Salt crystallization in cold sulfate saline soil

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ABSTRACT

The effect of sodium sulfate crystallization on soil freezing temperature, and the changes in salt expansion and frost heave pressure with temperature were analyzed experimentally and using crystallization theory. The Pitzer ion model was used to find the supersaturation ratio of a sodium sulfate solution in soil. The relationship between the initial supersaturation ratio and temperature was obtained, which provided criteria for the presence of salt crystals over the entire temperature range. Experiments were carried out to determine the effect of cooling the sodium sulfate saline soil as well as the location of salt crystallization. Analysis of the location and shape change of salt crystals based on the experiments clarified the interaction between salt crystallization and ice-water phase change. A formula relating the surface free energy of a crystal to its critical nucleation radius was deduced based on the assumption of homogeneous nucleation. Finally, equations for the salt expansion force and frost heave pressure were obtained and their rationalizations were provided.

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1. Introduction

Sulfate saline soil is widely distributed in the cold western regions of China (Xu et al., 1995), where the temperature changes dramatically. Saline soil is often located in seasonal frozen or permafrost regions. Salt expansion, caused by the chemical and physical properties of saline soil, can seriously damage infrastructure such as roads, canals, and airports. Frost heaving can increase the salt concentration of the soil solution, thus accelerating the precipitation of salt crystals and intensifying salt expansion. With economic development in western China, roads are increasingly being constructed in saline soil. Therefore, studies on salt expansion in sulfate saline soil in cold regions (Deng and Zhou, 2009) are of great significance for improving the safety of infrastructure. However, because of complicated temperature variations, there are a number of unanswered questions about sulfate saline soil in cold regions.

The fundamental cause of salt expansion is crystallization, as salt heaving cannot occur without the presence of salt crystals. Domestic studies on salt expansion in sulfate saline soil have mainly focused on experimental measurements of the salt expansion rate, which is influenced by the salt and water contents, the types of salt, and temperature (Yuan and Li, 1995; Wu et al., 2001; Chen et al., 2006; Xu et al., 2010; Zhang et al., 2010). There is little discussion on the fundamental mechanism of salt crystal formation and growth in soil. In the literature, calculations of salt crystallization and salt expansion are mostly based on

the phase diagram of the corresponding salt solutions (Niu and Gao, 2008, 2015). Equations used in these papers consider only the steady state of the solution, and not its metastable state or results of lower veracity and accuracy. Research shows that regardless of cooling or salt transfer, sodium sulfate can combine with ten or seven water molecules to form sodium sulfate decahydrate (mirabilite) or heptahydrate, respectively, as long as the supersaturation ratio of salt in soil is greater than or equal to the initial value (Steiger and Asmussen, 2008). Consequently, swelling deformation occurs in the soil. However, the formation of mirabilite is not only influenced by temperature, but also by the ambient humidity (Hamilton and Hall, 2008; Oswald et al., 2008; Steiger and Asmussen, 2008), and it will crystallize only when the humidity is >50%.

International researchers of salt expansion usually consider salt crystallization and the initial supersaturation ratio in brick, concrete, rock and other building materials, instead of soil (Koniorczyk, 2010). When the supersaturation ratio is close to the start value, crystals formed from the solution will fill the pores, thereby reducing the durability of such building materials. Crystallization also creates crystallization pressure (Rijniers et al., 2005; Chatterji, 2005; Espinosa et al., 2008; Koniorczyk, 2012; Derluyn, 2012; Saidov et al., 2012), wherein if the deformation of soil is constrained by the foundation, great internal pressure (salt expansion force) is accumulated because of salt crystallization, which damages civil engineering constructions.

Frost action in civil engineering constructions is caused by the coupling of solid, liquid, and gaseous matter as well as heat in a porous medium (Li et al., 2001). In saline soil, ions mainly exist in soil solutions. When the soil temperature falls below the freezing point of the salt

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solution, the water molecules form pure crystalline ice and cause frost heaving. The combination of salt expansion and frost heaving results in uneven expansion of the structural foundations, reducing the stability of the constructions. The freezing point, therefore, is a key parameter in determining the phase of the saline soil (Wan et al., 2015a). In previous studies (Xu et al., 2010; Bing and Ma, 2011), the effect of ions on the freezing temperature of saline soil, but not the effect of salt crystallization, has been considered.

So far, there are relatively few studies on both salt crystallization and crystal growth in saline soil at low temperatures. Only salt crystallization in soil at room temperature has been discussed. In light of the presence of sulfate saline soil, which can be very destructive, in the Tibetan Plateau, this paper reports the crystallization condition of sulfate in saline soil, the interaction between salt crystallization and ice–water phase change, and the force from salt and ice crystals using crystallization theory and experiments. This work aims to deduce the rules of salt crystallization in saline soil, and to provide theoretical and experimental references for engineering in cold regions.

2. Supersaturation ratio of sodium sulfate solution

2.1. Theory

This paper considers saline soil containing sodium sulfate, which crystallizes when the solution is in a supersaturated state. The condition of salt crystallization is usually judged from the value of the supersaturation ratio. Crystallization takes place when the solution is supersaturated with respect to the crystallizing phase. The mass balance equation of salt crystals by Espinosa et al. (2008), which expresses the change in crystal mass with time using the supersaturation ratio U_a, is as follows:

$$\frac{dm_s}{dt} = K_{crystal}(U_a - 1)^n, U_a \geq U_0 \tag{1}$$

where m_s is the mass of crystal mass, $U_0 > 1$ is the initial supersaturation ratio. $K_{crystal}$, a parameter that decreases with temperature (Espinosa et al., 2008). n is the rate index, whose value can be found in Derluyn (2012). Usually secondary crystallization will occur when $U_a > 1$.

Since Eq. (1) indicates that the growth of crystal mass is closely related to the supersaturation ratio in the solution, we start by considering U_a. A supersaturated solution is in an unstable state, and crystallization is the process that leads to stability. In our study, the mean ion activity is used to calculate the supersaturation ratio. The effect of relative humidity on crystal morphology is not considered in this study. Another assumption is that only sodium sulfate decahydrate is formed in sulfate saline soil in the cooling process. When both the ions and water are considered, the supersaturation ratio can be expressed as:

$$U_a = \left(\frac{a_\pm}{a_\pm^*}\right)^v \cdot \left(\frac{a_w}{a_w^*}\right)^{v_0} \tag{2}$$

where $a_\pm$ is the mean ion activity of the given solution, $a_\pm^*$ is the mean ion activity of the saturated solution, v is the number of ions produced per solute molecule ($v = 3$ in Na$_2$SO$_4$), a_w is the water activity, a_w^* is the water activity at saturation, and v_0 is the number of crystallized water molecules per salt molecule ($v_0 = 10$ in Na$_2$SO$_4$·10H$_2$O).

The mean ion activity is defined as:

$$a_\pm = c_\pm \gamma_\pm \tag{3}$$

where $c_\pm$ is the mean molality of ions, it is the function of concentration of solution (Prausnitz et al., 1999), and $\gamma_\pm$ is the mean-ion activity coefficient.

The definition of the mean-ion activity coefficient is:

$$\ln \gamma_\pm = |z_M z_X| f^\gamma + 2c \frac{|v_M v_X|}{v} B_{MX}^\gamma + 2c^2 \frac{(v_M v_X)^{3/2}}{v} C_{MX}^\gamma \tag{4}$$

where

$$f^\gamma = A_\phi \left(\frac{I^{1/2}}{1 + bI^{1/2}} + \frac{2}{b} \ln\left(1 + bI^{1/2}\right) \right)$$

$$B_{MX}^\gamma = 2\beta_{MX}^{(0)} + \frac{2\beta_{MX}^{(1)}}{a_1^2 I} \left[1 - \left(1 + a_1 I^{1/2} - 0.5a_1^2 I\right) \times \exp\left(-a_1 I^{1/2}\right) \right] + \frac{2\beta_{MX}^{(2)}}{a_2^2 I} \times$$
$$\left[1 - \left(1 + a_2 I^{1/2} - 0.5a_2^2 I\right) \times \exp\left(-a_2 I^{1/2}\right) \right]$$

$$C_{MX}^\gamma = \frac{3}{2} C_{MX}^\phi$$

MX is the corresponding salt, and the interaction parameters $\beta^{(0)}_{MX}$, $\beta^{(1)}_{MX}$, $\beta^{(2)}_{MX}$, and C^ϕ_{MX} are specific to salt MX (consisting of v_M cations M of charge z_M, v_X anions X of charge z_X). The relationship of these parameters with temperature was discussed by Steiger et al. (2008). $b = 1.2$ kg$^{1/2}$ mol$^{-1/2}$ is a constant, and z_M, z_N are the charges of the electrolyte ions. c is actual concentration of the solution, and α_1, α_2 are test parameter, their value is 1.2 and 0.2 respectively (Steiger et al., 2008). I, the ionic strength, is defined as:

$$I = \frac{1}{2} \sum_i c_i z_i^2 \tag{5}$$

where z_i is the charge of ion type i, and c_i is the molar concentration of ion type i.

A_ϕ is the Debye-Hückel parameter for the osmotic coefficient, which has a nonlinear relationship with temperature T (Clegg and Whitfield, 1991).

The relation between water activity a_w and osmotic coefficient ϕ is expressed by the following equation (Steiger, 2005):

$$\ln a_w = -\phi \frac{M_w}{1000} \sum_i c_i \tag{6}$$

where M_w is the molar mass of water. In the Pitzer approach (Steiger and Asmussen, 2008), the osmotic coefficient for a single electrolyte is given by:

$$\phi - 1 = |z_+ z_-| f^\phi + 2c \frac{v_+ v_-}{v} B_{MX}^\phi + 2c^2 \frac{(v_+ v_-)^{3/2}}{v} C_{MX}^\phi \tag{7}$$

where:

$$f^\phi = -A_\phi \frac{I^{1/2}}{1 + bI^{1/2}}$$
$$B_{MX}^\phi = \beta_{MX}^{(0)} + \beta_{MX}^{(1)} \exp\left(-\alpha_1 I^{1/2}\right) + \beta_{MX}^{(2)} \exp\left(-\alpha_2 I^{1/2}\right)$$

In the absence of salt crystallization, the solution concentration will increase below the freezing temperature due to ice formation. Hence, the relation between the unfrozen water content and temperature should be analyzed before calculating the supersaturation ratio.

Based on the saturation curve of sodium sulfate solution (Xu et al., 1995), there will be little salt crystallization below the initial freezing temperature of soil, compared to that at room temperature. The content of unfrozen water below the freezing temperature is mainly determined by the ice-water phase change, and can be studied through Nuclear Magnetic Resonance (NMR) (Wan et al., 2015b). The equation of unfrozen water content θ_f obtained by fitting experimental data is as follows:

$$\theta_f = \chi e^{\omega T} + \delta \tag{8}$$

where $\chi = -1.763 \ln c + 1$, $\omega = -0.645 \ln c + 0.7787$, and $\delta = 0.0265$. T refers to centigrade temperature.