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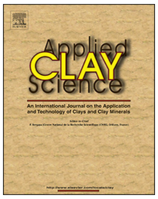

Research paper

A method for calculating unfrozen water content of silty clay with consideration of freezing point

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ABSTRACT

A physical calculation model for the content of unfrozen water of silty clay was proposed with a consideration of freezing point. The freezing point of bulk water, capillary water and bound water was calculated. The freezing point of bulk water was assumed to be constant in the calculation. The Kelvin equation and the theory of water activity were used to calculate the freezing-point changes of the capillary and bound water during the volume decrease, respectively. The influence of soil-particle size on the freezing point was taken into account in the model. In the calculation, the unfrozen water content at a negative temperature was defined as the sum of the volume of capillary and bound water whose freezing point was lower than the given temperature. By using silty clay from the Qinghai-Tibet Plateau as an example, the results of the model calculations were validated by using the measured data from time-domain reflection and nuclear magnetic resonance. The calculations for four existing models as proposed by other scholars were listed for comparison with our model. The results show that the calculated results of our model are precise and reflect the hysteresis effect of the unfrozen water content during freezing and thawing. The model validated an order of freezing in soil: bulk water froze first, most capillary water froze next, and most bound water froze last. This paper explains the existence of unfrozen water from the perspective of freezing-point change and provides a theoretical basis for the calculation.

1. Introduction

Frozen soil is soil or rock which has a temperature below 0 °C. At a negative temperature, not all water transforms into ice, but a certain amount of water exists in soil because of capillarity and the surface energy of soil particles, and this water is termed unfrozen water (Xu et al., 2001). The factors that influence unfrozen water include the soil properties (mineral components, particle size), the initial water content, the dry density, the solute, the temperature, the load and the freezing–thawing history (Xu et al., 2001). The content of unfrozen water affects the structure of pore ice and the cementing of soil particles and ice skeleton in the frozen soil (Wen et al., 2012). For the engineering practice, the unfrozen water content in soil during the freezing and thawing process or state affects the mechanical properties of soil (Xu et al., 2016; Xu et al., 2017). Because of differences in thermal conductivity and heat capacity, the unfrozen water significantly influences the results of the heat-moisture calculation. In summary, the calculation of unfrozen water content is significant to reveal the existence mechanism of unfrozen water and provide a theoretical basis for the numerical calculation.

Some scholars have proposed empirical and semi-empirical equations in the calculation of unfrozen water content with temperature change depending on the fitting of measured data. Early in 1966, Dillon and Andersland (1966) used empirical equations that contain two parameters to calculate content of unfrozen water. Then, some researchers have used the specific surface to calculate the unfrozen water content for different soils (Akagawa, 1998; Anderson and Tice, 1972; Anderson and Tice, 1973; Patterson and Smith, 1981; Tice et al., 1973). Tsytovich (1975) set a plastic index, the water content at a plastic limit and the temperature as parameters, and proposed an equation for the calculation of unfrozen water content. Afterwards, Xu et al. (1985) derived a calculation equation based on Dillon and Anderson's work; it contained two parameters, namely, the initial water content and the initial freezing temperature. In 1993, Michalowski (1993) established an equation that contains one parameter, i.e. temperature, to calculate the unfrozen water content. Based on differential scanning calorimetry, Kozlowski (2007) analyzed 141 tests on six mono-mineral soil samples and proposed a semi-empirical calculation model for clay. The model divided the calculation process into three intervals according to the freezing and critical temperatures (the temperature at which all pore

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water froze).

The equations mentioned above were devised by fitting the unfrozen water content with influencing factors. Their forms are simple, they converge easily in numerical calculations and they have been applied extensively in calculations of the heat moisture in the active layer (Romanovsky and Osterkamp, 2000), analysis of the thermodynamic stability of constructions in permafrost regions of Qinghai-Tibet Plateau (Zhang et al., 2005) and estimation of the infrastructure settlement over permafrost or frozen ground (Qin and Hiller, 2011; Qin and Zhang, 2010). From the perspective of the proportion of unfrozen water, some scholars have calculated quantitatively the unfrozen water content. Williams (1964) proposed a calculation model by differential scanning calorimetry and an incremental method. Liu and Li (2012) calculated the unfrozen water content from temperature changes during thawing based on Newton's law of cooling. These studies have provided a theoretical basis for calculations of unfrozen water content. However, in these calculations, the difference in proportion, thermal capacity and thermal conductivity between ice, water and soil was taken into account to calculate the unfrozen water content. The existence mechanism of unfrozen water was not considered. In this paper, we set the change in freezing-point as the basis for the existence of unfrozen water and proposed a physical model to calculate the content of unfrozen water. The freezing points of bulk water, capillary water and bound water were calculated separately. The freezing point of bulk water was assumed as constant, and the freezing point of capillary water and bound water decreased with a decrease of each volume. At a negative temperature, the unfrozen water content was defined as the sum of the capillary water content and the bound water content whose freezing point was lower than the given temperature. Data that were measured by the time-domain-reflection (TDR) and nuclear-magnetic-resonance (NMR) techniques were obtained to validate the calculation results.

2. Theoretical model

According to its form of existence, water in silty clay is divided into bulk water, capillary water and bound water. We assume that when all other conditions are the same, the freezing point of bulk water is constant. We neglected the influence of soil-particle size on the thickness of the bound water film. When the initial water content exceeded the bound water content, the influence of initial water content on the bound water content was neglected. When the soil temperature was below 0 °C, the bulk water was frozen and the unfrozen water contained only capillary water and bound water. The picture of scanning electron microscope of Qinghai-Tibet silty clay selected in this paper is shown in Fig. 1. The soil particles laminated with each other. Therefore, the shapes of the capillary and bound water can be simplified as a two-dimensional schematic diagram, shown in Fig. 2. With a difference in water content and saturation, the shape of the capillary water can be divided into three types. The menisci of the capillary water were unconnected (Fig. 2a), connected (Fig. 2b) and merged when bulk water appeared (Fig. 2c).

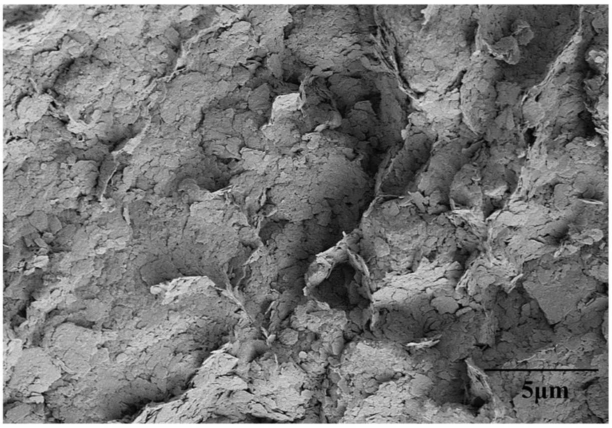

Fig. 1. Scanning electron microscope picture of Qinghai-Tibet silty clay (×5000).

The calculation process was as follows. According to the geometrical relationship of the meniscus radius, particle size, particle distance and bound-water film thickness, we have built some equations to calculate the meniscus radius of a given particle size at a certain volumetric water content. After the meniscus radius was substituted into the Kelvin equation, the molar free energy was calculated. Then, the freezing point of the capillary water was obtained. The freezing point of bound water was calculated from the water activity theory. After the calculation, the relationship between freezing point and water content was built. The unfrozen water content was obtained from the sum of capillary water content and bound water content.

2.1. Calculation of freezing point of capillary water and bound water

Based on the literature (Luan et al., 2006), we have modified the geometrical schematic by considering the bound water distribution. The parameters and a schematic diagram are shown in Fig. 3.

The parameters in Fig. 3 can be described as,

$$x^2 + (y - b - r)^2 - r^2 = 0 \tag{1}$$

$$y' = -\frac{x}{y - b - r} = \tan\left(\frac{\pi}{2} - \theta - \sin^{-1}\frac{y}{R_0 + h}\right) \tag{2}$$

$$(x - R_0 - h - a)^2 + y^2 = (R_0 + h)^2 \tag{3}$$

where r is the meniscus radius of capillary water, $2b$ is the distance between the top and bottom meniscus, R_0 is the radius of a soil particle, h is the thickness of the bound water film, $2(a + h)$ is the distance between soil particles, θ is the contact angle between the meniscus and the soil particle and P is the contact point of the meniscus and the bound water film in which x and y are coordinate values. Each parameter satisfies the conditions as follows,

$$0 < b < R_0 + h,\ a < r < R_0 + h,\ a < x < R_0 + h,\ 0 < y < R_0 + h \tag{4}$$

The thickness of the bound water film is determined from the following equations,

$$h = \frac{w_a}{A_s \rho_{bw}} \tag{5}$$

where w_a is the content of absorption water by soil particles, A_s is the specific surface area, ρ_{bw} is the bound water density, which can be calculated by the initial water content w_0, the equation is as follows (Cui et al., 2010; Li, 2004),

$$\rho_{bw} = 0.0002w_0^2 - 0.0272w_0 + 1.8005,\ (R^2 = 0.9911) \tag{6}$$

In Eqs. (1), (2) and (3), R_0 can be obtained from the particle-size-distribution curve. For a given value of θ and b, the three equations have three unknown variables, x, y and r. With a change in θ and b, the solution of x, y and r was obtained by the fixed-point interaction method. The equations were solved as follows,

$$r = \frac{x}{\tan\left(\frac{\pi}{2} - \theta - \sin^{-1}\frac{y}{R_0 + h}\right) - b + y} \tag{7}$$

$$x = \sqrt{2y(b + r) - y^2 - 2br - b^2} \tag{8}$$

$$y = \sqrt{(R_0 + h)^2 - (x - R_0 - h - a)^2} \tag{9}$$

When θ and b are constant, the water content increases with an increase in particle distance. The particle distance was simplified for convenient calculation (Fig. 4). The relationship between the particle distance $2(a + h)$ and the saturated water content w_{sr} is as follows,