Can clays ensure nuclear waste repositories?
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Research on argillite as a possible host rock for nuclear waste disposal is still an open subject since many issues need to be clarified. In the Underground Research Laboratories constructed for this purpose, a damaged zone around the excavation has been systematically observed and characterized by the appearance of micro-fissures. We analyse here - at nanoscale level - the calcite/clay assembly, the main constituents of argillite, under storage conditions and show the fragility of the montmorillonite with respect to calcite. Under anisotropic stress, we have observed a shear deformation of the assembly with the presence of broken bonds in the clay mineral, localised in the octahedral rather than the tetrahedral layers. The stress/strain curve leads to a failure strength point at 18.5 MPa. The obtained in-plane response of the assembly to perpendicular deformation is characterized by smaller perpendicular moduli $E_\perp = 48.28$ GPa compared to larger in-plane moduli $E_\parallel = 141.39$ GPa and $E_\parallel = 134.02$ GPa. Our calculations indicate the instability of the assembly without water molecules at the interface in addition to an important shear deformation.
minimizations are performed allowing all individual ionic coordinates and lattice parameters to vary. In this study, we analyse, first, the behaviour of the montmorillonite (001)/calcite (104) interface under the effect of anisotropic stress at a fixed temperature of 90°C. In the second experience, we apply a shear stress (xy, xz and yz) to the assembly. These simulations are carried out in the presence of water at the interface.

In the first experience, we have applied an anisotropic stress to the calcite/clay interface with $\sigma_{xx} = 13$ MPa, $\sigma_{yy} = 16.9$ MPa, while the vertical stress $\sigma_{zz}$ varies from 0 to 20 MPa. For each value of $\sigma_{zz}$, we compress the assembly then we release the constraint and leave the system to relax. The obtained stress/strain response is shown in Fig. 3a.

We notice that the deformation of the assembly is anisotropic, more pronounced along the vertical direction. This anisotropy is caused by compression of the interlayer space along the z direction, which requires much smaller forces than the compression of aluminosilicate layers in-plane. The in-plane response of the assembly to perpendicular deformation is characterized by smaller perpendicular moduli $E_z = 48.28$ GPa compared to larger in-plane moduli ($E_x = 141.39$ GPa, $E_y = 134.02$ GPa). Thus the ratio (the perpendicular moduli over the in-plane moduli) is equal to 2.8. This value is in agreement with the experimental measurement of the anisotropic ratio of the Young’s modulus, which is equal to $2^{19}$. This explains the easier deformation of the assembly along z direction rather than the horizontal one (more resistance to deformation).

As shown in Fig. 3a, the stress/strain curves deal with three phases: elastic, plastic and a failure phase. The obtained failure strength corresponds to 18.5 MPa for both the vertical and the horizontal direction. We have observed that the plastic behaviour of the assembly is obtained when the vertical stress $\sigma_{zz}$ varies between 18 and 20 MPa. The corresponding strains variations are: from 0.02 to 0.04 along x direction, between 0.05 and 0.1 along y direction and between 0.08 and 0.13 along the vertical direction. These can be the conditions to have a deformation of the assembly without the formation of fissures.

Previous hierarchical simulation techniques at the electronic and atomistic levels show the strength and possible failure mechanisms of Layered Silicates over the range of cation densities $^{20}$. Their study on pyrophyllite, montmorillonite and mica showed a large mechanical anisotropy, kinks, cation intrusion, and shear flow in the aluminosilicate layers. Besides intense research efforts have been dedicated to the mechanical properties of clay minerals on the macroscale $^{21-30}$.

We present in Fig. 3b the relaxed atomistic assembly after the application of the storage stress conditions ($\sigma_{xx} = 13$ MPa, $\sigma_{yy} = 16.9$ MPa and $\sigma_{zz} = 13.4$ MPa). We observe, first, that the damage is present in the clay layers part and not in calcite. These broken bonds (in the clay layers) are noticed in the octahedral rather than the tetrahedral layers. We note that the bonding distances of Si-O and Al-O are 1.58 Å and 1.98 Å, respectively, which could explain the difficulty to break the tetrahedral bond. Moreover, we observe from Fig. 3b that the assembly has a shear deformation.

In Fig. 4, we plot the variation of the interfacial distance and the thickness of the first interlayer depending on the vertical stress. It appears that under the application of a vertical constraint between 5 MPa and 13.4 MPa, the thickness of the clay layer increases by 1.39 Å, while the interfacial distance undergoes a slight increase (0.42 Å). Besides, when applying a stress from 13.4 MPa to 18.5, the clay layer undergoes a slight compression of 0.38 Å, while the interfacial distance decreases with 0.30 Å. From 18 MPa to 20 MPa, the thickness of the interlayer layer increases rapidly with 1.63 Å; for the interfacial distance it undergoes a sudden compression of 1.21 Å.

Regarding the response of the interface to the vertical deformation, we remark that, in the presence of water molecules at the interface, (see Fig. 5a and b) no damage is observed neither in the tetrahedral clay layer nor in the calcium carbonate one. Furthermore we noticed a slight shear deformation of the aluminosilicate as well as in calcium carbonate layers.
In Fig. 5b, we plot the relaxed interface of the assembly without water molecules (at the interface) after the application of anisotropic stress. We clearly observe the presence of broken bonds in the first tetrahedral clay layer. Note that the shear deformation in the clay layers is more pronounced in the case of an assembly without water at the interface. Our calculations show the instability of the assembly in the last case (without water at the interface) with a total energy of 27680 eV and an expansion of the system about 0.7%.

We have already studied the water role in our recent work. From the variation of the total energy versus the interfacial distance, we have shown that the presence of water has the effect of absorbing the excess energy provided by the system and thereby stabilize the interface. We note that our study of calcite/clay interface with the presence of water is the first work in such area. However, there are many other papers interested into the role of water on calcite surface. Experimental studies have given considerable information concerning the structure of the carbonate-water interface and the growth mechanisms. Other computational calculations have shown that the incorporation of water into the amorphous calcium carbonate nanoparticles make the system thermodynamically more stable. Using a new force field, Raiteri et al. have examined the thermodynamics of calcium carbonate-water system.

Responses to shear stress in the presence of water molecules at the interface were analysed in Fig. 6 in the xy, xz and yz planes. We remark that the assembly is more resistant to shear in the xy and xz planes compared to yz plane. Besides, we noticed that the system
In summary, a nanoscale tool is used to analyse at the atomic level the mechanical behaviour of the calcite/clay interface under storage conditions. The assembly of the calcite (104) with montmorillonite (001) subject to storage conditions showed the fragility of the montmorillonite with respect to calcite, which resist to these conditions. The assembly calcite/clay is more deformable in the direction perpendicular to the interface (z-direction), which is due to the lamellar clays structure. Moreover, when applying an anisotropic stress, a failure point appears at 18.5 MPa with a compression of the interlayer space leading the breaks of the aluminosilicate bonds, which explains the damage around galleries in the Callovo-Oxfordian argillite. We have concluded that the presence of water molecules give more stability of the assembly since no damage at the interface has been observed in the tetrahedral clay layer neither in calcium carbonate part. Therefore, it is necessary to intensify studies on other mineral rocks, which do not lead damage under storage conditions and hence ensure the safety of nuclear waste repository.

**Methods summary**

To ensure a good accommodation at the interface, we built what we call the “supercell” by duplicating the unit cell of calcite 11 times in the x direction and 4 times in the y direction. For clay system, we duplicate the unit cell 3 times in the x direction and 5 times in the y direction. Therefore, the obtained lattice mismatch is 1.58% for the x direction and 2.9% for the y direction. Thus, the dimension of the simulation box is (5.53 × 10.39 × 70.50) nm, and nx = 90’, the number of atoms is 26 280.

**Potential model for the clay/calcite interface:** The clay mineral model considered here is a Wyoming-type Montmorillonite, with the unit cell formula Na0.75[Si2.75Al0.25](Al2Si3Mg6.53)O10(OH)2·1.5H2O. To describe the Montmorillonite (001)/calcite (104) interface, we have developed existing models for calcite and clay by adding terms describing the interatomic interactions between constituents of calcite and clay at the interface. We have used the ClayFF potential model\(^\text{37}\), well tested for clays\(^\text{38–49}\) and the Xiao forcefield for calcite \(^\text{50}\), that we have previously used in the analysis of bulk and surface state of calcite rock\(^\text{1}\). This is a new forcefield taking into account the aqueous environment using the TIP3P water model\(^\text{52}\). At the interface, we have described the interactions between the last layer of the calcite (Ca\(^{2+}\), CO\(_3^{2-}\)) and the first layer of clay (SiO\(_2\)) using the model of Guillot-Sator\(^\text{53}\).

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Author contributions

A.Z. conceived and designed the study. W.S. performed the theoretical studies and simulations. W.S. and A.Z. analysed and discussed the results. W.S. and A.Z. wrote the manuscript. A.Z. conceived and designed the study. W.S. performed the theoretical studies and simulations. W.S. and A.Z. analysed and discussed the results. W.S. and A.Z. wrote the manuscript. All authors discussed the conceptual and practical implications of the method at all stages.

Additional Information

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