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# Kinetic model for crystallization in porous media

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**Abstract**—A kinetic model for analyzing phase front propagation during freezing of a fine porous medium under conditions of moisture diffusion is presented. Crystallization is assumed to take place in a kinetic zone according to an experimental function characterizing the crystallization rate. The method was demonstrated for the crystallization of a 1-D fine-grained soil medium subject to constant boundary conditions. The numerical results were validated against experimental data from the literature. The following conclusions were inferred from the theoretical results: (1) in a closed system the rate of phase front propagation can oscillate even under constant boundary conditions; (2) as the phase front reaches a stationary state, the diffusional moisture flux from the non-frozen zone to the kinetic zone vanishes. Copyright © 1996 Elsevier Science Ltd.

## 1. INTRODUCTION

An understanding of the process of freezing and thawing of fluids in porous media is important in many branches of science and engineering, for example in biological applications such as cryopreservation of biological materials and cryosurgery [1] and in the environmental sciences in connection with the crystallization and melting of water in soil in cold climates [2]. This paper focuses on the process of water crystallization in fine-grained soil.

The peculiarities of the cryogenic structure of fine-grained soils depend greatly upon the conditions of freezing. Formation of an ice layer creates a water concentration gradient, which is the driving force behind the moisture diffusion process and causes moisture and temperature profile redistribution in both the frozen and non-frozen regions [2–5]. Since the moisture diffusion coefficients in the frozen zone are significantly smaller than those in the non-frozen zone, most theoretical models neglect the effect of mass transfer in the frozen regions in such systems. The phase front is usually modeled as a mathematical surface. Introduction of a boundary condition relating to the moisture flux at the phase front interface makes it necessary to perform extensive numerical calculations to reach a solution.

The various numerical methods for solving phase-change with moving boundary problems have been reviewed in a number of works, including refs. [6, 7]. Recently, Voller [8, 9] developed a new computational scheme, which modified the source-based method by introducing a new source term, defined as a liquid volume fraction, as a function of temperature. The

method was illustrated for a pure material [8] and a binary alloy [9] and was found to be an accurate computation method, which can be applied efficiently for many solidification problems.

In this paper, a kinetic model is presented for solidification in a fine-grained porous medium. The model includes a kinetic function, describing the rate of ice crystallization, as a function of supersaturation. Crystallization is assumed to take place in the kinetic zone which is defined as the range within which supercooling occurs, thereby eliminating the discontinuation at the boundary and simplifying the numerical calculations. Moreover, allowance for water diffusion in the kinetic and frozen zones makes it possible to investigate the process of cryogenic texture formation in the frozen state. Preliminary results relating to this model and details about the numerical method were presented in [10, 11]. Recent investigations [3, 12–14] show that modeling the phase front as a mathematical surface does not yield a satisfactory representation of the system. Unless moisture diffusion in the supercooling zone is also taken into consideration, it is impossible to properly describe such phenomena as a moisture redistribution process or a Schlieren formation in the frozen zone, as reflected in the experimental results presented in [4, 12, 13].

The present paper is focused on utilization of the model for the purpose of studying the instability of phase front propagation and is divided into the following sections: firstly, description of the theoretical model and validation against experimental results from the literature and secondly, theoretical results relating to the effect of Lewis and Stefan numbers on redistribution of the temperature and moisture profiles, as well as theoretical analysis of the instability of phase front propagation.

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## NOMENCLATURE

$a_0$	coefficient in equation (9)	$x$	coordinate [m]
$C$	volumetric specific heat [ $\text{J m}^{-3} \text{K}^{-1}$ ]	$X^*$	thermal front position [m]
$D$	diffusion coefficient [ $\text{m}^2 \text{s}^{-1}$ ]	$X^{**}$	crystallization front position [m].
$H$	length of sample [m]		
$g$	kinetic function [ $\text{s}^{-1}$ ]	Greek symbols	
$q_w$	moisture migration flux [ $\text{kg m}^{-2} \text{s}^{-1}$ ]	$\Delta H$	latent heat [ $\text{J m}^{-3}$ ]
$k$	thermal conductivity [ $\text{W m}^{-1} \text{K}^{-1}$ ]	$\alpha$	thermal diffusivity [ $\text{m}^2 \text{s}^{-1}$ ]
$L$	ice, concentration [ $\text{kg kg}^{-1}$ ]	$\rho$	density [ $\text{kg m}^{-3}$ ].
$T$	temperature [K]		
$t$	time [s]	Dimensionless groups	
$t^*$	characteristic time of water crystallization [s]	$Fo = \alpha t/H^2$	Fourier number
$V$	thermal front velocity [ $\text{m s}^{-1}$ ]	$Ste = C(T_0^* - T_1)/W_0\Delta H$	Stefan number
$W$	moisture [ $\text{kg kg}^{-1}$ ]	$Le = D_0/\alpha$	Lewis number.
$W_s$	total moisture [ $\text{kg kg}^{-1}$ ]		
$W^*$	equilibrium liquid water concentration in frozen soil [ $\text{kg kg}^{-1}$ ]	Subscripts	
		0	initial
		1	left region boundary.

## 2. THEORETICAL MODEL

A schematic description of the system model is given in Fig. 1. We consider a transient 1-D problem relating to homogeneous fine-grained soil in the range  $0 < x < H$  (see Fig. 1). Initially the system is at the uniform temperature  $T_0$  and has the water content  $W_0$  (mass of water per unit mass of dry soil). At the time  $t = 0$  one side of the domain (at  $x = 0$ ) obeys the step function  $T = T_1$ , which is lower than  $T_0^*$ , defined as

the water freezing temperature corresponding to the moisture  $W_0$ . Freezing of the soil begins from  $x = 0$  and propagates in the  $x$  direction.  $X^*$  is the coordinate at which  $T = T_0^*$  and  $X^{**}$  is the coordinate at which water freezing starts,  $W_s = W^*$ . The diffusion coefficient of the moisture in the non-frozen and kinetic zones is considered to be a function of moisture concentration, but is independent of temperature. We also assume that the thermal diffusivity is constant. For the above-mentioned system, the energy balance

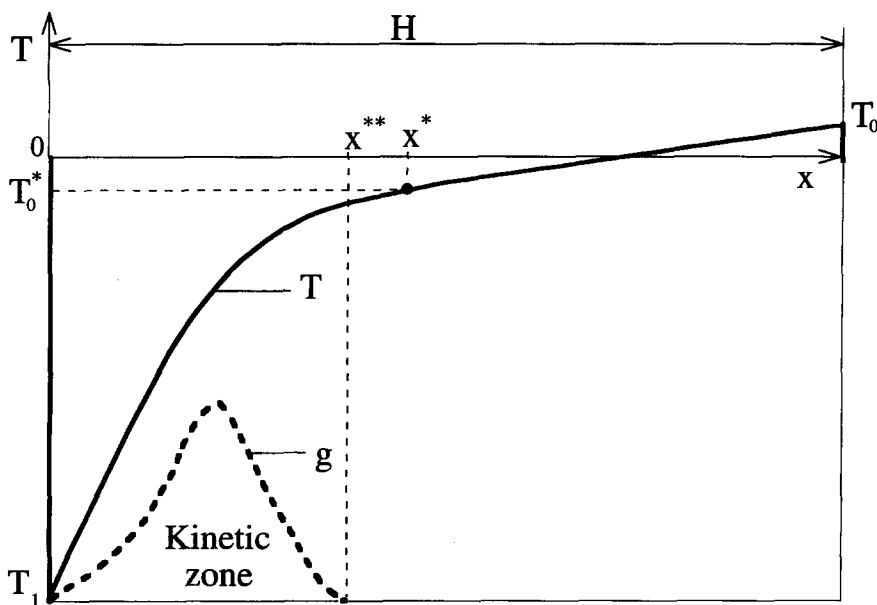


Fig. 1. Schematic description model system.

equation is given in equation (1), which has to satisfy the initial condition (1a) and boundary conditions (1b) and (1c)

$$\frac{\partial T}{\partial t} = \frac{\partial}{\partial x} \left( \alpha \frac{\partial T}{\partial x} \right) + \frac{\Delta H}{C} \frac{\partial L}{\partial t} \quad (1)$$

$$T(0, x) = T_0 \quad (1a)$$

$$T(t, 0) = T_1 \quad (1b)$$

$$T(t, H) = T_0 \quad (1c)$$

where  $\alpha$ ,  $\Delta H$ ,  $C$  and  $L$  are the thermal diffusivity, the volumetric latent heat of solidification, the volumetric specific heat, and the ice content (in mass of ice per mass of dry soil), respectively.

The mass balance of the system is given in equation (2), which has to satisfy the initial condition (2a) and the boundary conditions (2b) and (2c):

$$\frac{\partial W}{\partial t} = \frac{\partial}{\partial x} \left( D(W) \frac{\partial W}{\partial x} \right) - \frac{\partial L}{\partial t} \quad (2)$$

$$W(0, x) = W_0 \quad (2a)$$

$$\frac{\partial W(t, 0)}{\partial x} = 0 \quad (2b)$$

$$\frac{\partial W(t, H)}{\partial x} = 0 \quad (2c)$$

where  $D(W)$  is the diffusion coefficient of the moisture. We define the function  $g(T, W, L)$  by equation (3), which describes the rate of water crystallization:

$$\frac{\partial L}{\partial t} = g(T, W, L). \quad (3)$$

Furthermore, we assume that the function  $g(T, W, L)$  can be determined by equation (4).

$$g(T, W, L) = \frac{W - W^*}{t^*} \quad (4)$$

where  $W^*$  is the liquid water content in equilibrium at the temperature  $T$  for fine-grained soils, and  $t^*$  is the characteristic time of water solidification in the system. The equilibrium relations for  $W^*$  as a function of  $T$ , as well as the parameter  $t^*$ , have to be determined experimentally for each type of soil. Note that  $W - W^*$  is the degree of supersaturation and is the driving force behind the crystallization process.

In order to represent the above equations in dimensionless form, the following dimensionless parameters are defined:

$$\begin{aligned} \bar{T} &= \frac{T - T_0^*}{T_0^* - T_1} & \bar{W} &= \frac{W}{W_0} & \bar{W}^* &= \frac{W^*}{W_0} \\ \bar{x} &= \frac{x}{H} & \bar{L} &= \frac{L}{W_0} & \bar{D} &= \frac{D(W)}{D(W_0)}. \end{aligned} \quad (5)$$

Note that  $\Delta T_1 = T_0^* - T_1$  is the degree of supercooling at the initial time at the boundary  $x = 0$ . Substitution

of these dimensionless parameters in equations (1)–(4) yields:

$$\frac{\partial \bar{T}}{\partial Fo} = \frac{\partial^2 \bar{T}}{\partial \bar{x}^2} + \frac{\bar{g}}{Ste} \quad (6)$$

$$\bar{T}(0, \bar{x}) = \bar{T}_0 \quad (6a)$$

$$\bar{T}(Fo, 0) = -1 \quad (6b)$$

$$\bar{T}(Fo, 1) = \bar{T}_0 \quad (6c)$$

$$\frac{\partial \bar{W}}{\partial Fo} = Le \frac{\partial}{\partial \bar{x}} \left( \bar{D}(\bar{W}) \frac{\partial \bar{W}}{\partial \bar{x}} \right) - \bar{g} \quad (7)$$

$$\bar{W}(0, \bar{x}) = 1 \quad (7a)$$

$$\frac{\partial \bar{W}(Fo, 0)}{\partial \bar{x}} = 0 \quad (7b)$$

$$\frac{\partial \bar{W}(Fo, 1)}{\partial \bar{x}} = 0 \quad (7c)$$

where:

$$\begin{aligned} Ste &= \frac{C(T_0^* - T_1)}{W_0 \Delta H} & Le &= \frac{D_0}{\alpha} & \bar{g} &= \frac{\bar{W} - \bar{W}_0^*}{Fo^*} \\ Fo &= \frac{\alpha t}{H^2} & D_0 &= D(W_0). \end{aligned} \quad (8)$$

In order to solve equation (7), the equilibrium moisture content as a function of temperature has to be given in dimensionless form. Using the available experimental data from the literature [2, 3, 15], we have determined that in the temperature range we are concerned with i.e.  $T_1 < T < T_0^*$ , the experimental equilibrium data related to the crystallization of water in fine-grained soils can be represented by the correlation:

$$\bar{W}^*(\bar{T}) = (1 - a_0 \bar{T})^{-1} \quad (9)$$

where  $a_0$  is a constant parameter related to the type of the soil. The coupled energy and mass balance equations (6) and (7) were solved numerically, employing a non-implicit scheme of approximation based on central differences with respect to space and one-sided differences with respect to time.

The diffusion coefficient  $D(W)$  is approximated for points half-way between every two adjacent nodes. A simple rapidly accomplished recursive computation named ‘the double sweep-method’ [16] was combined with iterations to solve the finite difference equations. The boundary conditions for the moisture transfer equation were approximated by using both the central difference with fictitious nodes and the subsequent grid function. More details about the numerical method are given in ref. [11].

### 3. RESULTS AND DISCUSSION

The numerical model was solved for a loamy soil type with the following thermophysical properties:

thermal conductivity  $k = 1.2 \text{ W m}^{-1} \text{ K}^{-1}$ , volumetric specific heat  $C = 2835 \text{ kJ m}^{-3} \text{ K}^{-1}$ ,  $\rho = 1750 \text{ kg m}^{-3}$ , initial moisture content  $W_0 = 0.26$ , diffusion coefficient (for  $W_0 = 0.26$ )  $D_0 = 1.25 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$ . The Lewis number (for  $W_0 = 0.26$ )  $Le = 0.3$  and the equilibrium water freezing temperature  $T_f^* = -0.15^\circ\text{C}$ . The characteristic time of water crystallization  $t^* = 900 \text{ s}$ . The equilibrium data from refs. [2, 15] were found to fit the correlation form of equa-

tion (9) with constant  $a_0 = 7.7$ . The experimental data for the diffusion coefficient as a function of moisture was found to fit the dimensionless empirical correlation  $\bar{D} = 0.92 \bar{W}^8$ . The initial condition  $T_0 = 3^\circ\text{C}$  and boundary conditions  $T_1 = -12.5^\circ\text{C}$  ( $\bar{T} = 0.25$  and  $Ste = 0.23$ ) were used in validation of the model.

The numerical results for the dimensionless temperature profile are compared with the experimental data in Fig. 2(a), and the results for the dimensionless

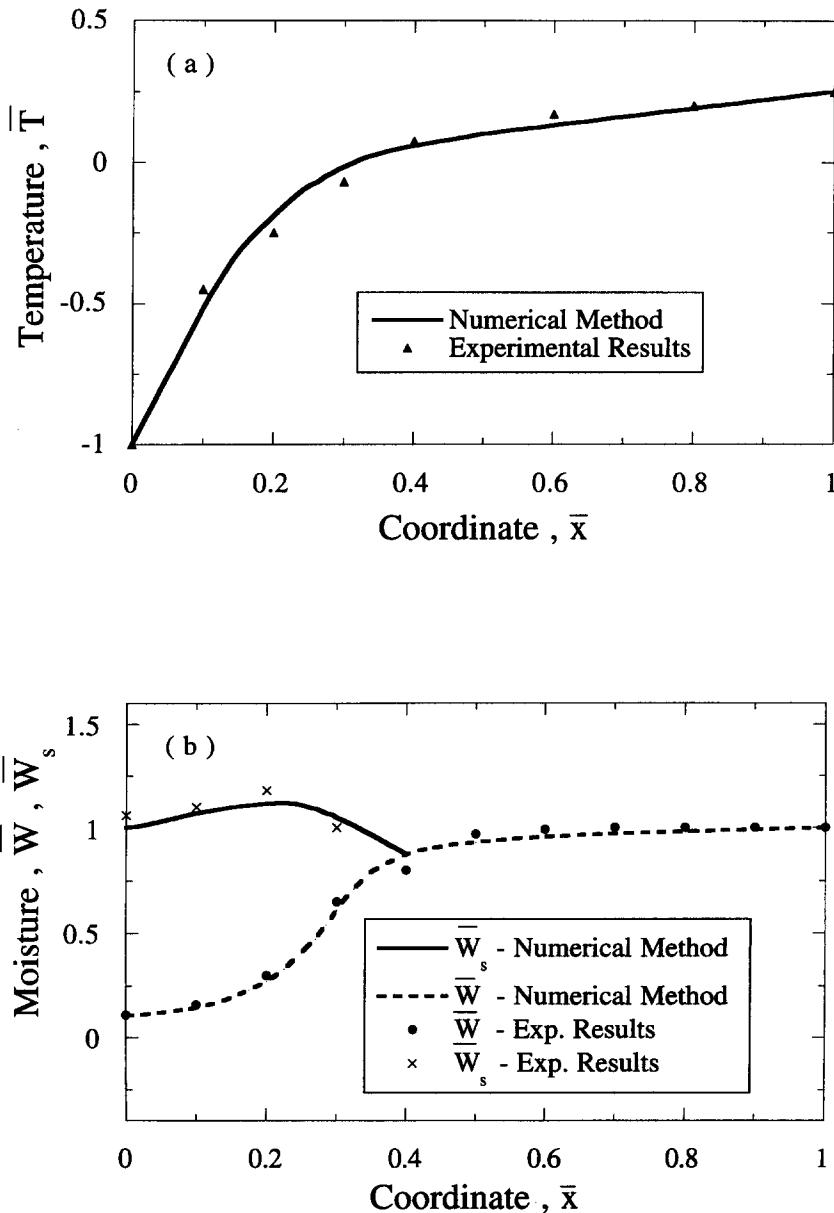


Fig. 2. Comparison between theoretical results of this work with experimental data from refs. [2, 15]. Temperature profile (a) moisture and (b) total moisture.  $Fo = 0.2$ ,  $Le = 0.3$ ,  $Ste = 0.23$ ,  $\bar{T}_0 = 0.25$ .

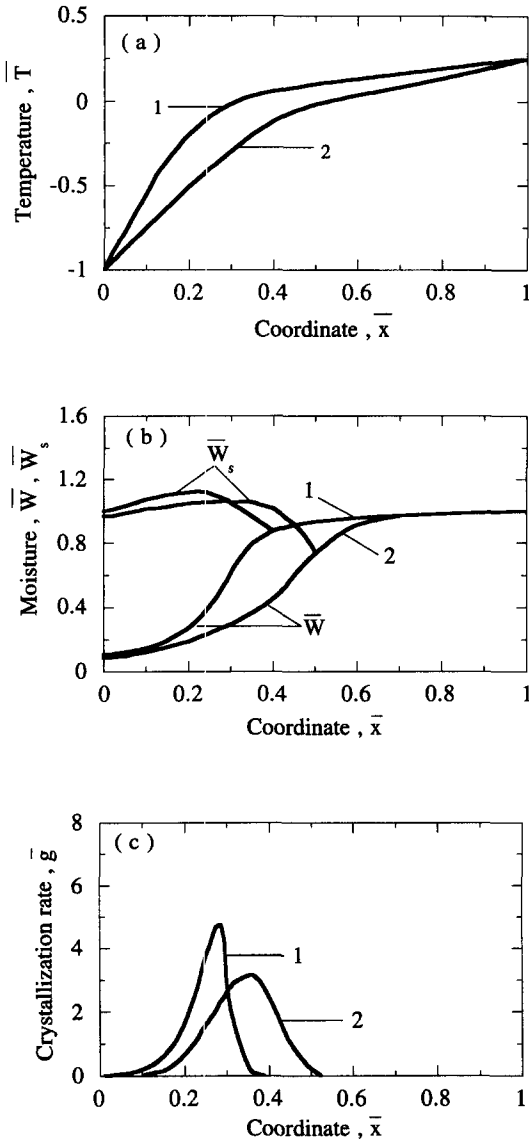


Fig. 3. Distribution of temperature (a) moisture (b) total moisture and (c) crystallization rate for two different Lewis numbers:  $Le = 0.30$  and  $Le = 0.15$  (curve 1 and curve 2, respectively).  $Fo = 0.2$ ,  $Ste = 0.23$ ,  $T_0 = 0.25$  in both cases.

moisture and total water in Fig. 2(b). It is evident that there is good agreement between the theoretical and the experimental results.

The principal characteristics of the crystallization process in a system at a fixed time ( $Fo = 0.2$ ) for two different Lewis numbers are shown in Fig. 3(a)–(c). Figure 3(a) shows that the temperature profile has a linear form in domains beyond the transformation zone. This confirms the existence of quasi-steady heat transfer conditions in those domains. The moisture content distribution (Fig. 3(b)) is essentially non-linear, and is described by an S-curve. The value of  $\bar{W}$  increases monotonously with increasing distance from

the cold side  $\bar{x}$ , up to a value corresponding to the soil moisture in the non-frozen zone. The sharp increase of  $\bar{W}$  in the kinetic zone reflects the diffusion of moisture from the non-frozen zone due to crystallization. This process increases the moisture content gradient and moisture flux in the direction of the cold boundary, resulting in an increase in the total moisture in the frozen zone  $\bar{W}_s$  ( $\bar{W}_s = \bar{W} + \bar{L}$ ). As can be seen from the form of curve 1 in Fig. 3(b), the total moisture distribution behaves in a complex manner: at first,  $\bar{W}_s$  increases with the increasing  $\bar{x}$ , but subsequently it decreases to a value corresponding to the equilibrium moisture concentration.

The profile of the crystallization rate is presented in Fig. 3(c). Beyond the kinetic crystallization zone, the rate of crystallization is negligible. The absence of a solid phase in the range  $\bar{X}^{**} < \bar{x} < \bar{X}^*$  is a result of the decrease in water content to values below those of equilibrium, due to migration of moisture to the freezing zone.

For  $Ste = 0.23$  and  $Le$  in the range of 0.3–1.0, the transformation zone has a width of about 10% of the overall dimension of the system,  $H$ . These results indicate that simulation of the phase transformation zone as an infinitely thin front of freezing, which is the approach incorporated in most theoretical models, is not suitable for water crystallization in fine-grained soil, thereby confirming the validity of the kinetic approach proposed in this paper.

As the  $Le$  number increases from 0.15 to 0.3, the overall behavior of the system remains essentially the same Fig. 3(a)–(c). However, the significance of an increase in the  $Le$  number is intensification of the moisture flux. As a result, there is visible displacement of the abnormally high ice capacity zone (Fig. 3(b)), together with movement of the location of the maximum value of the crystallization rate towards the cold boundary and narrowing of the width of the kinetic zone (Fig. 3(c)). These results are in agreement with experimental results reported in [2, 5, 12].

Figure 4 shows the influence of the  $Ste$  number on the dimensionless total moisture profile. An increase in the temperature head ( $\Delta T_1 = T_0^* - T_1$ ), leading to a decrease in the  $Ste$  number results in localization of intensive ice formation in a narrow zone near the freezing front (Fig. 4).

The thermal front velocity  $\bar{V}$ , the moisture flux  $\bar{q}_w$  and the positions of the thermal front  $\bar{X}^*$  and crystallization front  $\bar{X}^{**}$  (all in dimensionless form) vs the Fourier number  $Fo$  are presented in Fig. 5(a)–(c) where:

$$\bar{V} = \frac{d\bar{X}^*}{dFo} \quad \text{and} \quad \bar{q}_w = \bar{D} \left. \frac{\partial \bar{W}}{\partial \bar{x}} \right|_{\bar{x}=\bar{X}^*} \quad (10)$$

The changes in the velocity of the thermal front  $\bar{V}$  and in the water migration flux  $\bar{q}_w$  are non-monotonous in character. The oscillations in  $\bar{V}$  and  $\bar{q}_w$  appear to be caused by the disparity between the moisture and the heat transfer rates, which is due in turn to significant

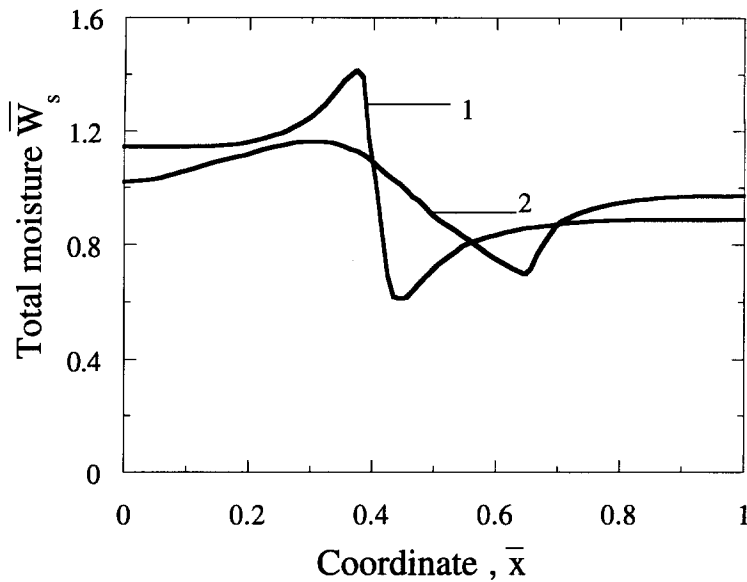


Fig. 4. Total moisture profile for  $Ste = 0.23$ ,  $\bar{T}_0 = 0.25$  (curve 1) compared with  $Ste = 0.114$ ,  $\bar{T}_0 = 0.875$  (curve 2), at constant  $Fo = 1.8$ ,  $Le = 0.3$ .

differences in the mass and heat diffusivity (under these humidity conditions, the former is moisture dependent whereas the latter is taken as constant). As the front moves away from the cold boundary, the moisture content in the vicinity of the front drops, due to water crystallization in the transformation zone. This leads to a decrease in the diffusion coefficient and, accordingly, to reduction of the moisture flux. Assuming that  $\alpha = \text{const.}$ , any decrease in  $q_w$  will lead to an increase in the propagation velocity and subsequently to rapid front transference in the direction of the moisture field, where the propagation velocity again decreases. Increases in the  $D_0/\alpha$  ratio promote singularity of the oscillations, as moisture decrease is completely or partly compensated for by moisture flow away from the melted zone due to crystallization (Fig. 3(c)).

As mentioned before, increases in the  $Le$  number result in intensification of moisture transfer and movement of the high ice capacity zone towards the cold boundary, creating conditions permitting formation of schlieren texture near the cold boundary. The latter phenomenon was observed experimentally by Feldman [17] and is typical of open and closed systems.

The final stage of the freezing process results in disappearance of the thermal and crystallization phase fronts at a certain distance from the cold boundary (Fig. 5(c)), which depends on the temperature head and on thermophysical and transport soil properties. Furthermore, the results (Fig. 5(b)) show that the diffusional flux from the non-frozen zone  $\bar{q}_w$  decreases to zero as the Fourier number  $Fo$  goes to infinity. This

phenomenon is also observed in the experimental studies described by Feldman [17]. It could be explained on the basis of the results of the kinetic model as follows: crystallization in the kinetic zone causes a reduction in water content in the vicinity of the front, which produces a moisture concentration gradient that is the driving force for water migration. However, as the solid phase front become stationary ( $Fo > 1.6$ , Fig. 5(c)), this driving force is eliminated and accordingly the water flux is also terminated.

#### 4. CONCLUSIONS

(1) A kinetic model is developed for heat and mass transfer in fine-grained soils under freezing conditions. This approach is based on introduction of the kinetic function to describe the rate of crystallization in a kinetic zone. Our results show that this approach is appropriate for theoretical analysis of such a system.

(2) Theoretical analysis based on this method shows oscillation of the rate of propagation of the phase front under specific conditions. This phenomenon corresponds to the process of intensive segregative ice formation. These results are in agreement with experimental results reported in the literature.

(3) From the theoretical results we infer the existence of an important phenomenon, namely termination of the water migration flux from the non-frozen zone as the phase front reaches a stationary state.

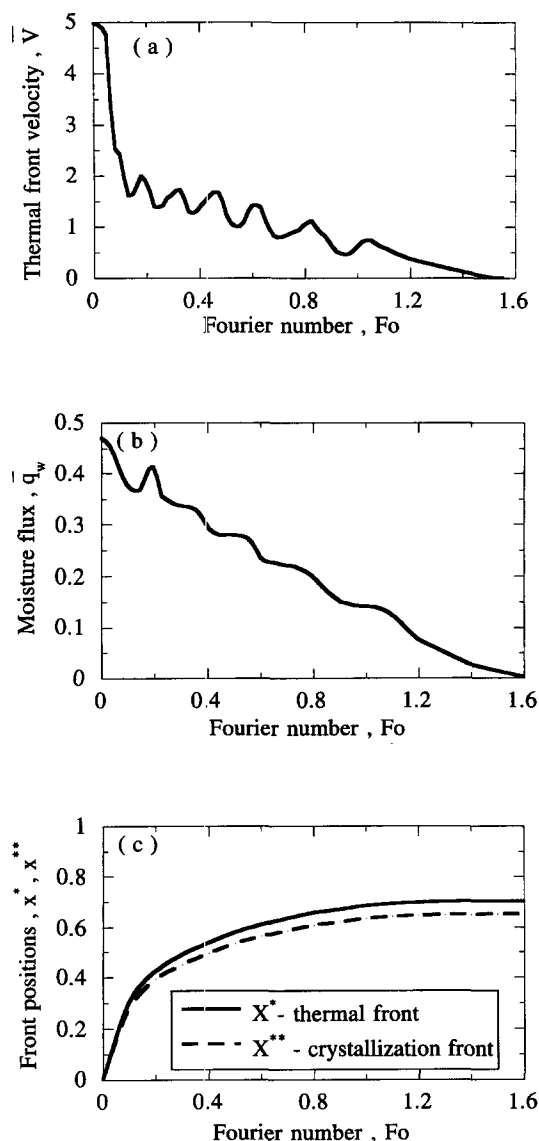


Fig. 5. Thermal front velocity (a) moisture flux (b) position of thermal and crystallization fronts (c) vs Fourier number.  $Le = 0.3, Ste = 0.23, \bar{T}_0 = 0.25$ .

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