

Elevated temperature effects on microstructure of compacted smectite

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Introduction

In the context of engineered barrier systems (EBS) in geological disposal concepts for high level nuclear waste (HLW), the clay buffer can be exposed to an elevated temperature sourcing from the heat generated by the HLW (heating) and the water intrusion at the interface with the host rock (hydration). Understanding the effects of elevated temperature on porosity and pore-water in the system of clay buffer (compacted bentonite) is crucial for predicting the evolution of buffer during the operational phase. The pore system of compacted bentonite can be simplified by two scales of porosity: i) the interlayer porosity that includes the spaces between the unit layers of smectite (microstructure) and ii) the macro porosity that represents the pore spaces between the particles and aggregates of particles (Fig. 1). The interlayer hydration or dehydration process can only alter the distance between the clay microstructure units (interlayer distance) by adding or removing discrete layers of water (Push and Yong, 2006). Water molecules can be exchanged between these two scales of porosity. Elevated temperature can affect the equilibrium state of water in the interlayer and induce an exchange of water between the interlayer porosity and macro porosity. Predictive models for the interlayer porosity and its variation in compacted bentonite are very limited and they are usually based on XRD results at ambient temperature. A new approach for modelling the evolution of interlayer water of compacted bentonite with temperature is presented that is based on the geochemistry of interlayer hydration and dehydration of smectite.

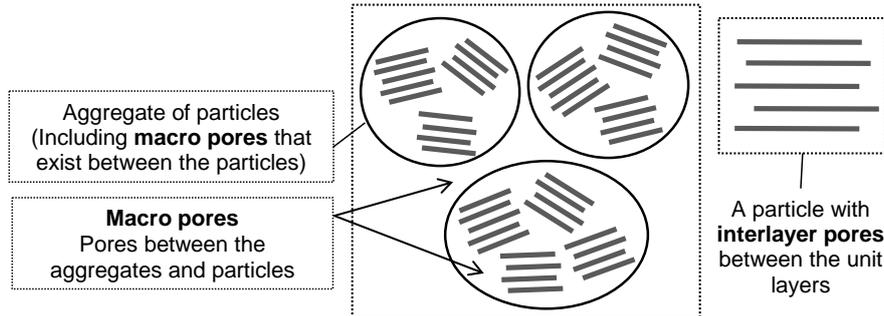


Fig. 1: Schematic of interlayer porosity and macro porosity in compacted bentonite

Interlayer porosity evolution – a geochemical modelling approach

The interlayer hydration and dehydration of smectite can be described as a solid solution geochemical reaction between the interlayer water molecules and a symbolic hydrous and its homologous anhydrous counterparts of smectite (Ransom and Helgeson, 1995):

$$\log K_{eq} = \log \left(\frac{1 - X_{hs}}{X_{hs}} \right) + \frac{W_s}{2.303RT} (2X_{hs} - 1) + n_m \log a_w \quad (1)$$

where, K_{eq} represents the equilibrium constant of the reaction and X_{hs} represents the mole fraction of hydrous smectite. W_s denotes the Margules parameter for the binary regular solid-solution of hydrous and anhydrous smectite components at reference temperature and pressure. R refers to gas constant and T is temperature. n_m is the number of water moles in the interlayer, given as the moles of water per smectite half formula unit, i.e. $O_{10}(OH)_2$. a_w is the activity of water.

The thermodynamic parameters of the solid-solution model, including the equilibrium constant of the reactions and Margules parameters are derived from water/vapour adsorption experimental data. Temperature effects are reflected directly in the model ($\frac{W_s}{2.303RT}$) and indirectly on the equilibrium constant of the reaction ($\log K_{eq}$), given as (Langmuir, 1997):

$$\log K_{eq} = (\log K_{eq})_{T_r} + \frac{\Delta H_{r,T_r}^0}{2.303R} \left(\frac{1}{T_r} - \frac{1}{T} \right) + \frac{\Delta C_p^0}{2.303R} \left(\frac{T}{T_r} - 1 \right) + \frac{\Delta C_p^0}{2.303R} \ln \left(\frac{T}{T_r} \right) \quad (2)$$

where, $\Delta H_{r,T_r}^0$ is the standard enthalpy of reaction at reference temperature (T_r) and ΔC_p^0 is the standard heat capacity of the reaction at constant pressure.

The interlayer porosity is calculated as a function of mole fraction of hydrous smectite from the interlayer hydration/dehydration reaction (i.e. Eq. 1) (Sedighi and Thomas, 2014):

$$\theta_{il} = X_{hs} \frac{n_m v_{il}}{m_{sm}} \rho_d^{sm} \quad (3)$$

where, v_{il} denotes the specific molar volume of the interlayer water, m_{sm} is the molar mass of dry smectite and ρ_d^{sm} represents the bulk dry density of smectite.

Temperature effects on interlayer porosity of compacted bentonite

The model proposed was applied to calculate the interlayer porosity of compacted MX-80 bentonite (dry density around 1.6 Mg/m³) and at a range of temperatures (20, 40, 60 and 80 °C). Thermodynamics parameters of the solid solution model (K_{eq} and W_s) were adopted from values reported by Sedighi and Thomas (2014) for compacted MX-80. $\Delta H_{r,T_r}^0$ and ΔC_p^0 were those reported by Ransom and Helgeson (1995). Fig. 2 (left) presents the variations of activity of water versus mole fraction of the hydrous smectite that was calculated by using the solid solution model. Experimental water adsorption data reported in the literature for compacted MX-80 at different temperatures (Jacinto et al. 2009; Villar and Gómez-Espina, 2008) was also used to derive a_w versus X_{hs} . The variations predicted by the model are close to those calculated from the experiment especially at high relative humidity (RH). During re-saturation process, the variation of interlayer porosity with relative humidity is considerably affected by the temperature increase (Fig.2- right). Based on the results, it is anticipated that an exchange of water from the interlayer porosity to macro porosity can occur when the interlayer porosity reduces from 22% at 20 °C to 18% at 80 °C at saturated conditions (more than 20% decrease). Similar trend is observed at different relative humidity values for up to 30% RH

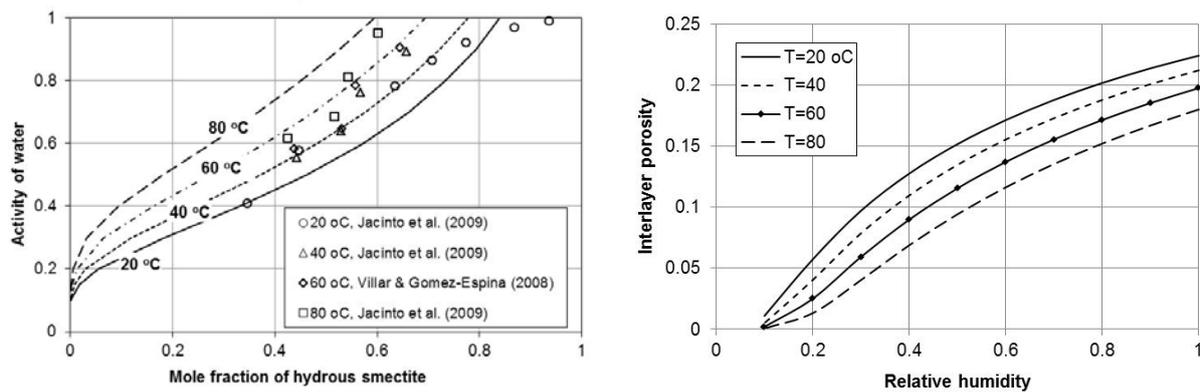


Fig. 2: a_w versus X_{hs} (left) and θ_{il} versus RH at different temperatures (right) for compacted MX-80

Conclusions

The model presented provides a theoretical approach for calculating the variations of interlayer porosity with relative humidity and temperature in compacted bentonite. The model is based on thermodynamics of hydration and dehydration of smectite that is described as a regular solid solution geochemical reaction. The application of the model for the case of compacted MX-80 bentonite highlights a strong potential for the exchange of water between the interlayer water and macro pores. Under constant volumetric conditions, the macro porosity provides larger pathways at elevated temperatures for the flow of moisture and transport of chemicals at ambient temperature. The new findings provide a better understanding of the impacts of elevated temperature on compacted bentonite that can be adopted in predictive coupled models.

References

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