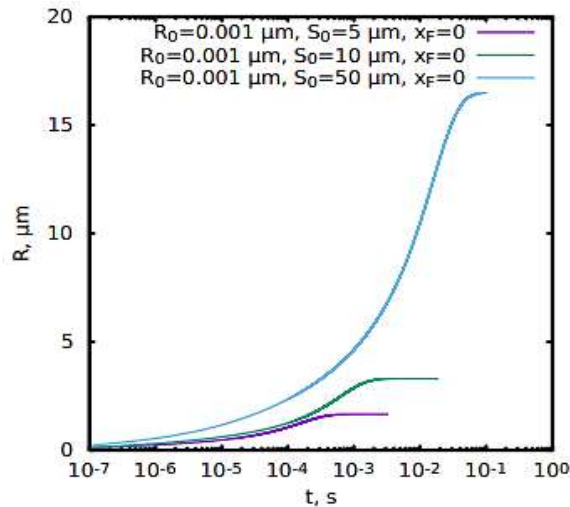


FIG. 2. Bubble radius versus time for three cases of the initial domain size  $S_0$  in the case of complete release of hydrogen ( $x_F = 0$ ).

Fig. 2 shows the bubble radius versus time for three cases of the initial domain size  $S_0$  in the case of complete release of hydrogen ( $x_F = 0$ ). For  $S_0 = 5 \mu\text{m}$ , the characteristic time of the hydrogen solution decomposition is  $\sim 5 \cdot 10^{-4}$  s. When  $S_0 = 10 \mu\text{m}$ , this time equals  $\sim 2 \cdot 10^{-3}$  s, and for  $S_0 = 50 \mu\text{m}$  it increases to  $\sim 5 \cdot 10^{-2}$  s. According to the obtained data, the hydrogen content of the coolant may reduce by several orders of magnitude during time  $\tau \sim 10^{-3}$  s or  $\sim 10^{-1}$  s depending on the concentration of bubbles. In actual situations, however, the minimum concentration of critical nuclei in the reactor coolant at conditions under consideration according to our estimates is close to  $10^{11} \text{cm}^{-3}$ . This corresponds to  $S_0 \sim 5 \mu\text{m}$ , and thus the characteristic time of the hydrogen solution decomposition will be  $\sim 5 \cdot 10^{-4}$  s.

### 3. JOINT SOLUTION OF THE PROBLEMS OF RADIOLYSIS AND THE KINETICS OF HYDROGEN RELEASE INTO BUBBLES

To estimate the change in the concentrations of  $\text{H}_2\text{O}_2$  and  $\text{O}_2$  with a sharp decrease in the concentration of hydrogen in the liquid phase, it is necessary to jointly solve the diffusion and the radiolysis problems.

The kinetic model describing the change in the concentrations of radiolysis products over time is a system of nonlinear differential equations (8) for all components [4]. The last term in this equation corresponds to the convective and diffusion transfer of solution components.

$$\frac{\partial c_i}{\partial t} = (J_Y G_Y^i + J_n G_n^i + J_\alpha G_\alpha^i) + \sum_{p,q} k_{pq} c_p c_q - \sum_r k_{ir} c_i c_r + F_i; \quad (8)$$

$$F_i = -\text{div}(c_i \vec{v}) + \text{div}(D_i \text{grad} c_i).$$

Here  $c_i, c_p, c_q, c_r$  – are the concentrations of particles of types  $i, p, q, r$ ;  $k_{pq}$  and  $k_{ir}$  – respectively, the rate constants for the formation and annihilation of particles of type  $i$  in reactions between particles  $p, q, r$ ;  $\sum_{p,q}$  – means the summation over all reactions leading to the formation of particles of the type  $i$ ;  $\sum_r$  – summation over all reactions in which particles of type  $i$  disappear.

Track outputs  $G_i$  are recommended for use by IAEA technical documents [5].  $D_i$  – is the diffusion coefficient of component  $i$ ;  $\vec{v}$  – is the velocity field.

The hydrogen concentration in the coolant changes very quickly, almost stepwise, and this allows us to significantly simplify the solution. In accordance with this, we approximate the function  $F_i$  in equation (8) using the relation:

$$F_i = -k c_m \delta_{im} \theta(t - t_0), \quad (9)$$

$$\theta(t - t_0) = \begin{cases} 0, & t < t_0; \\ 1, & t \geq t_0, \end{cases}$$

where index  $m$  – refers to molecular hydrogen;  $\theta(t - t_0)$  – Heaviside function;  $k = 1/\tau$ ,  $\tau$  – is the characteristic time of hydrogen release into bubbles;  $t_0$  – is the start time of the hydrogen yield jump.

The numerical integration of the system of equations (8) with condition (9) was carried out in [6]. Fig. 3 shows the evolution of six relative concentrations of the components  $\text{H}_2, \text{H}, \text{H}^+, \text{O}_2, \text{OH}^-, \text{H}_2\text{O}_2$  under the action of radiolysis of an aqueous solution of  $\text{H}_2 - 4,4 \cdot 10^{-5}$ ;  $\text{O}_2 - 4,4 \cdot 10^{-9}$  (moles

fractions) in the presence of a sharp drop in the concentration of hydrogen. The dotted line shows the behavior of the lines in the absence of a jump in the  $H_2$  concentration.

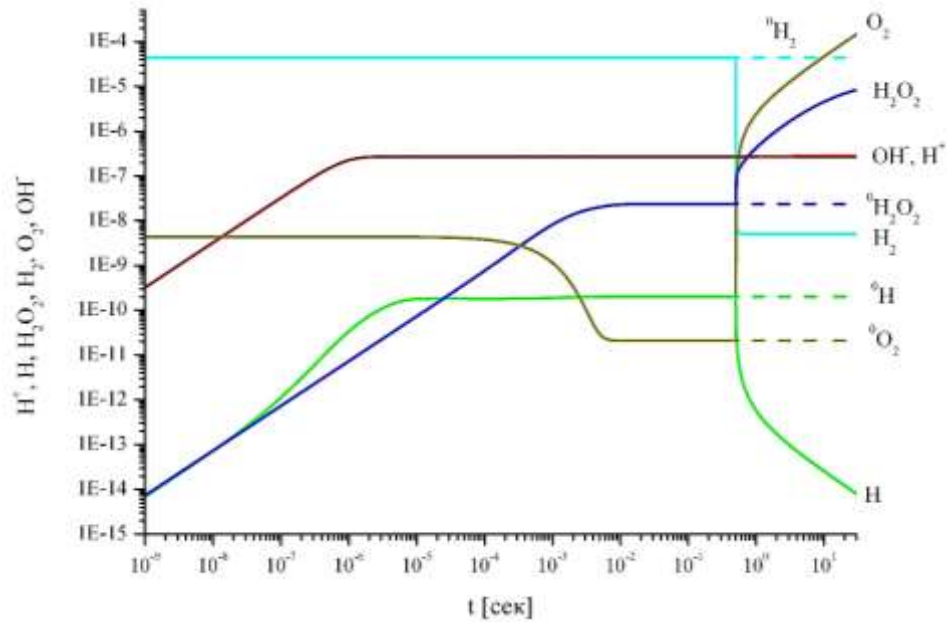


FIG. 3. Radiolysis of an aqueous solution of  $H_2 - 4,4 \cdot 10^{-5}$ ;  $O_2 - 4,4 \cdot 10^{-9}$ . Jump parameters of  $H_2$ :  $t_0 = 0,5$  s;  $\tau = 5 \cdot 10^{-4}$  s.

A decrease in the hydrogen concentration occurs until the flow of hydrogen into the bubbles is equal to the production of hydrogen due to radiolysis. According to Fig. 3, a jump in the hydrogen concentration leads to a sharp restructuring of the entire picture of the time dependences of the component concentrations. In particular, this concerns the behavior of the concentrations of  $O_2$  and  $H_2O_2$ , i.e. basic oxidizing agents for zirconium fuel rod claddings. The mole fraction of oxygen by the time of 1 s jumps approximately by five orders of magnitude up to  $\sim 5 \cdot 10^{-6}$ .

Note that the admissible for operation at power  $>50\%$   $N_{nom}$ . oxygen concentration does not exceed  $0.005 \text{ mg/dm}^3$  [7] or  $\sim 2.8 \cdot 10^{-9}$  in mole fractions. Thus, the oxygen concentration relative to the allowable value when the reactor is operating at a power of  $>50\%$   $N_{nom}$ . can increase more than 1000 times. Similar behavior is demonstrated by hydrogen peroxide  $H_2O_2$ . However, here the increase in its relative concentration by the same time is somewhat more than one order of magnitude.

#### 4. CONCLUSION

The analysis carried out in this work has shown that a sharp local decrease in the hydrogen concentration and a corresponding increase in the radiolytic oxygen content may cause the oxide layer build-up on the surfaces of VVER fuel element claddings. This is due to two phase transitions occurring in the reactor coolant at successive temperatures – decomposition of hydrogen solution in the coolant in the neighborhood of the saturation temperature, followed by the liquid–vapor phase transformation. In this case, the coolant may in some zones deviate from the strict water-chemistry regime aimed to suppress radiolysis. It has been shown that the hydrogen concentration in the coolant may decrease by orders of magnitude in a short time. In this case the efficiency of radiolytic oxygen suppression reduces drastically, and concentration of the radiolytic oxygen and hydrogen peroxide in the coolant may increase considerably, thus promoting local oxidation of fuel element claddings.

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