FREEZING IN SATURATED BENTONITE –
A THERMODYNAMIC APPROACH

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A thermodynamic description of the response of a saturated bentonite system to changes in external variables has successfully been adopted in several different cases. Examples include correspondence between swelling pressure and water retention properties of unconfined bentonite (Bucher and Müller-Vonmoos, 1989), pressure response due to changes in salt concentration of an external solution (Karnaand et al., 2005) and criteria for gas entry in gas migration experiments. In the present work we apply the same view to predict the behavior of confined bentonite below 0°C, the freezing point of water.

The chemical potential of water in unconfined bentonite can be written

$$\mu_{\text{clay}}(w, T) = \mu_{p.w.}(T) + RT \ln RH_{\text{unconf}}(w, T)$$

where $RH_{\text{unconf}}(w, T)$ is the water retention curve for the specific material, giving the equilibrium relative humidity for a specified water ratio and temperature. The variation of $RH_{\text{unconf}}(w, T)$ with temperature is known to be minor. This strongly indicates that interlayer porewater as a phase resembles liquid water. It is reasonable to assume that interlayer pore water will resemble a liquid phase also at temperatures below 0 °C. However, the vapor pressure of ice has a faster decline with temperature than has (supercooled) liquid water. Consequently, for a given temperature below 0°C, there exists a maximum water ratio

$$w_{\text{max}}(T) = w_{\text{unconf}} \left( \frac{P_{\text{vapor}}(T)}{P_{\text{vapor}}(T)} \right)$$

where $P_{\text{vapor}}(T)$ and $P_{\text{vapor}}(T)$ are vapor pressures of ice and super cooled liquid water respectively and $w_{\text{unconf}}(x, T)$ is the inverse of the retention curve introduced above. The behavior is illustrated in Figure 1.

A confined system, specified by a void ratio $e$, in equilibrium with an external water reservoir, exercises a swelling pressure in order to equalize the chemical potentials of water in the clay and in the reservoir,

$$P_s(e, T) = -\frac{RT}{V_w} \ln RH_{\text{unconf}}(w_{\text{sat}}, T) \quad T > 0°C.$$  

**Figure 1:** Schematic illustration of vapor pressure variation with temperature for ice, pure water and montmorillonite porewater at two different water ratios ($w_1 > w_2$). Freezing of pure water occurs at a). Temperatures for which $w_1$ and $w_2$ are the maximum water ratios are indicated by b) and c) respectively.
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Here \( w_{sat} = \frac{\rho_{water}}{\rho_{solid}} \) is the saturated water ratio. Below 0°C, the clay water chemical potential should instead be equalized with that of an ice phase at the prescribed temperature. Because the ice vapor pressure, and hence its chemical potential, is a much more steep function with temperature (figure 1) the result is a drop of swelling pressure with temperature

\[
P_s(e, T) = P_s^0(e) + \frac{RT}{V_w} \ln \left( \frac{p_{vap}^\text{ice} (T)}{p_{vap}^\text{p.w.} (T)} \right) \quad T < 0°C
\]

Where \( P_s^0(e) \) denotes the swelling pressure above 0°C (whose temperature dependence here is neglected). From this expression it is seen that the resulting swelling pressure is completely lost at a critical temperature \( T_c \), where

\[
-\frac{RT_c}{V_w} \ln \left( \frac{p_{vap}^\text{ice} (T_c)}{p_{vap}^\text{p.w.} (T_c)} \right) = P_s^0(e)
\]

This temperature corresponds to the point on the \( w_{max} (T) \)-curve from above where \( w_{max} = w_{sat} \).

At temperatures below \( T_c \), water will be transported out of the interlayer pores and add to (or form) an external ice phase. In a confined system this ice phase will contribute to an increase of the pressure since water expands as it freezes. The amount of ice formed, and hence the pressure increase, is directly related to the water retention properties of the unconfined clay system. Figure 2 shows the predicted total pressure as a function of temperature for a confined system originally at a swelling pressure of 7MPa.

![Figure 2: Predicted total pressure as a function of temperature of a confined bentonite sample whose swelling pressure at below 0°C is 7 MPa.](image)

References