Supporting information for “Reaction mechanisms in swelling clays under ionizing radiation: influence of the water amount and of the nature of the clay”

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SI-1: Infrared spectroscopy of synthetic montmorillonite and saponite

Infrared (IR) spectra were recorded in the 4000-500 cm\(^{-1}\) energy range with a Bruker Tensor 27 FT-IR spectrophotometer using the ATR (attenuated total reflectance) technique equipped of a Golden Gate accessory with a diamond crystal. All the spectra were collected with a 4 cm\(^{-1}\) resolution from 100 scans and data were analyzed using the OPUS software. The background (ambient atmosphere, no sample on the ATR accessory) was subtracted in all cases. A standard correction of the ATR signal was performed by multiplying the ATR signal by the corresponding wavenumber in order to take into account the variation of the penetration depth of the evanescent wave into the sample.

Figure 1 presents the IR spectra of synthetic montmorillonite and saponite as a function of the relative humidity (RH). The corrected ATR signal of the band of the vibrational modes of water (O-H stretching and H\(_2\)O bending) increases with RH, meaning that the amount of water in the sample increases, as expected. Infrared bands are identified thanks to literature data\(^{1-5}\) and are described in Table 1.

Figure 1. IR spectra of (a) synthetic montmorillonite and (b) synthetic saponite at five relative humidities: 0% RH (black line), 3% RH (red line), 11% RH (blue line), 43% RH (dark cyan line), 74% RH (magenta line) and 97% RH (orange line). Spectra are normalized using the isolated \(\nu_{\text{Mg-O}}\) band at 527 cm\(^{-1}\) (montmorillonite) and at 650 cm\(^{-1}\) (saponite).
<table>
<thead>
<tr>
<th>Wavenumber range (cm⁻¹)</th>
<th>Vibration mode</th>
<th>Signal’s intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>νMgO-H ≈ 3700</td>
<td>isolated MgO-H stretching</td>
<td>Medium</td>
</tr>
<tr>
<td>4000-3000</td>
<td>O-H stretching mode</td>
<td>Strong or medium</td>
</tr>
<tr>
<td>1630</td>
<td>H₂O bending mode</td>
<td>Medium</td>
</tr>
<tr>
<td>1115-950</td>
<td>Si-O-Si assymetric stretching</td>
<td>Strong or medium</td>
</tr>
<tr>
<td>920-843 (montmorillonite)</td>
<td>O-H deformation –linked to cation</td>
<td>Strong or medium</td>
</tr>
<tr>
<td>805 (saponite)</td>
<td>Si-O-Si symmetric stretching</td>
<td>Weak</td>
</tr>
<tr>
<td>798 (montmorillonite)</td>
<td>Si-O deformation perpendicular to optical axis</td>
<td>Weak</td>
</tr>
<tr>
<td>650 (Saponite)</td>
<td>Si-O deformation parallel to optical axis</td>
<td>Medium</td>
</tr>
<tr>
<td>527 (montmorillonite)</td>
<td>Mg-O stretching</td>
<td>Weak</td>
</tr>
</tbody>
</table>

Table 1. IR bands (position, assignment) detected in montmorillonite and saponite.

Noteworthy, the maximum of the O-H stretching band is shifted towards lower wavenumbers when RH increases. This corresponds to a strengthening of the hydrogen bond network with the water content.¹⁵
SI-2: Example of Differential Thermal Analysis (DTA)

Figure 2 represents the DTA curve of saponite at 97% relative humidity allowing us to identify the different weight loss regions.

Figure 2. DTA curve for saponite at 97% relative humidity.
SI-3: X-Ray Diffraction (XRD) of synthetic montmorillonite and saponite

A Bruker D8 Advance diffractometer equipped with a grazing parabolic Göbel mirror, a Cu emitter ($\lambda_{\text{CuK}\alpha} = 1.541$ Å, 40 kV/40 mA) and a Vantek detector (position sensitive detector) was used to collect powder X-ray patterns of synthetic montmorillonite and saponite. From XRD measurements, the intercalation of 0, 1 or 2 layers of water molecules in the interlayer space around the cations can be determined.\textsuperscript{6-12} The interlayer distance ranges from 9 to 10 Å if there is no water layer. Adding a water layer increases the distance by about 2.5 Å.

Figure 3 presents the assignments of different XRD diagrams, based on literature data.\textsuperscript{6-12} The attribution of the peaks changes with RH (Figure 3).

**Figure 3:** X-Ray diffraction diagrams of (a) saponite 11% RH, (b) saponite 97% RH, (c) montmorillonite 97% RH and (d) $d_{001}$ area of montmorillonite at three different RH.

As expected for these clays, the interlayer space distance, i.e. the number of water layers, globally increases with RH. Up to RH = 43%, only one water layer is present in both samples while increasing the relative humidity beyond, two water layers are formed within the...
interlayer space. The threshold of 43% RH is very particular for montmorillonite, as XRD results evidence the coexistence of 1 and 2 water layers (Figure 3d).
SI-4: Comparison of hydration of samples before and after irradiation

The influence of irradiation on the water content was monitored by TGA and XRD (Figures 4-5). All the results evidence that irradiation at a dose of 200 kGy has no influence on the water content of the sample.

**Figure 4.** Total water content determined by TGA for non-irradiated (reference) and irradiated (200 kGy) synthetic: montmorillonite (a) and saponite (b) as a function of RH.

**Figure 5.** $d_{001}$ distance determined by XRD as a function of RH for non-irradiated (reference) and irradiated (200 kGy) synthetic: (a) montmorillonite and (b) saponite.
SI-5: Measurements of dihydrogen radiolytic yield

The cumulated H₂ production as a function of the dose is presented in Figure 6 for synthetic montmorillonite and saponite. The H₂ production evolves linearly with the dose which enables us to deduce the corresponding H₂ radiolytic yield, expressed in mol.J⁻¹, from the slopes of the different lines.

*Figure 6. Cumulated H₂ production (symbols) for synthetic montmorillonite (a) and saponite (b) as a function of the dose at six different relative humidities. The corresponding linear fits are given.*
SI-6: Electron paramagnetic resonance (EPR) of synthetic saponite

Figure 7 presents EPR spectra at 90 K of synthetic saponite at three different RH. Observations and conclusions are the same as in the case of montmorillonite.

**Figure 7.** EPR spectra of synthetic montmorillonite at (a) 0% RH, (b) 11% RH and (c) 97% RH irradiated at 15 kGy. The spectra are recorded at 90 K. Effective experimental g-values are given directly on the figure.
References