

# 1-1 Degradation of Fuel Debris Under the Effect of Ionizing Radiation

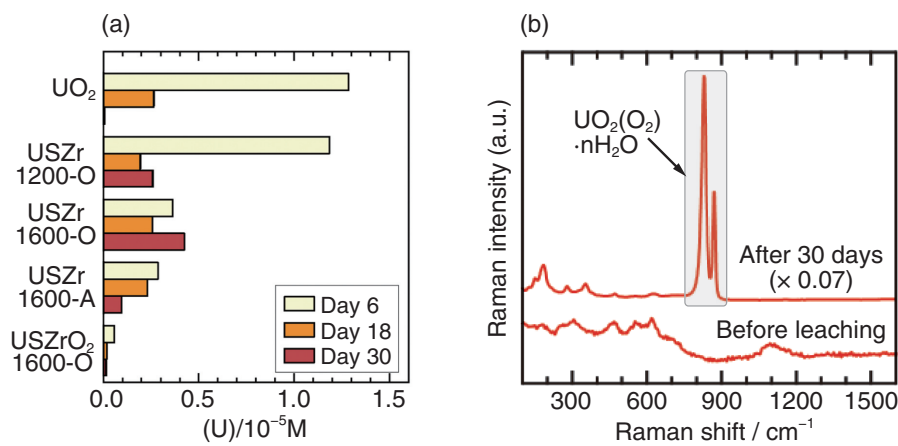
## — Formation of Solid Solution Improves Stability to Oxidative Degradation —

**Table 1-1 Examples of simulated debris samples prepared in this study**

The starting materials, heat treatment conditions, and typical phases formed in the samples are listed. Formation of a solid solution of  $\text{UO}_2$  with other metal ions, i.e.,  $\text{UO}_2(\text{s.s.})$ , was observed.

Sample	Starting materials*	Heat treatment	Major U phase
USZr 1200-O	$\text{UO}_2$ , Zr, SUS 304	1200 °C, 2% $\text{O}_2$	$\text{U}_3\text{O}_8$
USZr 1600-O	$\text{UO}_2$ , Zr, SUS 304	1600 °C, 2% $\text{O}_2$	$\text{UO}_2(\text{s.s.})$ (low Zr)
USZr 1600-A	$\text{UO}_2$ , Zr, SUS 304	1600 °C, Ar	$\text{UO}_2$
USZrO <sub>2</sub> 1600-O	$\text{UO}_2$ , ZrO <sub>2</sub> , SUS 304	1600 °C, 2% $\text{O}_2$	$\text{UO}_2(\text{s.s.})$ (high Zr)

\*The atomic ratio in the starting materials is as follows  
U: Zr: Fe+Cr+Ni (SUS 304) = 1: 1: 1



**Fig.1-3 (a) U concentrations in the leachate and (b) Raman spectra of uranyl peroxides formed on USZr1600-O by immersion in an aqueous  $\text{H}_2\text{O}_2$  solution**

Similarly, the formation of uranyl peroxides was observed on the other samples, except for USZrO<sub>2</sub>1600-O.

The fuel debris generated in the accident at TEPCO's Fukushima Daiichi Nuclear Power Station remains in the reactors, and substantial time and effort will be required for the retrieval of the debris. The debris has been most likely exposed to water since the accident. Contact with water results in the degradation of the debris matrix due to the radiolysis of water. Water radiolysis generates oxidants such as hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), which can oxidize uranium to hexavalent U(VI). According to previous studies on uranium (IV) oxide ( $\text{UO}_2$ ) and spent fuels, U oxidation proceeds at the interface with water, and the matrix gradually dissolves because U(VI) has a higher water-solubility than U(IV). Hence, to examine the possible degradation processes of fuel debris, we performed leaching experiments using simulated fuel debris.

The simulated debris samples were prepared from powders of  $\text{UO}_2$ , stainless steel (SUS 304), and zirconium metal (Zr) or oxide ( $\text{ZrO}_2$ ) by heat treatment under various conditions (Table 1-1). After analyzing the phase composition of the samples, the simulated debris samples were immersed in an aqueous  $\text{H}_2\text{O}_2$  solution for up to 30 days.  $\text{H}_2\text{O}_2$  was added because it is the water radiolysis product that has major impact on U oxidation. After certain periods of immersion, the

samples were analyzed by Raman spectroscopy, and chemical analysis of the leached elements was performed.

The analysis of the leached elements showed significant dissolution of U from the samples. The reaction of  $\text{H}_2\text{O}_2$  concurrently induced the precipitation of uranyl peroxides,  $\text{UO}_2(\text{O}_2) \cdot n\text{H}_2\text{O}$  ( $n = 2$  or  $4$ ). Because of these two processes, the dissolved U concentration once increased and then decreased with leaching time (Fig.1-3 (a)). The formation of uranyl peroxides was clearly confirmed by the Raman spectroscopy results (Fig.1-3 (b)). These results demonstrate that uranyl peroxides are the possible alteration products of fuel debris from the  $\text{H}_2\text{O}_2$  reaction.

In contrast, the sample in which formation of a U-Zr oxide solid solution proceeded to a remarkable degree (USZrO<sub>2</sub>1600-O) showed much less U dissolution and no Raman signal of uranyl peroxides. This finding indicates that formation of the oxide solid solution of Zr with  $\text{UO}_2$  improves the durability of fuel debris against the  $\text{H}_2\text{O}_2$  reaction.

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### Reference

Kumagai, Y. et al., Uranium Dissolution and Uranyl Peroxide Formation by Immersion of Simulated Fuel Debris in Aqueous  $\text{H}_2\text{O}_2$  Solution, Journal of Nuclear Science and Technology, vol.59, issue 8, 2022, p.961–971.