World Journal of Nuclear Science and Technology, 2015, 5, 102-106
Published Online April 2015 in SciRes. http://www.scirp.org/journal/wjnst
http://dx.doi.org/10.4236/wjnst.2015.52009

Thermodynamic Assessment of UO_2 Pellet Oxidation in Mixture Atmospheres under Spent Fuel Pool Accident

Dong-Joo Kim, Jong Hun Kim, Keon Sik Kim, Jae Ho Yang, Sun Ki Kim, Yang-Hyun Koo

LWR Fuel Technology Division, Korea Atomic Energy Research Institute, Daejeon, South Korea
Email: djkim@kaeri.re.kr

Received 3 November 2014; accepted 14 April 2015; published 15 April 2015

Abstract

For an analysis of the oxidation behavior of UO_2 nuclear fuel pellet under a loss of water coolant accident in a spent nuclear fuel pool of an LWR, thermodynamic assessments of UO_2 oxidation were carried out under various atmospheric conditions. In a steam atmosphere, it was assessed that UO_2 would not be fully oxidized into U_3O_8 due to the relatively lower oxygen partial pressure, while UO_2 will be fully oxidized into U_3O_8 in an air atmosphere. In an air and steam mixture atmosphere, the UO_2 oxidation was dominantly affected by the air volumetric fraction, because of the relatively higher oxygen partial pressure of air. In addition, the effect of H_2 volumetric fraction on the oxygen partial pressure under a mixture atmosphere was calculated, and it was revealed that UO_2 pellet oxidation could be reduced above the critical value of H_2 volumetric fraction.

Keywords

Spent Nuclear Fuel Pool, UO_2 Fuel Pellet, UO_2 Oxidation, Oxygen Partial Pressure

1. Introduction

Since the Fukushima Daiichi nuclear disaster on March 2011 [1], an accident in the spent nuclear fuel pool of an LWR has been extensively regarded an important concern [2] [3]. In particular, if a loss of water coolant accident in a spent nuclear fuel pool occurs, it can bring about a massive failure owing to a drastic increase in the temperature of the spent nuclear fuel. In addition, the possibility of an external leakage of a significant amount of radioactive materials can increase. Under a loss of water coolant accident, an air and/or steam oxidation reaction of the spent nuclear fuel leads to a failure of the fuel cladding, and air and/or steam oxidation of the spent fuel pellet will follow. An oxidized spent fuel pellet will be expanded and pulverized, and a failure of the fuel

How to cite this paper: Kim, D.-J., Kim, J.H., Kim, K.S., Yang, J.H., Kim, S.K. and Koo, Y.-H. (2015) Thermodynamic Assessment of UO_2 Pellet Oxidation in Mixture Atmospheres under Spent Fuel Pool Accident. *World Journal of Nuclear Science and Technology*, **5**, 102-106. http://dx.doi.org/10.4236/wjnst.2015.52009

cladding can additionally take place.

In terms of the accident analysis in a spent nuclear fuel pool, various accident scenarios can be suggested. Therefore, the oxidation data of the UO_2 and spent fuel pellet required for an accident analysis should be secured. The oxidation data of the UO_2 and spent fuel pellet should be verified by experiments under various atmospheres, because reliable experimental data are clearly helpful to achieve valuable results of an accident analysis.

Under an accident in a spent nuclear fuel pool, the UO_2 spent nuclear fuel pellet can be exposed to various environments. If the water coolant in the spent fuel pool is lost wholly or partially, the spent nuclear fuel will be exposed to the air atmosphere. The temperature of the spent nuclear fuel can increase by the loss of water coolant, and a steam atmosphere will be gradually generated. In addition, the hydrogen atmosphere can be generated by the reaction of the spent nuclear fuel clad-ding (Zr-based alloy) with air, steam or water (Zr oxidation).

In this study, for analysis of the oxidation behavior of UO_2 nuclear fuel pellet under a loss of water coolant accident in a spent nuclear fuel pool of an LWR, the thermodynamic assessments of UO_2 oxidation were carried out under various atmospheric conditions.

2. Thermodynamic Calculations

The thermodynamic calculations of UO_2 oxidation reaction under various atmospheres were performed using a chemical reaction and equilibrium software (Outokumpu HSC Chemistry for Windows, ver. 5.1). The thermo-chemical database in the software was utilized to calculate the intended reactions.

As mentioned above, the UO_2 oxidation reactions under various environments were anticipated, and the oxygen partial pressure is the most important factor in the oxidation reaction. Therefore, considering the various atmosphere conditions (steam, air + steam, air + steam + H_2 mixture), a thermodynamic calculation of the oxygen partial pressure in the mixture atmosphere was carried out. In addition, based on the calculated oxygen partial pressure, the equilibrium oxy-gen-to-uranium ratio as a function of temperature was assessed.

3. Results and Discussion

The oxygen partial pressure in a pure steam atmosphere as a function of temperature is shown in **Figure 1**. The temperature of the UO_2 nuclear pellet under nuclear reactor operation is typically in the range of 400˚C to 1200˚C. Therefore, it can be thought that the UO_2 pellets are exposed to low oxygen partial pressure (below ~10^{-4}).

The equilibrium oxygen-to-uranium ratio can be calculated using the oxygen partial pressure of the given environment and a phase diagram of the U-O system with superimposed oxygen pressure isobars (**Figure 2**). The isobars are indicated by index k in $p = 10^{-k}$ where p is in atm [4]. **Figure 2** shows that U_3O_8 and U_3O_{8-z} phases are observed above $p(O_2)$ = ~10^{-3}, that is, a UO_2 pellet can be fully oxidized in this oxygen partial pressure range.

According to the *p*-*C*-*T* relationships for the U-O system, Y.S. Kim suggested equations [4], where *p* is the

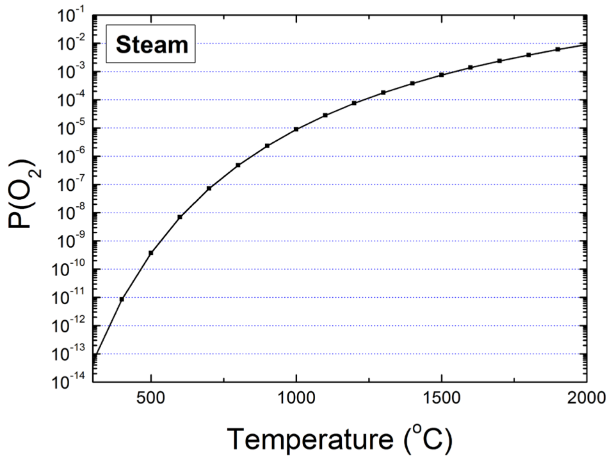

Figure 1. Calculated oxygen partial pressure in pure steam atmosphere as a function of temperature.

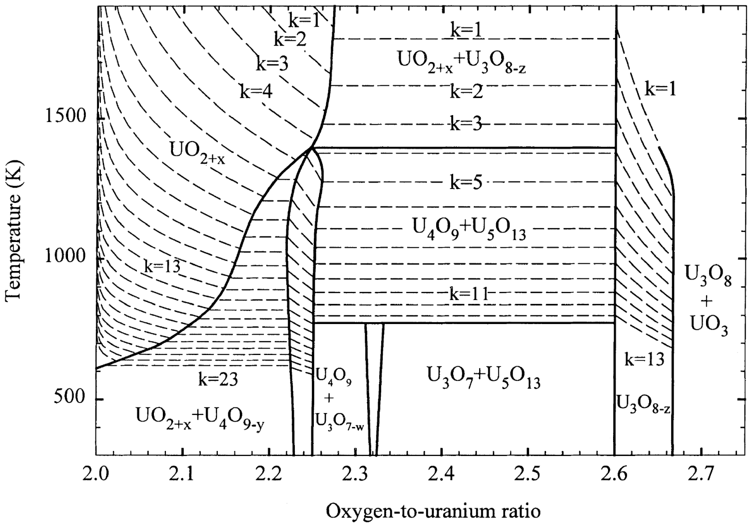

Figure 2. Phase diagram of the U-O system with oxygen pressure isobars superimposed. The isobars are indicated by index *k* in $p = 10^{-k}$ where *p* is in atm [4].

oxygen partial pressure, *C* is the oxygen-to-uranium ratio, and *T* is the temperature. The equilibrium oxygen-to-uranium ratio as a function of temperature was calculated using the equations (**Figure 3**), and the calculated results have a good agreement with the literature data [5]-[9]. In the UO_2 oxidation test under a pure steam atmosphere, the maximum weight gain of the uranium oxide pellet can be anticipated by the calculated results.

Figure 4 shows the oxygen partial pressures under air and steam mixture atmospheres as a function of temperature. It was calculated using various volumetric fractions of mixture atmospheres. **Figure 4** shows that the oxygen partial pressure is higher than $p(O_2) = 10^{-3}$ in the temperature range of concern (400˚C - 1100˚C), even though very small amounts of air were added into the environment. It can be thought that the equilibrium oxygen-to-uranium ratio of uranium oxide pellets in an air and steam mixture atmosphere is similar with that in an air atmosphere.

Figure 5 shows the partial pressures of H_2O, O_2, and H_2 in a (air + 50 vol% steam) + 10 vol% H_2 mixture atmosphere. Owing to the addition of H_2, $p(H_2O)$ in the environment increased and $p(O_2)$ decreased. It is thought that the oxidation of the UO_2 pellet can be affected by the $p(H_2)$, that is, the pellet oxidation reaction can be reduced owing to the $p(O_2)$ decrease.

Figure 6 shows that there is a critical value of $p(H_2)$ that can be drastically decreased $p(O_2)$ in the environment. In the case of an air + 50 vol% steam mixture, it was revealed that the critical value of $p(H_2)$ is 0.17. That is, at above 17 vol% H_2, the pellet oxidation reaction will be reduced. In addition, the critical value of $p(H_2)$ in an air and steam mixture environment is proportional to the amount of the air atmosphere.

4. Summary

To analyze the oxidation behavior of a UO_2 nuclear fuel pellet under a loss of water coolant accident in a spent nuclear fuel pool of an LWR, the thermodynamic assessments of UO_2 oxidation were carried out under various atmosphere conditions (steam, air + steam, air + steam + H_2 mixture).

Based on a phase diagram analysis, above $p(O_2) = \sim 10^{-3}$, a UO_2 pellet can be fully oxidized into U_3O_8 and U_3O_{8-z} phases. The oxygen partial pressures in the air and steam mixture environment are higher than $p(O_2) = 10^{-3}$ in the temperature range of concern (400˚C - 1100˚C). It can be thought that the equilibrium oxygen-to-uranium ratio of a uranium oxide pellet in an air and steam mixture atmosphere is similar with that in an air atmosphere.

In addition, in an air + steam + H_2 mixture environment, there is a critical value of $p(H_2)$ that can be drastically decreased $p(O_2)$. That is, the pellet oxidation reaction will be reduced, above the critical value of $p(H_2)$.

It is expected that these thermodynamic assessment results are contributed to establish more efficient experimental plan for simulation of the accident scenarios in spent fuel pool.

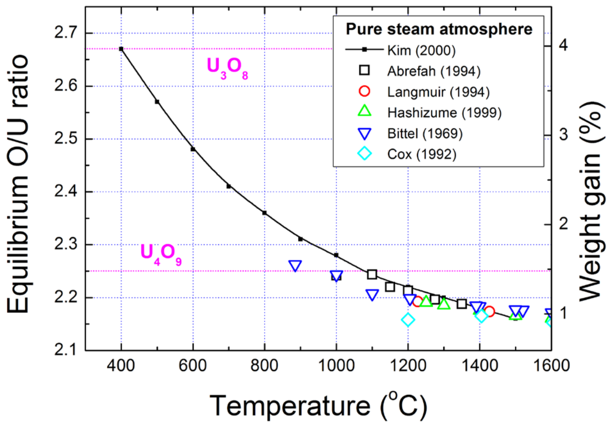

Figure 3. Calculated equilibrium O/U ratio and weight gain in pure steam atmosphere as a function of temperature.

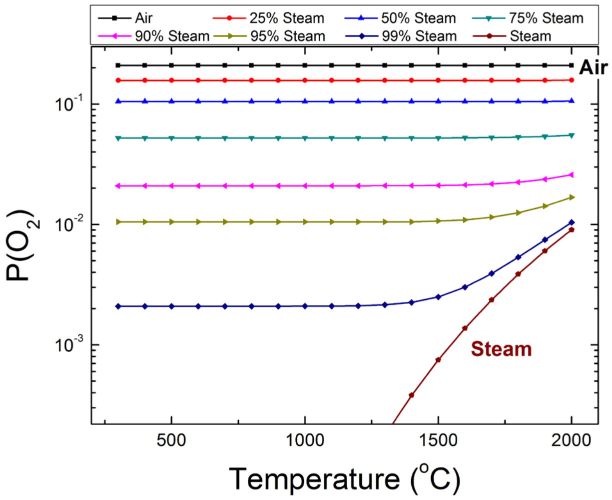

Figure 4. Calculated oxygen partial pressure in air and steam mixture atmosphere.

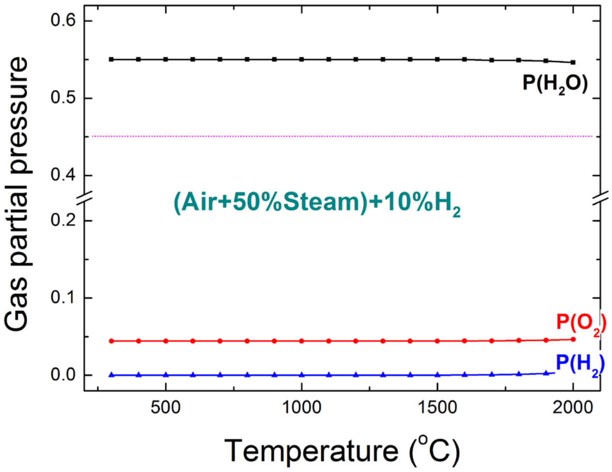

Figure 5. Calculated partial pressures of H_2O, O_2, H_2 in (air + 50 vol% steam) + 10 vol% H_2 mixutre atmosphere.

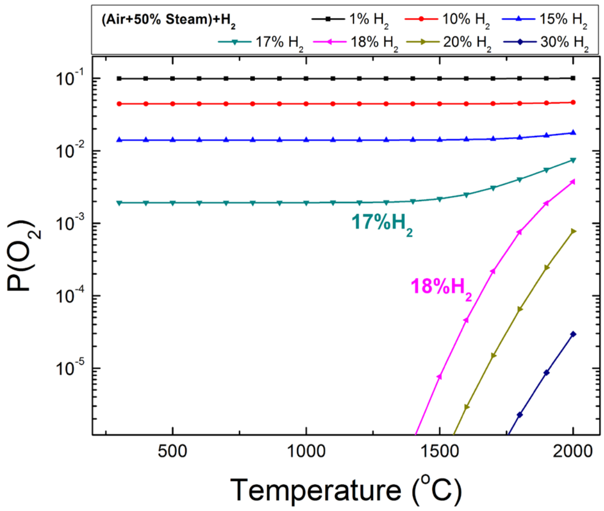

Figure 6. Calculated oxygen partial pressure in (air + 50 vol% steam) with various H_2 volumetric fractions.

Acknowledgements

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIP) (No. 2013000720).

References

[1] Koo, Y.H., Yang, Y.S. and Song, K.W. (2014) Radioactivity Release from the Fukushima Accident and Its Consequences: A Review. *Progress in Nuclear Energy*, **74**, 61-70. http://dx.doi.org/10.1016/j.pnucene.2014.02.013

[2] Bottomley, P.D.W., Walker, C.T., Papaioannou, D., Bremier, S., Pöml, P., Glatz, J.-P., Winckel, S., Uffelen, P., Manara, D. and Rondinella, V.V. (2013) Severe Accident Research at the Transuranium Institute Karlsruhe: A Review of Past Experience and Its Application to Future Challenges. *Annals of Nuclear Energy*, **65**, 345-356. http://dx.doi.org/10.1016/j.anucene.2013.11.012

[3] NNR-NRC (2013) Consequence Study of a Beyond-Design-Basis Earthquake Affecting the Spent Fuel Pool for a U.S. Mark I Boiling-Water Reactor. Office of Nuclear Regulatory Research, US Nuclear Regulatory Commission, Cover Note to Review.

[4] Kim, Y.S. (2000) A Thermodynamic Evaluation of the U-O System from UO_2 to U_3O_8. *Journal of Nuclear Materials*, **279**, 173-180. http://dx.doi.org/10.1016/S0022-3115(00)00019-2

[5] Blackburn, P.E. (1973) Oxygen Pressure over Fast Breeder Reactor Fuel (I) A Model for $UO_{2\pm x}$. *Journal of Nuclear Materials*, **46**, 244-252. http://dx.doi.org/10.1016/0022-3115(73)90038-X

[6] Abrefah, J., Braid, A.A., Wang, W., Khalil, Y. and Olander, D.R. (1994) High Temperature Oxidation of UO_2 in Steam-Hydrogen Mixtures. *Journal of Nuclear Materials*, **208**, 98-110. http://dx.doi.org/10.1016/0022-3115(94)90201-1

[7] Hashizume, K., Wang, W.-E. and Olander, D.R. (1999) Volatilization of Urania in Steam at Elevated Temperatures. *Journal of Nuclear Materials*, **275**, 277-286. http://dx.doi.org/10.1016/S0022-3115(99)00123-3

[8] Bittel, J.T., Sjodahl, L.H. and White, J.F. (1969) Steam Oxidation Kinetics and Oxygen Diffusion in UO_2 at High Temperatures. *Journal of the American Ceramic Society*, **52**, 446-451. http://dx.doi.org/10.1111/j.1151-2916.1969.tb11976.x

[9] Cox, D.S. and O'Connor, R.F. (1992) Measurement of Oxidation/Reduction Kinetics to 2100˚C Using Non-Contact Solid-State Electrolytes. *Solid State Ionics*, **53-56**, 238-254. http://dx.doi.org/10.1016/0167-2738(92)90387-5