

Analysis of the Oxidation State Change of High-Gd₂O₃-Content UO₂ Pellets under Simulated Fuel Rod Leakage Conditions

Tae-sik Jung*, Seong-woo Ha, Chae-rin Kim, Yeon-soo Na, Min-jae Joo, Kwang-young Lim
Technology and Engineering Division, KEPCO Nuclear Fuel, Daejeon 34057, Republic of Korea

*Corresponding author: taesik@knfc.co.kr

***Keywords :** High-temperature steam, Fuel rod leakage, UO₂ oxidation, High-Gd₂O₃-content UO₂

1. Introduction

The innovative Small Modular Reactor (i-SMR) currently under development in Korea adopts a soluble-boron-free concept, increasing the importance of control rods and burnable absorbers for reactivity control [1]. Two absorber materials are being considered: Highly Intensive and Discrete Gadolinia/Alumina Burnable Absorber (HIGA) [2] and UO₂ containing a high concentration of Gd₂O₃ [3]. While conventional UO₂ containing approximately 8 wt.% Gd₂O₃ has been widely used in commercial reactors, the oxidation behavior of UO₂ containing up to 20 wt.% Gd₂O₃ under steam conditions has not been sufficiently evaluated.

Substitution of U⁴⁺ by Gd³⁺ modifies the defect chemistry, oxygen stoichiometry, and oxygen-potential relationship of the (U,Gd)O_{2±x} fluorite solid solution. This modification may affect its oxidation behavior when steam enters a fuel rod through cladding leakage, whereas conventional UO₂ can progressively oxidize toward higher uranium oxides under sufficiently oxidizing conditions.

In this study, the oxidation behavior of UO₂ containing 20 wt.% and 8 wt.% Gd₂O₃ was evaluated thermodynamically and experimentally, respectively. Its thermodynamic stability was assessed in relation to the oxygen potential of steam, and steam oxidation experiments were performed at 1200°C using thermogravimetric analysis (TGA) to compare its oxidation resistance with that of conventional UO₂.

2. Calculation and Experimental method

Oxygen-potential calculations were performed to evaluate the oxidation behavior of fuel pellets exposed to steam following fuel rod leakage. The equilibrium oxygen partial pressure and oxygen potential of steam were calculated as functions of temperature at total pressures of 0.1 and 15.5 MPa using the thermodynamic approach proposed by Olander [4]. The effect of the H₂O/H₂ ratio was also considered because the oxygen potential inside a leaking fuel rod is strongly influenced by hydrogen generated through reactions between steam and fuel-rod components.

The calculated oxygen partial pressures were applied to the temperature-dependent PO₂-composition relationships of the U-O system [5] to determine the stable

uranium oxide phases. For UO₂ containing 20 wt.% Gd₂O₃, the effect of Gd³⁺ substitution on the oxygen stoichiometry and thermodynamic stability of the (U,Gd)O_{2±x} fluorite phase was additionally evaluated in relation to the oxygen potential imposed by the steam environment.

Steam oxidation experiments were performed using a thermogravimetric analyzer (TGA). UO₂ pellets containing 8 wt.% Gd₂O₃ were exposed to steam at 1200°C, and the mass change was continuously monitored during the test. Conventional UO₂ pellets were tested under equivalent conditions for comparison. After steam exposure, the macroscopic surface appearances of the pellets were also examined to assess oxidation-induced degradation.

3. Results and discussion

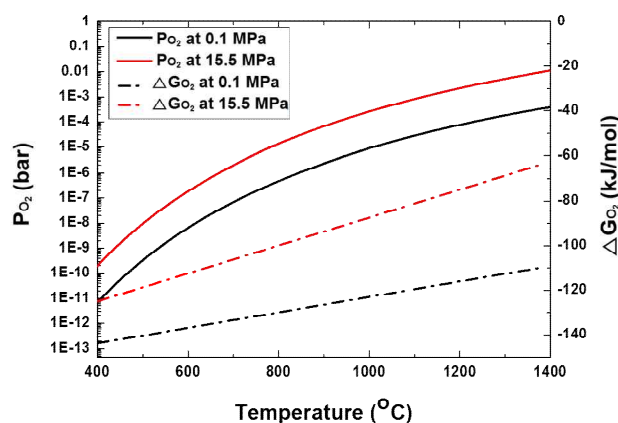


Fig. 1. Calculated oxygen partial pressure and potential of pure steam with temperature at total pressure of 0.1 and 15.5 MPa [6].

Figure 1 shows the calculated equilibrium oxygen partial pressure and oxygen potential of steam at total pressures of 0.1 and 15.5 MPa. Both values increased with increasing total pressure, indicating a stronger oxidizing environment at the PWR system pressure. Under an actual fuel rod leakage condition, however, hydrogen generated by steam reactions with fuel-rod components decreases the H₂O/H₂ ratio and consequently reduces the oxygen potential inside the rod.

The oxidation behavior of Gd₂O₃-containing UO₂ is also affected by its defect chemistry. Substitution of U⁴⁺ by Gd³⁺ modifies the uranium valence and oxygen

stoichiometry of the fluorite solid solution. Nevertheless, under the reducing conditions employed during pellet sintering and those prevailing inside an intact fuel rod, high-Gd₂O₃-content UO₂ remains predominantly within the (U,Gd)O_{2±x} fluorite region without extensive oxidation to higher uranium oxide phases.

The thermodynamic analysis indicates that the oxygen-potential–stoichiometry relationship of 20 wt.% Gd₂O₃-containing UO₂ differs from that of conventional UO₂. Oxygen potential of steam at 1200°C promotes oxidation of UO₂ toward higher uranium oxidation state, such as UO_{2+x}, however, Gd incorporation modifies the stability of the fluorite solid solution and reduces its tendency for further oxidation under the same steam environment.

This thermodynamic tendency was inferred from the steam oxidation experiment at 1200°C. As shown in Fig. 2, conventional UO₂ exhibited a pronounced change in surface roughness due to higher oxidation state after steam exposure, whereas the 8 wt.% Gd₂O₃-containing UO₂ pellet showed substantially less visible degradation and largely retained its original surface luster. As shown in the Fig. 3, UO₂ containing 8 wt.% Gd₂O₃ appears that lower weight gain is resulted.



Fig. 2 Macroscopic appearances of conventional UO₂ and 8 wt.% Gd₂O₃-containing UO₂ pellets after steam oxidation at 1200°C.

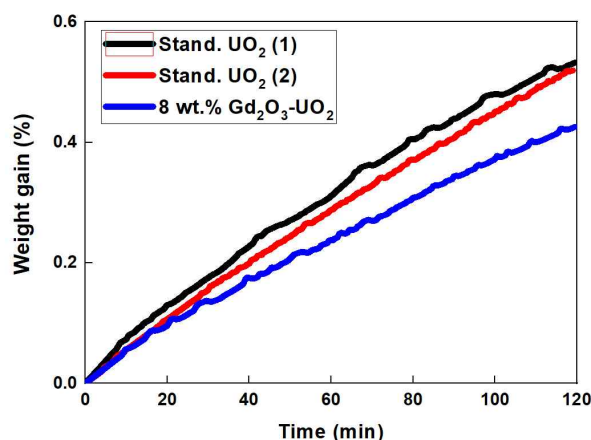


Fig. 3 Weight gain of conventional UO₂ and 8 wt.% Gd₂O₃-containing UO₂ pellets during steam oxidation at 1200°C.

The experimental results therefore support the thermodynamic prediction that high Gd₂O₃ addition suppresses further oxidation of UO₂ under high-temperature steam conditions. This enhanced oxidation resistance may be particularly beneficial under fuel rod leakage conditions, where the actual oxygen potential can be further decreased by hydrogen generation within the rod.

4. Conclusions

Calculations using thermodynamic data were performed to predict the behavior of the UO₂ 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 UO₂ 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 U₃O₈ even in the central temperature range of the pellets. However, unlike the result of thermodynamic calculation, it was confirmed that the oxidation of UO₂ would not develop very seriously due to the conversion to a reducing atmosphere by an increase in hydrogen partial pressure.

The steam oxidation experiment at 1200°C demonstrated that UO₂ containing 8 wt.% Gd₂O₃ exhibited greater oxidation resistance than conventional UO₂. Furthermore, based on the experimental observations and thermodynamic calculations, UO₂ containing up to 20 wt.% Gd₂O₃ is expected to exhibit even greater resistance to oxidation under high-temperature steam conditions.

REFERENCES

- [1] S.G. Lim, H.S. Nam, D.H. Lee, S.W. Lee, "Design characteristics of nuclear steam supply system and passive safety system for Innovative Small Modular Reactor (i-SMR)," Nucl. Eng. Technol., 57, 103697, 2025..
- [2] H.J. Kim, H. Bae, H.J. Ryu, "Improving hydration resistance of gadolinium-based burnable absorbers via cerium oxide additions," Nucl. Eng. Technol., 58, 104067, 2026.
- [3] J.H. Lee, J.H. Yang, D.S. Kim, J.-H. Yoon, D.-J. Kim, H.J. Kim, Y. Jung, "Effect of high Gd₂O₃ content on the thermal conductivity of UO₂-Gd₂O₃ fuels," Nucl. Eng. Technol., 58, 104261, 2026.
- [4] D.R. Olander, "Oxidation of UO₂ by High-Pressure Steam," Nucl. Technol., 74(2), pp. 215–217, 1986.
- [5] Y.S. Kim, "A thermodynamic evaluation of the U–O system from UO₂ to U₃O₈," J. Nucl. Mater., 279(2–3), pp. 173–180, 2000.
- [6] T.-S. Jung, Y.-S. Na, M.-J. Joo, K.-Y. Lim, Y.-H. Kim, S.-J. Lee, "Thermodynamic and experimental analyses of the oxidation behavior of UO₂ pellets in damaged fuel rods of pressurized water reactors," Nucl. Eng. Technol., 52, pp. 2880–2886, 2020.