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Alteration mechanisms of MOX samples: Studtite formation assessed by Raman Spectroscopy and ^{18}O Isotopic Labeling

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In the prospect of interim wet storage of the MOX spent fuel assemblies in water pools, the case of a defect affecting the clad must be considered. The high gamma irradiation field, slightly acidic pH of the aerated water (5 - 5.5) and presence of oxidizing species such as H_2O_2 arising from water radiolysis are so many parameters that need to be assessed in such a scenario [1]. The direct contact of the fuel with the pool water will lead to its oxidative dissolution and the formation of secondary phases that may affect the integrity of the assemblies. We aim in this study at understanding the mechanisms responsible for the formation of secondary phases on MOX fuels when in contact with radiolyzed water.

Non-irradiated MOX07 heterogeneous pellets (MIMAS MOX 7% Pu/(U+Pu)) were leached in aerated water under a gamma source (^{60}Co) in order to reproduce the interim storage environment in a hot cell. The initial pH of the solution was of 6.3 but was expected to acidify because of the oxic conditions. This experiment was followed by a second one performed in the same experimental conditions but with water enriched at 97% in ^{18}O .

Samples were analysed using Raman spectroscopy over time during the 3 months of the experiments. Punctual spectra as long as mappings of the samples were acquired in order to follow the sample's evolutions and link it to their chemical compositions. The Raman spectroscopy being sensitive to mass variations, the ^{18}O of the second experiment act as a marker for the oxidation/phase formation at the sample's surface.

These characterizations of the solids were combined with leachate analyses to follow the alteration markers.

During the leaching experiments, the uranium-rich zones are preferentially altered: they are dissolved prior to Pu-rich aggregates, which causes the appearance of holes at the surface of the samples. This result illustrates the preferential dissolution of the UO_2 grains in the presence of oxidizing species, the zones with a high plutonium content being much more stable with respect to dissolution.

In addition, we evidenced the heterogeneous formation of uranium peroxide at the surface of the samples accordingly to their chemical compositions (Figure 1). In the early stages of the precipitation, this selective dissolution of the UO_2 grains leads to a local precipitation of studtite on their surface and in the corrosion pits, indicating a localized process at the interface. Local supersaturation processes are possible, and preferential germination sites may be found in these corrosion pits. In the long term, the entire MOX fuel surface was covered, including the plutonium-enriched aggregates. We demonstrate here, thanks to Raman mappings, the local nature of the oxidative dissolution and secondary phases precipitation.

Concerning the formation of the uranyl and peroxide bonds, isotopic analysis of the Raman bands of the studtite precipitates highlighted very distinct exchanges (Figure 2). The oxygen atoms in the uranyl bond and in the peroxide bond do not have the same origin, which could be explained by the respective roles of radicals and hydrogen peroxide. The radicals would be mainly involved in the formation of the uranyl ion during the fuel surface oxidation, while the hydrogen peroxide would lead to the formation of peroxide bridges during the studtite precipitation. Finally, this work also demonstrated the feasibility of such an experimental approach, combining Raman imaging with isotopic labeling, to improve our understanding of dissolution mechanisms.

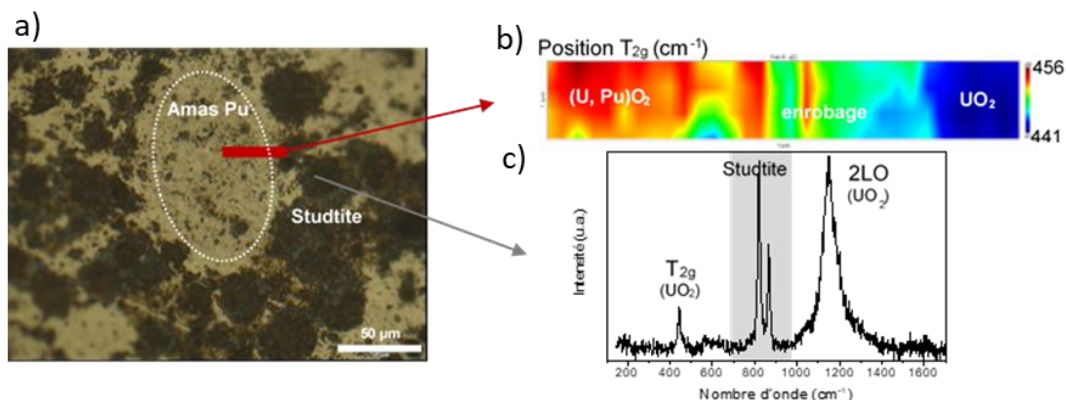


Figure 1: Heterogeneous precipitation of Studtite on U-rich zones of the MOX sample after 20 days of leaching in water with a natural isotopic composition; a) optical image b) Raman mapping and c) Raman spectra of the surface.

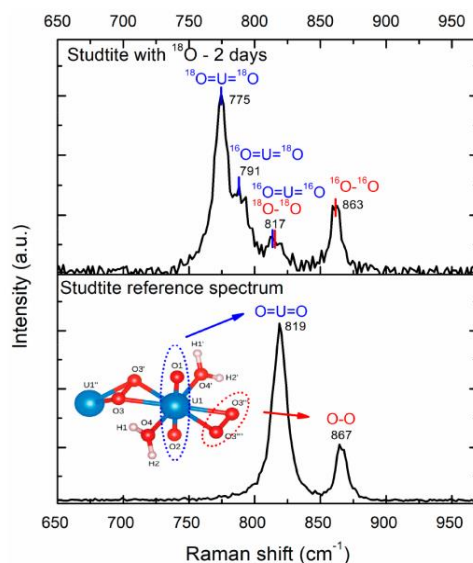


Figure 2: Raman spectra of studtite formed at the surface of the MIMASMOX sample after two leaching days in ^{18}O -enriched water (top) and formed in water with a natural isotopic composition (bottom), with band assignments and ball-and-stick representation [2].

[1] M. Magnin et al., Journal of Nuclear Materials 462 (2015) 230–241.

[2] L. Sarrasin et al., The Journal of Physical Chemistry C 2021 125 (35), 19209-19218.