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The release of radiotoxic species from future final geological nuclear waste repositories is governed by the oxidative dissolution of the UO2-matrix in the case of a canister failure. At the depths of a final geological repository, the conditions are reducing with very low oxygen concentrations [1]. In repositories built in granitic bedrock, as in the designs planned in Sweden, Canada and Finland, anoxic conditions are further ensured by the redox chemistry of the copper canister as well as with the surrounding biotite, magnetite and organic matter [2]. As the UO2 matrix is highly insoluble in the U(IV) state [3], the main mechanism of dissolution is through the formation of locally oxidizing conditions near the fuel surface through radiolysis. Even though radiolysis produces both reducing and oxidizing species, as both radicals (H·, e-aq, HO2·, O2·, ·OH) as well as molecular products (H2, H2O2) [4], the net redox conditions due to radiolysis are oxidizing at the immediate surface due to the higher reactivity of O2 compared to H2 [5]. Dissolution of the UO2 matrix leads to the release of radiotoxic fission products, which are to a large extent (>95%) contained in the matrix [6]. H2, which is formed in substantial amounts in the final repository through anoxic corrosion of the massive iron inserts, has in several studies been shown to protect the UO2-surface from radiolytic oxidation. The hydrogen effect is propagated through activation on the radioactive UO2 surface on active sites, or on metallic ε-particles (Mo, Pd, Ru, Rh and Tc).
It is not yet known if the radioactivity must be internal for the active surface sites to be present on the UO2-surface. This has been investigated using 241Am-sources separated from low-enriched UO2-pellets by 30μm using glass-threads in a 10mM NaHCO3-solution to externally irradiate the water volume close to the surface. The radiolytic oxidation of the UO2-matrix is studied under Ar- and H2-atmospheres. The dissolution of highly Pu-doped MOX has also been investigated, under both Ar- and D2-atmospheres and the extent of which the hydrogen effect protects this surface will be presented.

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