

¹⁴C DIFFUSION IN USED FUEL CLADDINGS

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The fuel claddings of pressurized water nuclear reactors (PWR) are made of zirconium alloy (mainly composed of 98% of Zr). In water, their oxidation reaction leads to the formation of an external zirconia layer (ZrO₂). Both Zr and ZrO₂ contain many activation products (AP) including ¹⁴C. The objective of this study is to identify and to characterize the possible carbon retention of Zr and ZrO₂ in order to improve the global performances of long-term safety of the deep storage of the radioactive waste.

More exactly, we determine the performances of the ¹⁴C retention in Zr and monoclinic ZrO₂. The modeling of C's behavior was done by the way of a multi-scale approach. First, Density Functional Theory (DFT), based on static simulations with the VASP code, was performed to identify the possible interstitial carbon sites, the migration energies as well as the jump frequencies between the neighbour interstitial sites. Second, a kinetic Monte-Carlo method was used to simulate the carbon macroscopic diffusion behaviour.

In the first step, the formation energies when a carbon atom was inserted in different positions in Zr bulk were calculated. It was found that a carbon atom always prefers to be in an interstitial position whether or not there is any vacancy. Two possible interstitial sites were pointed out, basal tetragonal and octahedral sites. In the perfect bulks, we performed the calculations of C's migration (with the Nudged Elastic Band approach) between the neighbour interstitial sites. Activation energies to migrate and attempt frequencies were also calculated and the possible migration paths in the bulk were identified. To study the macroscopic possibility of carbon diffusion, the results of the DFT simulations were used to simulate, with the Kinetic Monte Carlo (KMC) approach, the C's diffusion coefficient at different temperatures. It was proved that at the actual storage temperature (around 50 °C), it was very difficult for C to diffuse in Zr bulk so to exit from it.

The same work was also performed for C in monoclinic zirconia. It was found that when there was an atomic vacancy (O or Zr), the inserted carbon always preferred to go to the vacancy site than to be in an interstitial one. In the perfect ZrO₂ bulk eight interstitial sites were identified. The migration calculations were done by NEB simulations to get the activation energies, attempt frequencies and migration vectors. The preliminary simulations of C's diffusion in the monoclinic zirconia with the KMC approach showed that at the storage temperature, it was also very difficult for C to diffuse.

This work joins within the framework of several follow-up studies realized in collaborations with EDF, AREVA and with the National NEEDS program.