Non-isothermal water retention curve model for adsorption

Yi Liu 1,2, Guoqing Cai 1,2*, Jian Li 2, Rui Yang 2 and Chenggang Zhao 2

1 Key Laboratory of Urban Underground Engineering of Ministry of Education, Beijing Jiaotong University, Beijing 100044, China;
2 School of Civil Engineering, Beijing Jiaotong University, Beijing 100044, China.

Corresponding author’s e-mail: guoqing.cai@bjtu.edu.cn

Abstract. Non-isothermal water retention curve (WRC) in high suction range is a fundamental and interpretative tool to describe the behavior of bentonite and is crucial to ensure the safety and effective operation of high-level nuclear waste repository. In this study, an adsorption equation at given water content is proposed according to Kelvin equation, Clausius-Clapeyron equation and the adsorption enthalpy equation. Then, the proposed adsorption equation is incorporated into van Genuchten-Mualem model to establish a non-isothermal WRC model for adsorption. Four series of non-isothermal WRC data in a temperature range (293~353 K) and high suction range (>1 MPa) from four different soils are employed to illustrate the application and performances of the proposed model. The proposed WRC model provides good agreement between the calibrated/predicted and measured non-isothermal WRCs.

1. Introduction

Bentonite has been selected as a suitable material to backfill and seal high-level nuclear waste repository (Figure 1). Bentonite is initially unsaturated in the actual engineering, and the suction will attain tens or hundreds of MPa because of its strong water retention capacity. During the long-term operation of high-level nuclear waste repository, the bentonite will be gradually saturated by groundwater from the surrounding geological formations. Moreover, the radiogenic heat released from the waste container will change the water holding capacity of bentonite. Therefore, non-isothermal water retention curve (WRC) in high suction range is a fundamental and interpretative tool to describe the behavior of bentonite and is crucial to ensure the safety and effective operation of high-level nuclear waste repository.

Figure 1. Schematic view of a high-level nuclear waste repository (Sánchez [1] and Ye et al. [2]).

In the last decades, a number of laboratory studies reported in the literature focused on studying the WRCs under non-isothermal conditions [3-19]. In general, experimental results show that increasing temperature shifts WRC toward the direction of lower suction despite the soil types. This shift in WRC

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represents a decrease in the water holding capacity of the soil. In addition, a series of pioneering models attempting to consider the mechanisms of temperature effect have been proposed by scholars. For example, Philip and de Vries [20] firstly assumed that the surface tension was the sole temperature-dependent parameter in their model. Afterwards, Grant and Salehzadeh [21], Grant [22], Wu et al. [23], Salager et al. [9], Tong et al. [24], Gao and Shao [14], Roshani and Sedano [16] and Liu et al. [18] successively proposed non-isothermal WRC models considering various mechanisms such as temperature dependence of the surface tension, soil-water contact angle, liquid density and shape of air/gas bubbles. However, the abovementioned non-isothermal WRC models are mainly based on capillarity theory, and how to analyse the temperature effect in high suction range from the perspective of adsorption is still an unsolved problem. Only Jacinto et al. [7], Schneider and Goss [10], Sun et al. [19] and Vahedifard et al. [25] have done some related work based on the thermodynamics theory.

Based on the motivation issues mentioned above, a non-isothermal WRC model for adsorption is developed here. Firstly, an adsorption equation at given water content is proposed according to Kelvin equation, Clausius-Clapeyron equation [26-27] and the adsorption enthalpy equation. Then, the proposed adsorption equation is incorporated into van Genuchten-Mualem model [28] to establish a non-isothermal WRC model for adsorption. Finally, the proposed model is validated against four series of non-isothermal WRC data in a temperature range (293–353 K) and high suction range (>1 MPa) from four different soils.

2. Non-isothermal water retention curve model for adsorption

Soil suction \( \psi \) can be related to the relative humidity \( RH \) by Kelvin's law [29]:

\[
\psi = -\frac{\rho_wRT}{M_w} \ln RH = -\frac{\rho_wRT}{M_w} \ln \left( \frac{P_v}{P_{vs}} \right)
\]

(1)

where \( \psi \) is the soil suction, \( \rho_w \) is the water density, \( R \) is the universal gas constant, \( T \) is the absolute temperature, \( M_w \) is the molecular mass of water, and \( RH \) is defined as the ratio between the water vapor pressure in soil \( p_v \) and the saturated vapor pressure \( p_{vs} \). Assuming that the temperature effect on water density is ignored, and this leads to:

\[
\psi - T \frac{\partial \psi}{\partial T} = \frac{\rho_wRT^2}{M_w} \left( \frac{\partial \ln p_v}{\partial T} - \frac{\partial \ln p_{vs}}{\partial T} \right)
\]

(2)

According to Clausius-Clapeyron equation [26-27], the change with \( T \) in \( \ln p_v \) and \( \ln p_{vs} \) can be related to the differential enthalpy via:

\[
\frac{\partial \ln p_v}{\partial T} = -\frac{\Delta H_m}{RT^2}
\]

(3)

\[
\frac{\partial \ln p_{vs}}{\partial T} = -\frac{\Delta H_{m^{sat}}}{RT^2}
\]

(4)

where \( \Delta H_m \) and \( \Delta H_{m^{sat}} \) are the differential enthalpy of adsorption and the differential enthalpy of condensation/evaporation of pure water, respectively. Equations (2)-(4) can be combined to yield:

\[
\psi - T \frac{\partial \psi}{\partial T} = \frac{\rho_w(\Delta H_{m^{sat}} - \Delta H_m)}{M_w}
\]

(5)

Assuming the following relationship between \( \Delta H_m \) and \( RH \) based on the experimental results of Sun et al. [19] and Schneider and Goss [10]:

\[
\Delta H_m = -a + b \ln RH
\]

(6)

where \( a \) and \( b \) are fitting parameters. Equations (1), (5) and (6) can be combined to yield:

\[
T \frac{\partial \psi}{\partial T} = \left(1 - \frac{b}{RT}\right)\psi - \frac{\rho_w(\Delta H_{m^{sat}} + a)}{M_w}
\]

(7)

\( \psi \) is only a function of \( T \) at a given gravimetric water content, and solve Equation (7) yields the non-isothermal adsorption equation at given gravimetric water content:
\[
\frac{\psi - g}{\psi_0 - g} = \exp\left(\frac{\beta - \beta_0}{T - T_0}\right)
\]

(8)

\[
\beta = \frac{b}{R}
\]

(9)

\[
g = -\frac{R\rho_w(\Delta H_{m}^{sat} + a)}{bM_w}
\]

(10)

where \(T_0\) is the reference temperature, \(\psi_0\) is the soil suction at \(T_0\), \(\beta\) and \(g\) are the parameters controlling the temperature effect on suction. The van Genuchten-Mualem model [28] can be written as:

\[
w = \frac{w_s}{[1 + (\alpha\psi)^n]^{1-1/n}}
\]

(11)

where \(w\) is the gravimetric water content, \(w_s\) is the saturated gravimetric water content, \(\alpha\) and \(n\) are fitting parameters. According to Equation (8) and van Genuchten-Mualem model, \(w\) at various temperature can be written as:

\[
w = \frac{w_s}{[1 + (\alpha A)^n]^{1-1/n}}
\]

(12)

\[
A = T_0\left(\frac{\psi}{T} - g\right) \exp\left(\frac{\beta}{T} - \frac{\beta_0}{T_0}\right) + gT_0
\]

(13)

3. Validation and comparison

Four series of non-isothermal WRC data in a temperature range (293–353 K) and high suction range (>1 MPa) from four different soils are employed to illustrate the application and performances of the proposed model. The proposed model has 6 parameters (\(w_s\), \(\alpha\), \(n\), \(T_0\), \(\beta\) and \(g\)). Determination of the model parameters is summarised hereafter. The saturated water content \(w_s\), and fitting parameters (\(\alpha\) and \(n\)) can be obtained by fitting a measured WRC at reference temperature \(T_0\) (minimum temperature of each series data in this section). Parameters (\(\beta\) and \(g\)) controlling the temperature effects on suction at given water content can be determined by fitting a measured WRC at another selected temperature (maximum temperature of each series data in this section).

3.1. FEBEX bentonite (data from Villar and Lloret [6])

FEBEX bentonite was selected by the Spanish Agency for Radioactive Waste Management as a suitable material to backfill and seal high-level nuclear waste repository. FEBEX bentonite has a montmorillonite content higher than 90% and Ca is the major exchangeable cation. Villar and Lloret [6] measured the WRCs of FEBEX bentonite at constant volume and different temperatures. The measured WRCs with a dry density of 1.65 g/cm\(^3\) following a wetting path are used here. Figure 2 illustrates the comparisons between calibrated/predicted and measured WRCs at three different temperatures. Fitting parameters (\(w_s = 27.35\%\), \(\alpha = 0.067\), \(n = 1.274\)) can be calibrated by a reference WRC (\(T_0 = 293\) K). Parameters \(\beta\) and \(g\) are calibrated as 1086.40 K and −0.042 MPa/K by using the measured WRC at \(T = 333\) K. The other measured WRC at \(T = 313\) K is employed to validate the proposed WRC model. As can be seen from Figure 2, the calibrated/predicted WRCs are in good agreement with measured WRCs.
3.2. MX-80 bentonite (data from Jacinto et al. [7])

MX-80 bentonite extracted from America mainly has montmorillonite (65~82%) and Na is the major exchangeable cation. Jacinto et al. [7] measured the WRCs of MX-80 bentonite at constant volume and different temperatures. The measured WRCs with a dry density of 1.6 g/cm$^3$ are used here. Comparisons between calibrated/predicted and measured WRCs at three different temperatures are showed in Figure 3. Fitting parameters ($w_s = 26.20\%$, $\alpha = 0.062$, $n = 1.541$) can be calibrated by a reference WRC ($T_0 = 293$ K). Parameters $\beta$ and $g$ are calibrated as 7.55 K and $-12.501$ MPa/K by using the measured WRC at $T = 353$ K. The other measured WRC at $T = 313$ K is employed to validate the proposed WRC model. As can be seen from Figure 3, the calibrated/predicted WRCs are in good agreement with measured WRCs.

3.3. Bentonite-sand mixture (data from Fang et al. [13])

Fang et al. [13] performed WRC tests on bentonite-sand mixture at various temperatures. Bentonite used in the test is produced from Gaomiaozi area in Inner Mongolia of China, and quartz sand aggregate is the manually processed local quartz sand. The measured WRCs with a dry density of 1.8 g/cm$^3$ and sand mix ratios of 30% are used here. Comparisons between calibrated/predicted and measured WRCs at four different temperatures are showed in Figure 4. Select the value 293 K as the reference temperature ($T_0 = 293$ K), and measured WRCs at reference temperature and another temperature ($T = 353$ K) are employed to calibrate parameters ($w_s = 24.28\%$, $\alpha = 0.062$, $n = 1.505$, $\beta = 1147.37$ K, $g = -0.032$ MPa/K). The other measured WRCs at $T = 313$ K and 333 K are employed to validate the
proposed WRC model. As shown in Figure 4, the proposed WRC model gives a good prediction to the test results.

![Figure 4](image)

**Figure 4.** Comparisons between calibrated/predicted and measured WRCs of bentonite-sand mixture (data from Fang et al. [13]).

### 3.4. GMZ bentonite (data from Wan et al. [15])
Wan et al. [15] performed WRC tests on GMZ bentonite at various temperatures. GMZ bentonite mainly has montmorillonite (75.4%) and Na is the major exchangeable cation. The measured WRCs with a dry density of 1.7 g/cm³ following a wetting path are used here. Comparisons between calibrated/predicted and measured WRCs at four different temperatures are showed in Figure 5. Select the value 293 K as the reference temperature \( T_0 = 293 \text{ K} \), and measured WRCs at reference temperature and another temperature \( T = 353 \text{ K} \) are employed to calibrate parameters \( w_s = 24.49\%, \alpha = 0.066, n = 1.383, \beta = 1034.94 \text{ K}, g = -0.062 \text{ MPa/K} \). The other measured WRCs at \( T = 313 \text{ K} \) and \( 333 \text{ K} \) are employed to validate the proposed WRC model. As shown in Figure 5, the proposed WRC model gives a good prediction to the test results.

![Figure 5](image)

**Figure 5.** Comparisons between calibrated/predicted and measured WRCs of GMZ bentonite (data from Wan et al. [15]).

### 4. Conclusions
Non-isothermal water retention curve (WRC) in high suction range is a fundamental and interpretative tool to describe the behavior of bentonite and is crucial to ensure the safety and effective operation of high-level nuclear waste repository. Most non-isothermal WRC models are mainly based on capillarity theory, and how to analyse the temperature effect in high suction range from the perspective of adsorption is still an unsolved problem.
In this study, an adsorption equation at given water content is proposed according to Kelvin equation, Clausius-Clapeyron equation [26-27] and the adsorption enthalpy equation. Then, the proposed adsorption equation is incorporated into van Genuchten-Mualem model [28] to establish a non-isothermal WRC model for adsorption. The proposed model has 6 parameters (\(w_s, \alpha, n, T_0, \beta \) and \(g\)) and can be obtained via WRC data at two selected temperatures.

Four series of non-isothermal WRC data in a temperature range (293–353 K) and high suction range (>1 MPa) from four different soils are employed to illustrate the application and performances of the proposed model. The proposed WRC model provides good agreement between the calibrated/predicted and measured non-isothermal WRCs.

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