

Oxidation behaviour of UO_2 under dry storage controlled conditions: the impact of temperature and oxygen partial pressure.

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The short-term management of spent nuclear fuel (SNF) may include dry temporary storage until a Deep Geological Repository (DGR) becomes available. Particularly, in Spain, the fuel is not reused once irradiated (open cycle) [1], and the temporary management of SNF includes Decentralized Temporary Storage (DTS) facilities at the sites of the nuclear power plants [2]. During this period, the integrity of the SNF must be ensured, particularly against the fuel matrix oxidation from UO_2 to U_3O_8 , which occurs in the presence of oxygen at relatively high temperatures. This phase represents the terminal thermodynamic state under such conditions for a fresh UO_2 surrogate, whose representativeness is proved in terms of its conservatism in relation to actual spent fuel [3]. The formation of U_3O_8 from UO_2 , the primary constituent of SNF (approximately 95%), leads to a ~36% increase in volume. This expansion is associated with the spallation and cracking of the original fuel pellet, which, depending on pre-existing conditions (e.g. failed cladding), could potentially lead to radionuclides release. Accurately determining the conditions under which U_3O_8 could be formed is essential for ensuring safety during transport, unloading, or dry storage of SNF. While this reaction has been extensively studied in air, the combined effect of temperature and varying oxygen concentrations on the formation of U_3O_8 remains unclear, with limited experimental data available. Investigating the potential oxidation of the fuel matrix at lower oxygen partial pressures, might bring to light other alternatives to air that might delay or even prevent this oxidation. However, the literature regarding the effect of lower oxygen partial pressures than air on UO_2 oxidation is scarce [4-6].

In order to study the fuel oxidation in the presence of oxygen and high temperatures, experimental oxidation data for unirradiated UO_2 , emphasising the induction time for the U_3O_8 formation, were obtained using various complementary techniques for monitoring oxidation, both *in situ* and *ex situ*. These studies have provided key variables, including the degree of oxidation, temperatures, U_3O_8 formation times, and other physicochemical parameters. This study investigates the effects of three temperatures at or below 400 °C limit [7, 8] (i.e. 200, 300 and 400 °C), each under different oxygen concentrations (0.1, 1, 10, and 21% O_2), on the U_3O_8 formation from unirradiated UO_2 . Isothermal *in situ* tests (by thermogravimetry (TGA) and Linkam-Raman (LR)) and *ex situ* tests (batch-type reactors (BR)) were conducted to determine the induction time for U_3O_8 formation. Each experimental setup offered a unique analytical perspective, and collectively, the setups provided complementary insights when conducted systematically across overlapping timeframes. The length of the experiments was 10 hours for TGA (Figure 1), around 3 days for Linkam-Raman and 14 days for batch-type isothermal reactors. After a systematic analysis of the UO_2 oxidation reaction, the results obtained from both *in situ* (TGA and LR) and *ex situ* (BR) experiments, reveal the impact of temperature on U_3O_8 formation [9]. The data provided (U_3O_8 formation time as a function of temperature and O_2 concentration) allow for understanding how the oxidation rate varies according to oxygen availability and temperature. The time required for U_3O_8 formation (>90%), was found to depend on temperature and oxygen concentration.

At 300°C, oxidation times drastically depend on the oxygen concentration, with rapid oxidation in atmospheres with more oxygen (21% and 10%) and very slow oxidation at low concentrations (1% and 0.1%). In fact, at 10% O_2 and 21% O_2 concentrations, the formation of U_3O_8 (>90%) at 300 °C is achieved in a relatively short time (10 h). When the oxygen concentration is reduced to a low level (1% O_2), a significant increase in the time required to form a similar percentage of U_3O_8 (93%) is observed. In this case, U_3O_8 was firstly detected after 168 h (7 days), reflecting the importance of oxygen availability in the kinetics of the oxidation process. At the lowest concentration evaluated (0.1% O_2), 90% U_3O_8 formation was identified in the same 168 hours, showing that oxidation is even more slowly at this concentration. This indicates that when a significant amount of oxygen is available, the oxidation of UO_2 to U_3O_8 is faster than at 1% O_2 or lower. The adaptation of these observations into analytical expressions shows consistency with

results from other experiments conducted on irradiated fuel and provides valuable insights into the time limit at which an irradiated fuel rod with an undetected defect can remain exposed to an oxidizing agent (such as O_2).

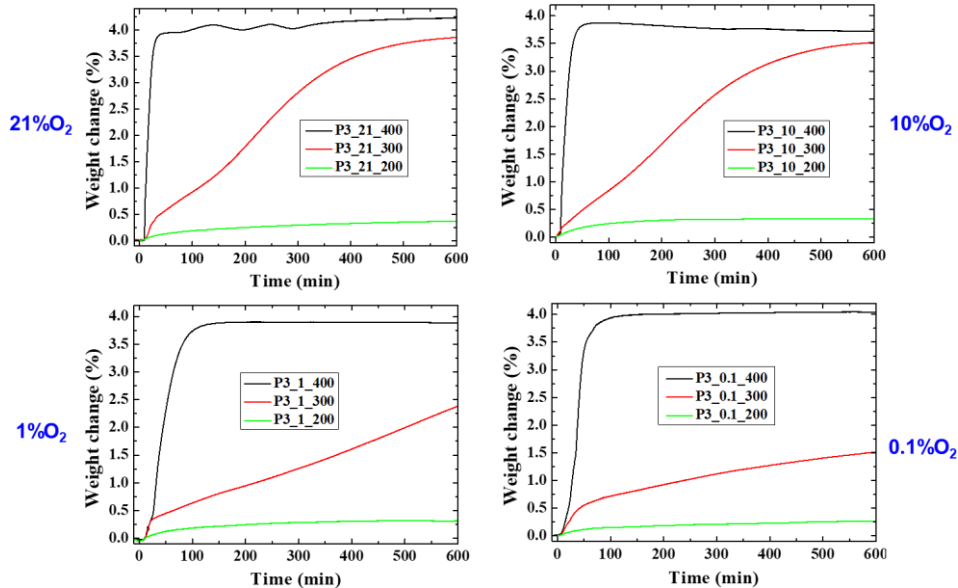


Figure 1 Weight change curves vs time acquired by in situ TGA of powdered UO_2 as a function of % O_2 and temperature.

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