Modeling of Oxygen Potential in Uranium-Oxygen System.

Soyoung Kim [a*,] Kwangheon Park[a]
aGreen Nuclear Research Laboratory, Kyung-Hee University, South Korea
Corresponding author:mhsy65@hanmail.net

1. Introduction

Nuclear fuels used in PWR and CANDU are uranium oxides (UO_2).

The dry storage of spent fuels is preferred to the wet storage as a long term storage method due to the limit of storage space.

There is a possibility that the pellet inside the cladding can be oxidized, if the cladding has pinholes or small cracks during the dry storage period.

And in a hypothetical accident (LOCA), the pellet can be exposed to the ambient steam or even air at the high temperature.

The oxidation state of the fuel depends on the equilibrium oxygen pressure surrounding the pellet.

Especially, there occurs about 33% volume increase of the fuel when UO_{2+x} turns U_3O_8, leading to the severe damage to fuel rods.

Hence, the oxidation state of uranium oxides (pellets) under a given oxygen potential at a temperature was modeled based on many data available up to date.

2. Data Review

2.1 Two-phase region.

2.1.1 $UO_{2+x} + U_4O_{9-y}$

Lindemer and Besmann[2] obtained the following equilibrium oxygen pressure when both UO_{2+x} and U_4O_{9-y} phases exist together.

$$\ln p_{O_2}(UO_{2+x} + U_4O_{9-y}) = 22.80 - \frac{4.7 \times 10^4}{T}. \quad (2)$$

The equation above shows a discrepancy in temperature (600-1400K) compared to Labroche's results [3].

We modified equilibrium oxygen pressure to eliminate the discrepancy and obtained the follow equation.

$$\ln p_{O_2}(UO_{2+x} + U_4O_{9-y}) = 27.63 - \frac{50864}{T}. \quad (3)$$

2.1.2 $UO_{2+x} + U_3O_{8-z}$

According to Kim [1], fitting the data for the $UO_{2+x} + U_3O_{8-z}$ phases taken from Ref. [4] yields

$$\ln p_{O_2}(UO_{2+x} + U_3O_{8-z}) = 20.18 - \frac{4.01 \times 10^4}{T}. \quad (4)$$

Kim [1] obtained the Eq. (4) that is more accurate than Roberts and Walter[8] in UO_{2+x} + U_3O_{8-z} phases.

Therefore, Eq. (4) is selected for the phase region in this study.

2.1.3 $U_4O_{9-y} + U_5O_{13}$

Blackburn [5] presented the expression for this region as :

$$\ln p_{O_2}(U_4O_9 + U_5O_{13}) = 19.40 - \frac{3.94 \times 10^4}{T}. \quad (5)$$

It was also verified in Kim [1] that the equation well satisfies the enthalpy constraint.

And Eq. (5) is based on more extensive database than Saito[7], Roberts and Walter[8].

Therefore, Eq. (5) is selected for the U_4O_{9-y} + U_5O_{13} region in this paper.

2.1.4 $U_3O_{8-z} + UO_3$

In this region, we used the database of HSC Chemistry 7 and the data from Ref. [6].

The data from HSC Chemistry 7.0 and Ref. [6] were quite similar.

Therefore, we applied the data from HSC Chemistry to derive Eq. (6)

$$\ln p_{O_2}(U_3O_{8-z} + UO_3) = 25.4 - \frac{24211.8}{T}. \quad (6)$$

2.2 Single-phase region.

2.2.1 UO_{2+x}

Kim [1] provided in this region:

$$\ln p_{O_2} = -39.14 + 26.69C + 2\ln\frac{C-2}{3-C} - \frac{3.99 \times 10^4}{T}. \quad (7)$$

The Eq. (7) shows a discrepancy compared to Labroche's results [3] which was similar to that of Lindemer and Besmann [2].

In this study, Thus, we derived the equation below based on Eq. (7), correcting it so that the result is almost the same as Labroche's [3] data.

$$\ln p_{O_2} = -39.14 + 26.69C + 2\ln\frac{C-2}{3-C} - \frac{3.78 \times 10^4}{T}. \quad (8)$$

2.2.2 U_4O_{9-y} and U_3O_{8-z}

In these two region (U_4O_{9-y} and U_3O_{8-z}), it was found that the boundary values at the two-phase region were not the same when Sievert's law was applied. Therefore, in these two regions, Eqs. (9)-(10) was selected to determine the equilibrium oxygen

pressure(p_{o2}) value using linear analysis in U_4O_{9-y} and U_3O_{8-z} regions.

U_4O_{9-y} region applies to Eq. (9) and U_3O_{8-z} region applies to Eq. (10).

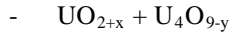$$\ln p_{O_2}\big|_y = \left(\frac{\ln p_{O_2}\big|_2 - \ln p_{O_2}\big|_1}{y_2 - y_1}\right)(y - y_1) + \ln p_{O_2}\big|_1. \quad (9)$$

Or

$$\ln p_{O_2}\big|_z = \left(\frac{\ln p_{O_2}\big|_2 - \ln p_{O_2}\big|_1}{z_2 - z_1}\right)(z - z_1) + \ln p_{O_2}\big|_1. \quad (10)$$
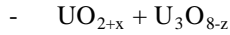
where the y is the non-stoichiometric in U_4O_{9-y}, the z is the non-stoichiometric of U_3O_{8-z} and the subscript, 1 and 2, indicate each point randomly selected at the both boundaries of U_4O_{9-y} or U_3O_{8-z} region The subscripts, y or z, indicate the O/U ratio at the point of calculation.
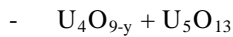
3. Conclusions

The equilibrium oxygen pressure of the UO_{2+x}, U_4O_{9-y}, U_3O_{8-z}, $UO_{2+x} + U_4O_{9-y}$, $UO_{2+x} + U_3O_{8-z}$, $U_4O_{9-y} + U_5O_{13}$ and $U_3O_{8-z} + UO_3$ phases were reviewed. Satisfactory U_aO_b - T - P_{O2} relationships were reassessed using the available experimental data.
For analysis of the phase stability of uranium oxide (e.g,. UO_{2+x}, U_4O_{9-y}, U_3O_{8-z}, UO_3), the best U_aO_b-T-P_{O2} relationships for each phase region are
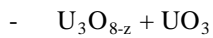
- $UO_{2+x} + U_4O_{9-y}$

$$\ln p_{O_2}(UO_{2+x} + U_4O_{9-y}) = 27.63 - \frac{50864}{T}.$$

- $UO_{2+x} + U_3O_{8-z}$

$$\ln p_{O_2}(UO_{2+x} + U_3O_{8-z}) = 20.18 - \frac{4.01 \times 10^4}{T}.$$

- $U_4O_{9-y} + U_5O_{13}$

$$\ln p_{O_2}(U_4O_9 + U_5O_{13}) = 19.40 - \frac{3.94 \times 10^4}{T}.$$

- $U_3O_{8-z} + UO_3$

$$\ln p_{O_2}(U_3O_{8-z} + UO_3) = 25.4 - \frac{24211.8}{T}.$$

- UO_{2+x}

$$\ln p_{O_2} = -39.14 + 26.69C + 2\ln\frac{C-2}{3-C} - \frac{3.78 \times 10^4}{T}.$$

- U_4O_{9-y}

$$\ln p_{O_2}\big|_y = \left(\frac{\ln p_{O_2}\big|_2 - \ln p_{O_2}\big|_1}{y_2 - y_1}\right)(y - y_1) + \ln p_{O_2}\big|_1.$$

- U_3O_{8-z}

$$\ln p_{O_2}\big|_z = \left(\frac{\ln p_{O_2}\big|_2 - \ln p_{O_2}\big|_1}{z_2 - z_1}\right)(z - z_1) + \ln p_{O_2}\big|_1.$$

Fig. 1 shows the Uranium – Oxygen Phase Diagram using the U_aO_b - T - P_{O2} relationships presented in this study.
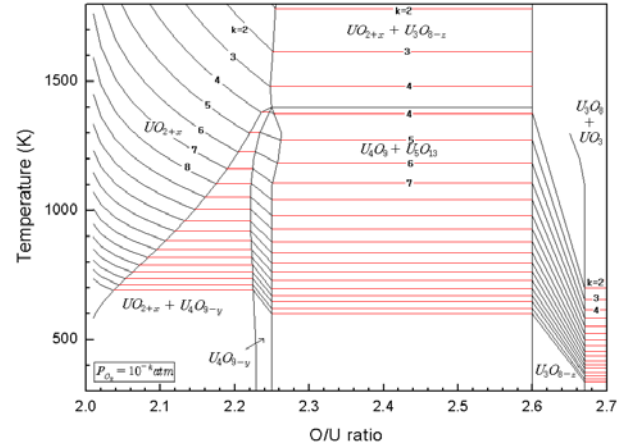

Fig 1. Uranium – Oxygen Phase Diagram.

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