Oxidation in air/steam mixtures of pre-oxidized Zircaloy-4 in the 750 -950°C temperature range: experimental data and modeling for ASTEC code application

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Spent fuel pools (SFPs) are large structures equipped with storage racks designed to temporarily store irradiated nuclear fuel removed from the reactor. In case of prolonged loss of cooling conditions or in case of a loss of coolant accident, the pool water may drop below the top of the spent fuel assemblies. The uncovered part of the fuel would be exposed to a steam/air mixture and the exothermal oxidation process of the cladding would result in a fast degradation of the fuel assembly and to the release of fission products.

In the frame of the French DENOPI project, an experimental study was carried out to study the oxidation at high temperature (750 - 950°C) of pre-oxidized Zircaloy-4 in air/steam (ie O₂/N₂/H₂O) mixtures. Specimens of Zircaloy-4 (15 mm×10 mm) were firstly oxidized at 425°C in an oxygen/steam mixture to form a pre-oxide scale with thicknesses of approximatively 30 µm. This low temperature oxidation scale simulates the corrosion oxide formed during normal operation. It was followed by corrosion tests in O₂-N₂ (in air proportion)-He-H₂O flowing mixtures in a symmetrical microbalance to measure the mass gain of the samples. The tests have confirmed the detrimental role of nitrogen when added to oxygen and/or to steam. A protective effect of the pre-oxide regarding subsequent high temperature oxidation has been observed in the first moments. But the protective effect is lost with the spalling of the pre-oxide scale that initiates at the edges of the sample. The influence of oxygen, nitrogen and steam partial pressures on the degradation kinetics was determined thanks to the jump method. The hydrogen content was measured by the hot extraction technique and was correlated to the steam partial pressure, indicating that both oxidant (oxygen and steam) contribute to the oxidation. Moreover, during the high temperature oxidation, the morphology of the sample strongly evolves with the spalling of the pre-oxide scale and the creep of the sample. From all these experimental observations, a kinetic model is proposed for the severe accident code ASTEC. This model relies on the lost of the protective effect of the pre-oxide scale and to the formation of a "porous" zirconia layer at a high oxidation rate. The model was implemented in ASTEC and a sensitivity study was carried out at the fuel assembly scale to the parameters of the model. Main results will be presented as well as perspectives for further validation against experiments at a larger scale.