Effect of steam on UO\textsubscript{2} pellet oxidation in fuel rod using thermodynamic calculation

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1. Introduction

UO\textsubscript{2} pellets are exposed to steam injection resulting from fuel rod leakage that may mostly occur under transient and normal operating conditions [1]. As a result, fission fragments released as the UO\textsubscript{2} fragments by oxidation of UO\textsubscript{2} pellets can cause primary cooling water contamination [2]. Therefore, maintaining the integrity of the UO\textsubscript{2} in steam atmosphere lowers the radioactivity inside the reactor under normal operations [3-6].

When leakage occurs in fuel rod, coolant starts to get into the fuel rod and evaporates, as a result, the H\textsubscript{2}O(g) reacts with UO\textsubscript{2} pellets and zirconium tube inner wall. As a result, the gas mixture inside the fuel rod gradually becomes reducing by increasing the relative hydrogen partial pressure (P\textsubscript{H\textsubscript{2}}) due to the reaction between them. The oxygen partial pressure (P\textsubscript{O\textsubscript{2}}), determined by the ratio of water vapor and hydrogen gas partial pressures (P\textsubscript{H\textsubscript{2}O}/P\textsubscript{H\textsubscript{2}}) in the leaked fuel rod, is the factor that determines the tendency for the oxidation and reduction of the UO\textsubscript{2} pellets [7-9]. In general, UO\textsubscript{2} (oxygen to uranium ration, O/U = 2.0) can be oxidized to U\textsubscript{3}O\textsubscript{8} (O/U = 2.67) within the steam.

In this study, the equilibrium oxygen partial pressure calculation at a pressure of 15.5 MPa, which is the system pressure in PWRs, was calculated to assess the tendency of oxidation for the UO\textsubscript{2} by steam. The results were applied to p-C-T diagram so that stabilized phased could be indicated in phase diagram of the U-O system with the oxygen isobars.

2. Calculation methods

Oxygen potential calculations were made using equilibrium oxygen partial pressures and performed to evaluate the UO\textsubscript{2} pellet oxidation behavior by the steam injected into the leaked fuel rod at the system pressure of the PWR [10]. This was done by using the thermodynamic data. The oxygen potential can be calculated with the following equation:

\[
\ln \frac{P_{O_2}}{P_{H_2O}} = \frac{\Delta G^0}{RT} + \ln \frac{X_{H_2}}{X_{H_2O}}
\]

where R, T, P, X, and P\textsubscript{O\textsubscript{2}} are the gas constant, temperature (in Kelvin), total pressure, total pressure coefficient, and equilibrium oxygen partial pressure (in atm), respectively. Through the Olander equation [10], the P\textsubscript{O\textsubscript{2}} and oxygen potential (\Delta G\textsubscript{O\textsubscript{2}}) were calculated according to the steam temperature at a pressure of 15.5 MPa. In addition, the calculations were also done for a pressure of 0.1 MPa. Furthermore, the oxygen potential sensitivity of each total pressure and temperature with PH\textsubscript{2}O/PH\textsubscript{2} conditions were calculated. The equilibrium gas mixture ratio at each temperature was calculated using the following equation [10]:

\[
\frac{P_{H_2O}}{P_{H_2}} = \frac{C_m}{RT}
\]

where \Delta G\textsuperscript{0}, PH\textsubscript{2}, and PH\textsubscript{2}O are the Gibbs free energy of the H\textsubscript{2}O formation, hydrogen partial pressure, and water vapor partial pressure, respectively.

The equilibrium oxygen partial pressure obtained was applied to the relationship between the temperature-dependent oxygen partial pressure and O/U [11] to determine the equilibrium oxide formed at the steam pressure conditions of 0.1 and 15.5 MPa. Specifically, MATLAB Symbolic Math ToolboxTM was used to obtain the O/U change with temperature. The equilibrium oxides at each temperature were indicated by superimposing on the revised phase diagram with the oxygen pressure isobars, referred to as the PO\textsubscript{2}-composition-temperature diagram (p-C-T diagram) [11].

3. Results and discussion

Figure 1 shows the results of calculating the equilibrium oxygen partial pressure of the steam at the total pressure of 0.1 and 15.5 MPa using D.R. Olander’s equation. The equilibrium oxygen partial pressure and potential at a pressure of 15.5 MPa are both higher than at 0.1 MPa.

![Fig. 1. Calculated oxygen partial pressure and potential of pure steam with temperature at total pressure of 0.1 and 15.5 MPa (12).](image-url)
The results of the oxygen potential changed by the enrichment of oxygen and hydrogen are shown in Fig. 2 in terms of the temperature and total pressure. It seems that oxygen potential at 0.1 MPa in the range of hydrogen-rich area, disappears, but it is just overlapped by the oxygen potential at 15.5 MPa and appear invisible. It can be observed that the higher the pressure, the higher the oxygen potential. However, this tendency is apparent in the oxygen-enriched region and converges in the hydrogen-enriched region. That is, in a reducing atmosphere with a high $H_2(g)$ partial pressure ($P_{H_2}$), there is no difference in the oxygen potential, regardless of the total pressure.

Typically, oxygen potential increases with temperature due to increase in the equilibrium oxygen partial pressure (see Fig. 1). However, the equilibrium partial pressure as a function of temperature is significantly lower than the amount of oxygen enrichment in the O-enriched region. Namely, it overwhelms the equilibrium oxygen partial pressure of steam so that the oxygen partial pressure remains constant as much as the oxygen enrichment.

As time goes by after the leakage, the atmosphere changes into reducing one. This trend can explain why $UO_2$ pellets are not heavily oxidized in leaked fuel rod. As shown in Fig. 2, as a result of the oxidation, oxygen potential can be sustained at lower value by consuming oxygen and generating hydrogen. As a result, $UO_2$ pellets are not oxidized after a certain time. Of course, there are other gaseous fission molecules but, there are no results of any effect on oxidation behavior in $UO_2$ pellets.

Figure 3 shows the p-C-T diagram presented in Y.S. Kim’s article [11] and the results of the oxygen partial pressures of 0.1 and 15.5 MPa, where O/U are superimposed. As calculated in Fig. 1, it can be seen that the lower total pressure has a low degree of oxidation owing to lower equilibrium oxygen partial pressure. When $UO_2$ pellets are cooled from 1400 to 400°C and exposed to pure steam at a pressure of 0.1 MPa, the $U_3O_8$ phase can form by passing through five phase boundaries, starting with $UO_2$. As the temperature from 1400 °C, the fluorate structure of the $UO_2$ is transformed in $U_3O_8$, having a high density of the layered structure from 463°C firstly, from which a serious breakage of $UO_2$ pellet occurs. That is, its integrity is maintained to a temperature of about 463°C or more; however, below this temperature, spallation in pellets occurs due to the decrease in density caused by a change in the crystal structure. On the other hand, at 15.5 MPa, $U_3O_8$ is produced more quickly at higher temperatures at about 1400 °C. It seems that $UO_2$ integrity is vulnerable to high pressure steam.

The calculation results of the steam injection due to the damage of the fuel rod maintain a certain ratio of mixed gases in the fuel rod, and as a result, it is possible to confirm how far the oxidation of the $UO_2$ pellet proceeded according to the equilibrium oxygen partial pressure with temperature through previous calculation result shown in Fig 1 - 3. However, the oxygen partial pressure maintained in the leaked rod according to the previous PIE results were reported [13,14], and through this, it can be seen that a reducing atmosphere is created by reaction with internal substances, and as a result, oxidation does not proceed much.

One limitation of this study is that the method to measure the oxidation tendency in leaked fuel has been dealt with in terms of thermodynamic approach without kinetic evaluation. Therefore, how fast the integrity of $UO_2$ is collapsed cannot be evaluated by using this method. In terms of dose rate increase by fuel rod damage, the approach to kinetically calculate the oxidation rate of $UO_2$ to $U_3O_8$ should be done.

4. Conclusions

Calculations using thermodynamic data were performed to predict the behavior of the $UO_2$ pellets
oxidized in a pure steam atmosphere due to fuel rod leakage used in the PWR reactors.

As the total pressure increases, the equilibrium partial pressure of oxygen increases, so the oxygen potential increases. Therefore, in PWR operating under 15.5 MPa, the integrity of the UO$_2$ pellet is more severe than oxidation at atmospheric pressure. In particular, in the case of 15.5 MPa, spallation may occur due to transformation to U$_3$O$_8$ even in the central temperature range of the pellets. However, unlike the result of thermodynamic calculation, it was confirmed that the oxidation of UO$_2$ would not develop very seriously due to the conversion to a reducing atmosphere by an increase in hydrogen partial pressure.

REFERENCES