1–4 Zirconium Hinders the Oxidative Dissolution of Nuclear Fuel

— Effect of Zirconium Incorporation in Uranium Oxide upon Inhibiting Oxidative Dissolution —

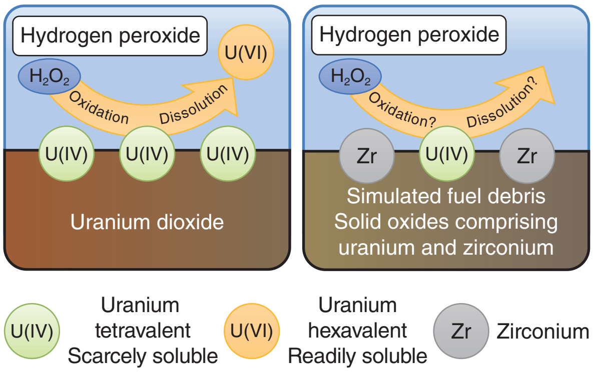

Fig.1-8 Reaction scheme of U dissolution by H_2O_2
Oxidative dissolution by H_2O_2 is a well-known degradation process for UO_2, but little is known about the process for fuel debris. Thus, the oxidative U dissolution was examined through experiments with simulated fuel debris.

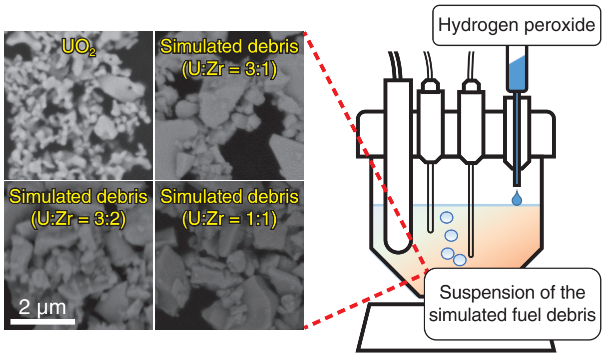

Fig.1-9 Scanning-electron-microscope (SEM) images of the U oxide samples and a schematic illustration of the setup for the H_2O_2 reaction experiment
The reactions of H_2O_2 with UO_2 and with the simulated fuel debris in aqueous solution were examined.

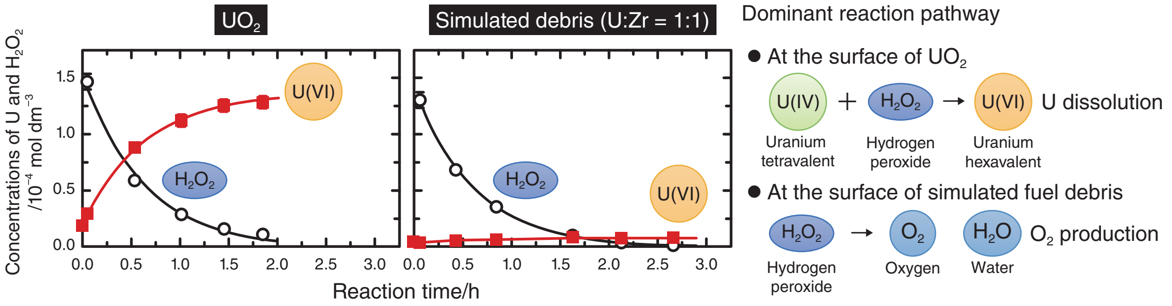

Fig.1-10 Comparison of the H_2O_2 reaction kinetics between UO_2 and the simulated fuel debris
The reaction of H_2O_2 with UO_2 results in the dissolution of U. However, the reaction with the simulated fuel debris scarcely caused the U dissolution and resulted in catalytic decomposition of H_2O_2, producing oxygen and water molecules.

We have shown that uranium dioxide (UO_2) becomes chemically stable by forming solid solution containing zirconium (Zr). The stabilization by Zr indicates that the molten fuel debris in the TEPCO's Fukushima Dai-ichi NPS (1F) would be stable against dissolution by chemical reactions and would remain in the reactors until it is retrieved.

Our research on the chemical reaction of the molten fuel debris is based on an understanding of the chemical degradation of spent nuclear fuel under the conditions of deep geological disposal. The spent fuel emits intense ionizing radiation and produces hydrogen peroxide (H_2O_2) by decomposing water molecules. In the case of direct contact of the fuel with water, H_2O_2 consequently reacts with the fuel, inducing dissolution of uranium (U). The U dissolution is induced by oxidation of U at the surface of the fuel (Fig.1-8). In the UO_2 matrix of the fuel, U is mainly in tetravalent state that is scarcely soluble in water. However, if tetravalent U is oxidized into hexavalent state, its solubility drastically increases. This sequence of chemical reactions is expected to occur for the fuel debris in 1F. However, little is known about the chemical behavior of the fuel debris in water, because the composition of fuel debris is far different from that of the usual UO_2 fuel due to melting with the materials in the reactor core.

We have performed experiments regarding the dissolution of U by H_2O_2, and shown that it is significantly inhibited by the incorporation of Zr (Fig.1-9). U oxide containing Zr was used as simulated fuel debris, because the fuel debris is expected to contain Zr by melting with the fuel-cladding material. When the simulated debris was exposed to H_2O_2, the reaction of H_2O_2 proceeded at a rate comparable with that of UO_2. However the dissolution of U was significantly inhibited (Fig.1-10). For example, the U dissolution from the simulated debris containing 50 % Zr in atomic ratio was only 4 % of that from UO_2. This inhibited dissolution resulted from the effect of Zr promoting H_2O_2 decomposition on the surface. This reaction mechanism was confirmed by analysis of gaseous products of the reaction. The reaction of H_2O_2 with the simulated debris produced nearly the stoichiometric amount of oxygen (O_2).

We are going to further investigate the basic chemistry of molten fuel in order to support technological development for the safe retrieval and management of the fuel debris in 1F.

Reference

Kumagai, Y. et al., Reaction of Hydrogen Peroxide with Uranium Zirconium Oxide Solid Solution–Zirconium Hinders Oxidative Uranium Dissolution, Journal of Nuclear Materials, vol.497, 2017, p.54–59.