Radiolysis in 2D-and ID-confining materials

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The influence of ionizing radiation on clay minerals is poorly known, in spite of their use as a major component of the engineered barrier in High Level Nuclear Waste Repositories (HLNWR).[1] In this context, the production of H_2 by clay minerals under ionizing radiation could be a real issue. It can, e.g., lead to the loss of radionuclide retention properties by creating cracks in the engineered barrier. It is thus important to determine H_2 formation reaction mechanisms and to understand the role of several parameters on this production, such as the water amount, the presence of impurities and the nature of the clay mineral.

Moreover, clay minerals provide a unique and very interesting system to study radiolysis in a model 2D-confining material. Indeed, clay minerals are hydrous silicates of aluminum, magnesium, or iron displaying a layered structure. In the sheets, TO_4 tetrahedral (T) sites usually occupied by Si^{4+}, Al^{3+}, or Fe^{3+} cations interconnected by three vertices, combine themselves into pseudo-hexagons $(TO_4)_6$ linked to a sheet of octahedral (O) sites, usually occupied by Al^{3+}, Fe^{3+}, Mg^{2+}, or Fe^{2+} cations and form 2D sheets (Figures 1a and 1b). By changing the nature of the atoms which are present, the amount of water can be tuned: in talc, no water is present (Figure 1a) whereas its amount can be varied in swelling clays such as montmorillonite or saponite for example (Figure 1b) due to the presence of cations in the interlayer space. We have shown that under irradiation by accelerated electrons, the dihydrogen production in synthetic talc, which is solely due to structure hydroxyl groups, is of the same order of magnitude as the one obtained in liquid water.[2] This yield is divided by 30 in the case of natural talc from Luzenac, evidencing the importance of the impurities as scavengers of the precursors of dihydrogen. In the case of synthetic montmorillonite and saponite, the radiolysis of water confined in the interlayer space, that has a thickness of a few Å, leads to H_2 yields which are two to three times higher than the one measured in water.[3] Moreover, these yields are similar for montmorillonite and saponite, evidencing that the charge location only plays a minor role in the H_2 production.

Layered double hydroxides (LDH) are analogous of clay minerals (Figure 1c). They are also a layered material, where the positive charges of the sheets are compensated by the presence of anions in the interlamellar space. In this case, the anion can play a role in the radiation chemistry, contrary to the case of clay minerals for which the cation (Na^+ in the present work) is inert towards ionizing radiation. We have shown that the nature of the anion controls the H_2 production in LDHs.

A last system of interest is imogolite[4] (Figure 1d) which is an aluminosilicate nanotube. It enables understanding the radiation chemistry of water confined in an 1D geometry.

Parallel to the H_2 production measurements, other characterization techniques such as electron paramagnetic experiments have enabled proposing reaction schemes. Reaction mechanisms accounting for H_2 production in confined media will be proposed and discussed according to the nature of the confining matrix, the amount of water.... All these results are of interest in the context of the disposal of radioactive waste.

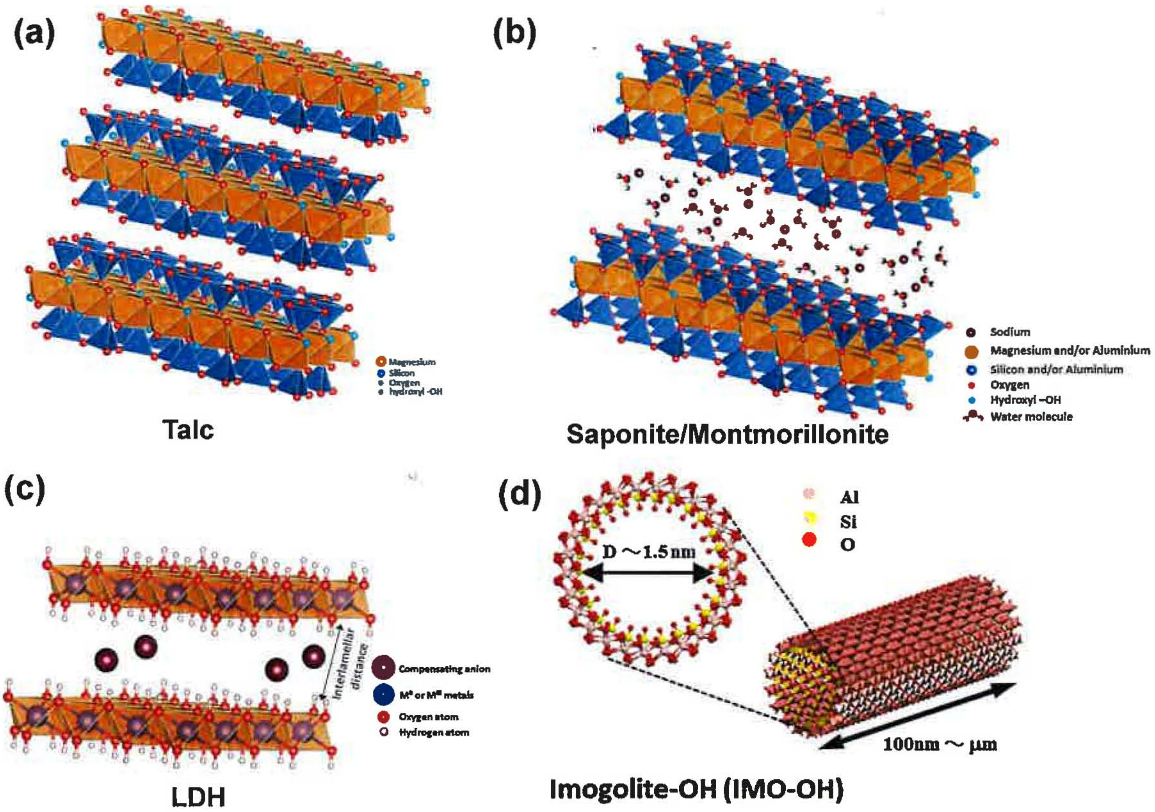

Figure 1. Different confining materials under study. 2D geometries: a) talc; b) swelling clays (saponite and montmorillonite); c) Layered Double Hydroxides (LDH). 1D geometry: d) imogolite.

References

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