Effect of steam on UO_2 pellet oxidation in fuel rod using thermodynamic calculation

Tae-sik Jung*, Yeon-soo Na, Min-jae Joo, Kwang-young Lim, Yoon-ho Kim, Seung-jae Lee
Materials Development Section of Nuclear Fuel Technology Department, KEPCO Nuclear Fuel, Daejeon 34057, Republic of Korea
**Corresponding author: taesik@knfc.co.kr*

1. Introduction

UO_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_2 fragments by oxidation of UO_2 pellets can cause primary cooling water contamination [2]. Therefore, maintaining the integrity of the UO_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 $H_2O(g)$ reacts with UO_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_{H_2}) due to the reaction between them. The oxygen partial pressure (P_{O_2}), determined by the ratio of water vapor and hydrogen gas partial pressures (P_{H_2O}/P_{H_2}) in the leaked fuel rod, is the factor that determines the tendency for the oxidation and reduction of the UO_2 pellets [7-9]. In general, UO_2 (oxygen to uranium ration, O/U = 2.0) can be oxidized to U_3O_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_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_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:

$$\Delta\bar{G}_{O2} = RTlnP_{O2} = RTln(XP_t),$$

where R, T, P_t, X, and P_{O_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_{O_2} and oxygen potential ($\Delta\bar{G}_{O2}$) 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 P_{H_2O}/P_{H_2} conditions were calculated. The equilibrium gas mixture ratio at each temperature was calculated using the following equation [10]:

$$\frac{P_{H2O}}{P_{H2}\sqrt{P_{O2}}} = \exp\left(\frac{-\Delta G^0}{RT}\right),$$

where ΔG^0, P_{H_2}, and P_{H_2O} are the Gibbs free energy of the H_2O 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 Toolbox^{TM} 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 P_{O_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.

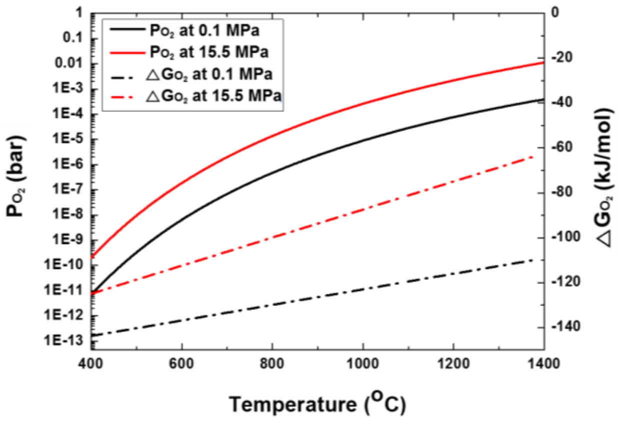

Fig. 1. Calculated oxygen partial pressure and potential of pure steam with temperature at total pressure of 0.1 and 15.5 MPa [12].

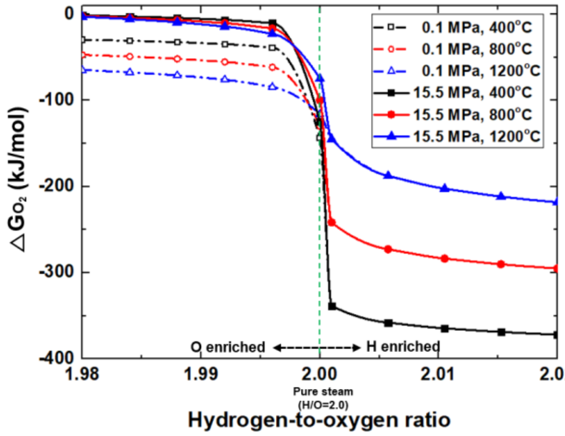

Fig. 2. Calculated oxygen potential with respect to the hydrogen to oxygen ratio at a given temperature and total pressure.

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 (PH_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.

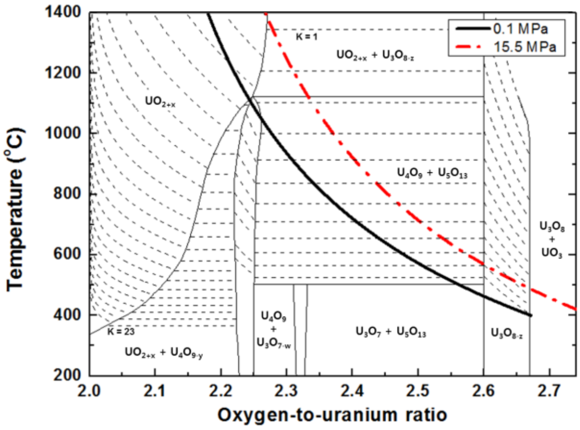

Fig. 3. p-C-T (PO_2-Composition-Temperature) diagram of U-O system with oxygen partial pressure isobars by Y.S. Kim. Black and red dash lines are the PO_2 of the pure steam condition at 0.1 and 15.5 MPa pressure with O/U. The dotted lines are $PO_2 = 10^{-K}$.

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+x}. As the temperature from 1400 °C, the fluorite structure of the UO_2 is transformed in U_3O_{8-z}, 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℃ 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_3O_8 even in the central temperature range of the pellets. However, unlike the result of thermodymic 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

[1] Z. Hozer, P. Szabo, B. Somfai, M. Cherubini, R. Aldworth, N. Waeckel, M. Jose (No. NEA-CSNI-R-2014-10). Organisation for Economic Co-Operation and Development, 2014.
[2] V. Inozemtsev, IAEA Nuclear Energy Series No. NF-T, 2, pp.1-175, 2010.
[3] R.J. Konings, T. Wiss, O. Benes, Nat. Mater., 14(3), pp.247, 2015.
[4] D.W. Shoesmith, S. Sunder, (No. SKB-TR-91-63). Swedish Nuclear Fuel and Waste Management Co., 1991.
[5] B.T. Tan, A.J. Popel, R.J. Wilbraham, J. Day, G.I. Lampronti, C. Boxall, I.J. Farnan, J. Nucl. Mater., 520, pp.41-55, 2019.
[6] O. Roth, M. Jonsson, Central European Journal of Chemistry, 6(1), pp.1-14, 2008.
[7] J.H. Davies, G.A. Potts, A. Proc. Int. Topical Meeting on LWR Fuel Performance, Avignon, April, 272, 1991.
[8] B. Cox, (No. AECL-8702). Atomic Energy of Canada Ltd., 1985.
[9] L.E. Thomas, C.E. Beyer, L.A. Chariot, J. Nucl. Mater., 188, pp.80-89, 1992.
[10] D.R. Olander, Nucl. Tech., 74(2), pp.215-217, 1986.
[11] Y.S. Kim, J. Nucl. Mater., 279(2-3), pp.173-180, 2000.
[12] T.S. Jung. Y.S. Na, M.J. Joo, K.Y. Kim, Y.H. Kim, S.J. Lee. Nucl. Eng. Tech., in press., 2020.
[13] K. Une, M. Imamura, M. Amaya, Y. Korei, J. Nucl. Mater., 223(1), pp.40-50, 1995.
[14] D.R. Olander, W.E. Wang, Y.S. Kim, C.Y. Li, S. Lim, S.K. Yagnik, J. Nucl. Mater., 248, pp.214-219, 1997.