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Research Paper

Estimating the freezing-thawing hysteresis of chloride saline soils based on the phase transition theory

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HIGHLIGHTS

- Theoretical models are developed based on the Pitzer model and thermodynamic theories.
- A hysteretic coefficient is introduced to quantitatively describe the freezing-thawing hysteresis.
- The depression of phase transition points changes versus the shape of pore geometries.
- The hysteresis of unfrozen water content can be divided into four stages.

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ABSTRACT

Knowledge of the freezing-thawing feature and hysteretic phenomenon is required to investigate frost heave, thaw collapse, and thermo-hydro transfer in soil-water systems in seasonally frozen regions. The freezing and melting points are important indexes to judge whether a soil-water system is in a frozen state or not, which are not constant but vary over a range and are determined by soil texture, water, salt content and etc. In this paper, a series of experimental studies have been carried out to test the freezing and melting points of three types of soils, i.e., sand, silt and silty clay, with various NaCl salt contents. Then, the theoretical models for estimating the freezing and melting points of the saline soils are proposed based on the Pitzer ion model and thermodynamic theories. In order to evaluate the theoretical models, the comparison between the predicted results by these models and the experimental results is made, and the agreement between them is seen to be good. In addition, a hysteretic coefficient is proposed to quantitatively describe the hysteretic phenomenon, which is affected by the pore size and water activity. And then, possible mechanisms are discussed for the hysteresis of phase transition temperatures and volumetric unfrozen water contents. Various pore shapes are assumed to explore the effect of pore geometry on the hysteretic phenomenon, and it can be found that soil-water systems have the smallest phase transition point depressions with needlelike pores and the largest with discoid pores. As a preliminary study, the research results may provide a basis for future investigations of the freezing-thawing process of soil-water systems in seasonally frozen regions.

1. Introduction

The freezing and thawing properties of soils are one of the most important soil hydrological characteristics required for both agriculture and engineering researches in seasonally frozen regions. The properties (e.g., freezing point, melting point, and hysteretic phenomenon) have widely been concerned in practice [1–4]. Although laboratory measures are the ultimate sources of information about freezing-thawing cycle characteristics, for many reasons the freezing and melting points are commonly estimated using various theoretical models [5,6]. The main reasons for using theoretical models instead of direct measurements are their universality and predictability. A typical theoretical model can be used to predict the freezing-thawing cycle characteristics of porous media under various situations, such as different initial water contents, different types of salts, and different salt contents.

For the freezing process of freezing-thawing cycles in soil-water systems, the freezing point and unfrozen water content, which represent the freezing characteristics of porous media, are crucial

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functions for determining both the soil hydraulic property and its coupled mechanical properties [7–9]. A number of efforts to study freezing temperature in soil-water systems can be found from the experimental and theoretical perspectives [5,10–12]. It is widely acknowledged that the freezing point is closely related to soil properties including the soil particle size and pore size distributions, soil texture (i.e., percentage of clay, silt, and sand), water content, pore solution type and the concentration of pore solution. For example, the experimental results indicated that the freezing point decreases with increasing salt content and increases with increasing water content [5,11–13].

For theoretical derivations, Wan et al. [5] proposed a theoretical model to calculate the freezing point of sulfate saline soils based on the thermodynamic theories and Pitzer ion model. In addition, an expression for calculating the freezing point of saline soils was developed by Xiao et al. [6], which is based on the phase transition theory in porous media. They found that the water activity and pore size can significantly affect the freezing point in saline soil-water systems. The above theoretical derivations are based on assumptions that the pores are spherical and the narrow pore connections between pores are neglected. However, the practical internal structure of soil-water systems cannot be represented by these assumptions perfectly. Hence it is important to consider the effect of pore geometry on the freezing point.

The thawing process as a branch of the freezing-thawing process in soil-water systems is crucial to the numerical modeling in cold region engineering. The melting point of ice is a characteristic property of pore media in the freezing-thawing cycle. Thermodynamically, the change in Gibbs free energy of the ice is zero at the melting point [14]. Essentially, the thawing process of porous media is the phase transition from pore ice to water. Generally, surface melting is considered as the classical melting type of ice crystals under various/variable external pressures and solution concentrations [15]. A nearly linear correlation between the reciprocal of the pore radius and the melting point depression of pore ice has been observed by previous studies [16–18]. For example, a theoretical model is derived by Morishige and Kawano [18], which enables the heat of fusion and surface tension of solids to be determined from a combined use of NMR and calorimetric measurements. Meanwhile, on the basis of thermodynamical principles, Khvorostyanov and Curry [15] developed general equations for the critical germ radius and finite size of freezing/melting particles, and the comparison between the theoretical results and the experimental data showed good agreements.

However, majority of researches focused on the melting of pore ice in the pores of nanometer materials, while a few studies discussed the melting in soil-water systems because it is complicated that the double-layer effect at the surface of soil particles. Especially for the saline soil-water system, the redissolving process of salt crystals is significant for the melting of pore ice. Tian et al. [19] investigated the thawing process of soil-water systems based on the nuclear magnetic resonance proton spin relaxation time distribution and free-induction decay measurements. The freezing and thawing cycle has been explained by referring to the energy status of the pore water. Lu et al. [20] investigated the change of unfrozen water contents during freezing and thawing processes for the silty clay from the Qinghai-Tibet Plateau. These researches put insight into the thawing characteristics of soil-water systems, but there is not a detailed explanation to reveal the thawing mechanism. Moreover, the effect of salt crystal redissolving, during the melting process of pore ice, is not investigated.

Similar to the drying-wetting cycle in porous media, the hysteresis phenomenon can also be found in the process of freezing-thawing cycle [19–21]. The freezing-thawing cycles of many porous materials exhibit hysteretic behavior, which means that there is a difference between the freezing characteristic and the thawing characteristic for the same subzero temperature. Numerous efforts on studying the freezing-thawing hysteretic phenomenon of porous media have been carried out based on experimental studies [15,18,19,22–26]. They found that the hysteresis in smaller pores can be negligible but that in larger pores becomes obvious. In other words, the freezing and melting points of the bound water are lower than those of free water which does not show any hysteretic effect [27]. Physical phenomena which result in the freezing-thawing hysteresis [19,20] include: (1) the geometric effect due to irregular shapes of pores, often called "ink-bottle" effect, (2) capillary condensation effect that originates from interfacial effect between pore water and solid particles, (3) metastable nucleation, nucleation of a new phase occurs if the size of the initial germ of new phase reaches a critical value, (4) expansion and contraction effect, the structure of fine grained soils will be changed in the process of freezing-thawing cycles, and (5) electrolyte effect, the water activity of pore solution will be lowered by electrolyte and the melting of pore ice will be affected by redissolving of electrolyte precipitate. However, little attention has been paid to the quantitative analysis of pore shapes. In addition, the mechanism to explain the effect of electrolyte on the freezing-thawing hysteresis phenomenon is still unclear.

The aim of this work is to derive theoretical models to estimate freezing points, melting points and related hysteretic coefficients of saline soils with various pore size distributions and salt contents. On the basis of Pitzer ion model and thermodynamic theories, these proposed models are related to pore size distributions, types of salts, and salt contents of soil-water systems. A series of tests are performed to verify the validity of the proposed models, which includes three types of soils (i.e., sand, silt, and silty clay) and seven NaCl contents. The predicted results by the proposed models in this study match the previous research results and the experimental results well. Various pore shapes are assumed to explain the hysteretic phenomenon in saline soil-water systems. In addition, the hysteretic phenomenon has been investigated from the perspective of the energy state of pore water. Furthermore, these new models can provide a reference for studying the freezing-thawing characteristics of saline soil-water systems in seasonally cold regions.

2. Experimental methodology

2.1. Materials and sample preparation

Three types of soils are used in the study: the silt is obtained from Lanzhou, West China (36°03′N and 105°50′E); the sand is taken from Delingha, West China (37°22′N and 97°21′E); and the silty clay is collected from the Beiluhe field site on the Qinghai-Tibet Plateau (34°54′N and 92°56′E), where saline soils are widely distributed. Before analyzing the grain-size distributions, salts are washed from the nature saline soils by distilled water for more than ten times. The desalinated soils are dried, crushed, and then sieved by a sieve with 2-mm holes. The soils with particle sizes below 2 mm are used in this study and analyzed by Master Sizer-2000 Laser particle size analyzer (Malvern, UK). The grain size distributions are shown in Fig. 1. The physical properties of the soils are summarized in Table 1.

In order to study the effect of salinity on the freezing and thawing properties, the soils with different sodium chloride contents are prepared for laboratory experiments. The salt contents w (the ratio of the mass of NaCl to the mass of dried soil, g/g) are 0.0, 0.1, 0.2, 0.4, 0.6, 0.8 and 1.0 percent for silty clay and silt, and those are 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0 percent for sand. The initial mass water contents for silty clay, silt and sand are 18%, 17% and 12%, respectively. The salt and water contents are referred to the soils in field. And solutes are mixed with deionized water to obtain the desired water and salinity levels. In order to make the distribution of ions and water more uniform, soil samples are put into plastic bags and stored in an incubator under the temperature of 20 °C for 24 h.

Soil samples are packed into iron boxes with 3.3 cm in diameter and 3.8 cm in height before the freezing and thawing tests start. Soil samples are compacted to get uniform bulk densities. The packed height of soil samples is 3.8 cm, and the dry densities of the samples are