# Rhythmic Ice Banding in Soil

R. TORRENCE MARTIN, Research Associate, Soil Engineering Division, Massachusetts Institute of Technology

A comprehensive theory to explain rhythmic ice banding, which produces frost heave in soil, is presented. For convenience in discussion the theory is divided into four stages which overlap and are interrelated. The stages are: (a) nucleation of ice at some distance from an existing ice front, (b) rapid growth of this nucleus into an ice lens, (c) termination of crystal growth, and (d) heat and water flow between the end of stage 3 and the beginning of a new cycle at stage 1. Consideration of all four stages is necessary to an understanding of frost heave.

The unsteady heat flow condition that exists in a freezing soil has an effect upon, and is effected by, nucleation and growth of ice crystals; this interrelationship produces rhythmic ice banding. Water transport through the soil and the accompanying latent heat of fusion are both an essential part of the net heat flow. The mechanism developed is completely analogous to the periodic precipitation of pure chemical systems. The behavior of such chemical systems, called Liesegang phenomena, occur when two solutions, upon diffusing into one another, react to form an insoluble product.

Utilizing the theory, it is possible to predict the distance between successive ice fronts; these predictions agree with experimental results.

For rhythmic banding to occur, the nucleation temperature just below the ice front must be lower than the nucleation temperature at a somewhat greater distance from the ice front. Consolidation and/or a lower degree of saturation below the ice front, which lowers the nucleation temperature, are caused by the tension that develops in the water during ice lens formation.

Soils that do not ordinarily heave (sands and clays) are treated as special cases of the proposed mechanism for which data on analogous Liesegang systems are available. The heave of a clay at a very low rate of freezing is also considered.

The theory is presented as a working hypothesis embracing the entire process in a freezing soil and including all soil types.

●LOSS OF strength in subgrades of highways and airfields (as well as in shallow structure foundations) during the spring thaw has been repeatedly demonstrated to be the result of frost heave. In engineering practice the usual procedure for preventing frost heave and the resultant strength loss has been to replace the frost-susceptible soil with a granular soil which is non-frost-susceptible. The Corps of Engineers, U.S. Army (Arctic Construction and Frost Effects Laboratory), has been doing research to determine just what constitutes a frost-susceptible soil and what might be done to make frost-susceptible soils non-frost-susceptible. For a number of years Lambe (1) has been working with ACFEL in an effort to find chemical additives that will reduce the frost susceptibility of soils.

Unfortunately, the mechanism of frost heave is not very well understood, which makes research on the elimination of frost heave doubly difficult. Numerous discussions of frost heave have been held by the M.I.T. soils staff: some of these were attended by engineers from ACFEL. These informal discussions provided the seed for the

present paper, which slowly grew and was brought to fruition as a lecture on theories of ice lens formation given by the author during a special summer program at M. I. T. entitled "Soil Engineering in Frost Areas."

Work by Taber (2) and Beskow (3), as well as the recent work of Chalmers and Jackson (4), Gold (5), Miller (6), and Penner (7), clearly showed that there was no one complete theory which explained ice lens formation. Each of the previously mentioned researchers has made a significant contribution to different aspects of the problem, without which the present theory could not have been evolved. Also, Simiakin and Miklalev (8) had demonstrated that ice lens formation and Liesegang rings were "absolutely analogous" processes. The fact that they proved the analogy by the use of Taber's experimental data may be taken as an independent verification of the present theory.

Basically the problem involves the interrelationship of (a) the phase change (liquid to solid), (b) the mass transport of liquid to the freezing front, and (c) the condition of a general unsteady heat flow found in a freezing soil. Any complete theory for the cyclic ice lens formation of necessity includes all stages of the cycle. For purposes of discussion the cycle may be conveniently divided into four stages, as follows:

1. Nucleation of ice at some distance from an existing ice front.
2. Rapid growth of this nucleus into an ice lens.
3. Termination of crystal growth.
4. Heat and water flow between the end of stage 3 and the beginning of a new cycle at stage 1.

Obviously, because the soil freezes, there must be heat flow throughout all four stages and, of course, water flows to the ice front during stage 2 in order to produce an ice lens, which points up the fact that all the stages overlap and are interdependent. Therefore, it may be well to briefly outline the discussion to be presented. Nucleation of a solid within a liquid phase is considered first in a bulk liquid and then in the soil water system. An investigation of possible growth mechanisms for the ice crystals just nucleated leads to a discussion of water flow in the soil water system. The unsteady heat flow of a freezing silt soil system (one in which rhythmic ice banding will occur) is examined while giving consideration to the stipulations of crystal growth and nucleation discussed in the preceding paragraphs. Following a discussion of the special cases for sands and clays, a consideration of an analogous chemical system, Liesegang rings, is presented.

## NUCLEATION

Freezing of a liquid involves the formation of small particles of solid phase, a process called nucleation. This process is followed by the growth of nuclei to crystals of finite size. The process of nucleation takes place at a measurable rate ( in a pure liquid) only at temperatures far below the normal freezing point, $T_0$. Precisely how far below the normal freezing point nucleation occurs, depends upon the physical system.

Nuclei form slightly below $T_0$, but because of the thermal energy the statistical odds are tremendously in favor of immediate disintegration; therefore, the temperature must be lowered before nuclei of sufficient size to produce a significant growth rate are formed. At some temperature, called the nucleation temperature, the thermal energy reaches a point where the statistical odds favor nuclei growth rather than nuclei disintegration. Instantaneously crystal growth becomes predominant. The nucleation temperature, $T_N$, must always be less than the freezing point in order to initiate ice formation.

In absolutely pure water, the temperature where this spontaneous nucleation occurs has been reported to be as low as -39C (9). However, the presence of foreign particles, even of molecular size, within a liquid may serve to stabilize the nuclei formed so that the temperature at which nuclei formation becomes significant is far above the temperature required for nucleation in the pure liquid.

In the process of nucleating ice in a soil-water system, there are, in addition to the conditions just discussed, other factors that have to be considered because the voids of a soil separate the water into small volumes that are interconnected by still smaller

volumes. For any temperature less than the normal freezing point, an important factor that governs the probability of nuclei formation is the ability of water molecules to move from the water structure to any incipient crystal embryo. The proximity of any surface influences the structure of the water, generally decreasing the freedom of water molecule movement, which in turn decreases the probability of nuclei formation. From a detailed study of the proximity of an interface (solid to liquid), Hosler and Hosler (10) demonstrated that the supercooling required to induce nucleation in glass capillaries increases very rapidly as the specific surface, area to volume, per unit length of capillary increases.

Nucleation of ice in the water of a soil system is fundamentally no different from bulk water; however, the nucleation is modified by the fact that the water is present as separated small volumes and the proximity of the water soil interface lowers significantly the temperature required to nucleate the ice. A further effect of the small partially separated water volumes is that the instantaneous volume of water available for ice formation is limited. In silts and clays where an appreciable fraction of the water is in the double layer, the volume of water available for ice formation is even further restricted. This vital factor is discussed further during the later examination of a freezing soil system.

Another factor that becomes important in the soil water system is the effect of pressure on the freezing temperature. By the use of thermodynamics, Edlefson and Anderson (11) showed that in a water-ice system if the pressure on the ice remains constant while the pressure on the water changes, the effect on the freezing temperature is:

$$\frac{dT}{dP} = +0.0824 \, C/atm \tag{1}$$

The conditions upon which Eq. 1 was derived are well satisfied in a freezing soil system. The freezing point is lowered rather than raised because (a) except where the soil permeability is greater than the rate of ice formation, the conversion of water to ice lowers the water content of the soil, which produces a mechanical tension in the water; and (b) the cations in the electrical double layer around the soil particles tend to be excluded from the ice, which produces an osmotic pressure in the water. Both of these pressures are negative, which lowers the freezing temperature.

The most important factor controlling nucleation is the specific surface, area of interface (solid-liquid and/or liquid-gas) to volume of water, which increases as the negative pressure in the soil water increases because of consolidation and/or a lowering of the degree of saturation. Therefore, the negative pressure that develops during the freezing of a soil-water system lowers the nucleation temperature.

## GROWTH

When ice is nucleated the instantaneous growth rate is.very large; however, in the soil-water system the amount of water within any one pore is limited, obviously restricting crystal growth. Growth of a nucleus can occur at a temperature well above the temperature required for nucleation, but will never exceed the normal freezing point. The driving force for growth is the temperature difference between the growing crystal and the normal freezing point of the liquid. Naturally, the greater this driving force the faster the growth rate.

The mass growth rate of a crystal is proportional to its area of contact with the liquid, which also increases with crystal size; therefore, it follows that at any specified temperature the rate of crystal growth increases rapidly as the size of the crystal increases, provided, of course, that the heat of crystallization can be dissipated and there is an adequate liquid supply.

A crystal growing within a relatively large soil pore rapidly freezes all the water that can be frozen at that temperature; however, in silt and clay soils this is only a fraction of the total water in the pore because the electrical double layer associated with these soil particles lowers the freezing temperature; (that is, freezing point depression). For example, imagine ice growing in a pore of a kaolinite soil. When the ice crystal has grown to within 30 Å (about 10 layers of water molecules) of the clay surface, the

freezing point of the water molecules adjacent to the ice will have been depressed about 0. 4 C below the freezing point of water at the center of the pore. If the ice crystal grows to within 10 $\overset{o}{A}$ the freezing point will be depressed approximately 4 C. From this it should be obvious that in silt and clay soils the ice crystal does not contact the soil particles (at least until the temperature is greatly reduced). The water film between the soil and the ice can withstand fairly high normal stresses (in the kaolinite example the normal stress that the water can withstand is 2. 5 and 25 atm for distances of 30 and 10 $_A$, respectively) and at the same time possess a marked mobility laterally along the soil surface.

There are two ways in which the growing crystal can obtain water to continue growth: (a) the crystal can propagate through a pore constriction, or (b) water can migrate through the pore to the ice crystal. The mechanism of water supply requiring the least expenditure of energy will naturally predominate.
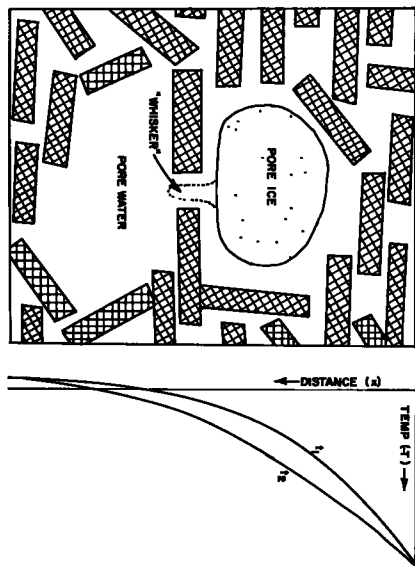


Figure 1. Ice growth in a clay pore; schematic diagram.

For ice to propagate through a pore requires the formation on a relatively large crystal of a much smaller whisker as shown in Figure 1. Water molecules adding at the point of the whisker are in effect being attached to a crystal which is small compared to the pore crystal. To obtain comparable growth rates on small and on large crystals the temperature of the small crystal must be much lower; therefore, to propagate through the pore the temperature must be lowered. For silts and clays the temperature must be lowered still further because of the freezing point depression in the pore constriction that arises from the double layer of the soil particles. As can be seen from Figure 1, the temperature at the point of the whisker, if the whisker could exist, would be in fact



Figure 2. Effect of water tension on soil permeability.

higher, not lower; therefore, propagation of ice through a pore constriction of a soil requires the expenditure of considerable energy. Because the temperature would have to be reduced appreciably for the ice to propagate through the pore constriction, it seems unlikely that ice would choose to advance to the water supply.

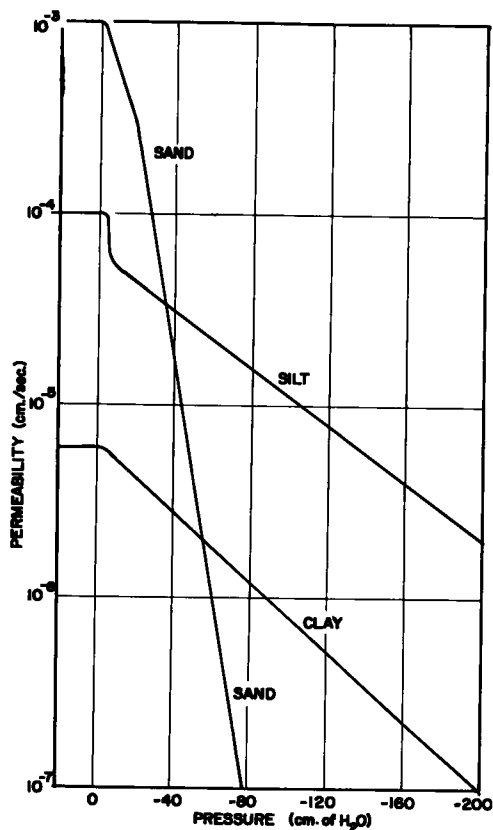The fact that water moves up a glass tube 1 mm in diameter to the ice rather than

ice growing down the tube (until the temperature is lowered considerably) indicates that water flow requires less expenditure of energy. That this is so is obvious from the very large volume increases that accompany the freezing of a frost-susceptible soil.

## WATERFLOW

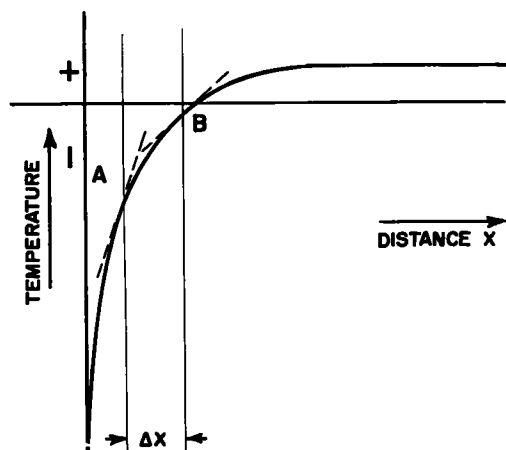The key to the water transport can be stated succinctly. When liquid water goes to ice, water is removed from the soil; to reestablish equilibrium, water flows to maintain a uniform water content in the soil. If the temperature stays below the freezing point, then as water flows, in an attempt to keep the water content of the soil constant, it is frozen into ice. The flow is triggered by the formation of ice, which instantaneously gives rise to a pressure deficiency at the ice front. The main driving force for flow is the pressure deficiency; the lower the temperature at the ice front, the greater the magnitude of the driving force.

An important feature of the water transport is how the pressure deficiency at the ice front influences the ability of the soil to transport water.

The soil permeability is a measure of water transport ability. Figure 2 shows permeability as a function of pore water pressure. These data are for agricultural soils where the bulk density is very low; nevertheless, the data are adequate to indicate that the ability of a soil to transport water decreases as tension develops in the water. In sand the void ratio remains essentially constant as tension develops in the water while the degree of saturation decreases. A tension of 50 to 70 cm of $H_2O$ lowers the degree of saturation in a sand to the point (-80 percent) where the liquid phase, probably no longer continuous, accounts for the rapid drop in permeability. The clay remains nearly 100 percent saturated up to a tension of 300 to 500 cm of water, and the liquid phase remains continuous. The decreased permeability with increased tension for the clay is predominantly due to the change in void ratio, because a small change in void ratio produces a large change in permeability. For the silt, quite likely both void ratio and degree of saturation change as the tension is increased; however, because the permeability falls off slowly with increasing tension, the liquid phase must remain continuous up to a tension of at least 200 cm of water.

The relative rate of water flow through different soil types as indicated in Figure 2 is: (a) sand, either very large or negligible; (b) silt, somewhat less than maximum for sand, any decrease (due to increased tension in the water) will be gradual; (c) clay, very slow and any decrease will be gradual.



Figure 3. Thermal gradient showing unequal heat flux through a volume element ( $\Delta X$ ).

## FREEZING OF A SOIL-WATER SYSTEM

The general unsteady heat flow situation, coupled with the conditions of crystal nucleation and growth is the necessary condition for rhythmic or periodic ice lens formation. In addition it is essential that the rate of heat extraction exceed the rate of heat supply (water flow) within certain limits.

To briefly recapitulate the nucleation and growth conditions:

i. The temperature at which ice will nucleate is significantly lower than the temperature at which ice crystals will grow at an appreciable rate. A corollary of this is that nucleation depends on the pressure in the water and the proximity of an interface (liquid-solid).

2. Growth of ice crystals occurs, if at all possible, by transport of water from adjacent soil to the ice crystals. The ability of a soil to provide adequate water transport depends on soil type, water content, and tension in the soil-water, which may change during freezing.

First, consider a silt soil system, because this is one that will give rhythmic banding. Subsequently the behavior of sand and clay soil systems will be discussed with regard to the theory developed for the silt soil system.

For a model, consider a thoroughly homogeneous silt at a uniform temperature $T^W$ and a uniform water content (saturated at $t = 0$) which is brought into contact with a heat sink at a uniform temperature $T^C$. Merely for convenience, a block of ice of sufficient size that at the completion of soil freezing the heat content of the ice block is virtually unchanged, is used as a heat sink. $T^C$ is appreciably lower than $T^W$. The problem is to examine the heat and water flow as a function of distance, $x$, where time, $t$, is a variable with the additional stipulations imposed by the conditions of crystal nucleation and growth previously discussed. The model is set horizontally, so that gravity is not a factor, and the soil column is connected to a water reservoir, corresponding to a water table, which is at the same temperature as the soil and is large enough that its temperature remains constant.

Neglecting ice formation for the moment, the heat extracted by the heat sink comes from the soil and the initial water present in the soil. It is well established that the thermal gradient is an unsteady state, as shown diagrammatically in Figure 3. The rate of heat extraction from the volume element $\Delta x$ in Figure 3 is determined by the slope at A, and the rate of heat supply to the same volume element is determined by the slope at B. Obviously, the rate of heat extraction exceeds the rate of heat supply; therefore, with time the temperature of this volume element is lowered.

When the ice block and soil are brought into contact, the actual temperature, $T_x$, at this point is less than the normal freezing point, $T_0$, so ice forms. A by-product of the freezing of ice is the latent heat of fusion, L, which raises the temperature at the ice front. This heat tends to flow to the left and somewhat to the right as well, which then slows or may even stop the time rate of change of the thermal gradient. The amount of temperature rise produced by the latent heat of fusion depends on how much water is instantaneously frozen, which in turn is determined by the nature of the soil.

Ice is now forming, which means that the volume of the soil water system must increase and/or the soil consolidate. Because water flows to the ice and is frozen, the volume increases far more than the 11 percent necessary for the change in density during freezing of the initial water, present in the soil. This positive volume change is not necessary to the mechanism of ice banding, and in fact, Taber (2) obtained very large heave from liquids with a negative volume change (liquid to solid). The soil may also consolidate, but data are lacking. For the volume to increase, displacing the soil and ice in the direction of decreasing temperature, work must be done.

In a silt, under normal freezing rates, the fraction of the water in the soil pores at the ice front that can be instantaneously frozen is not sufficient to raise the temperature to the normal freezing point, which means that water is being converted to ice at a certain degree of supercooling $(T_0 - T_x)$.

Below the freezing point, $T_0$, water would be more stable as ice. The lower the temperature, the more unstable the water and the greater the energy release when the water freezes. The energy released with the transformation of water into ice, L, is energy required to form ice from water and, therefore, is energy unavailable for doing work (heave). The available energy for doing the work of displacing the soil and drawing water to the ice comes from the change in free energy, $\Delta F$, of the system. It can be shown by thermodynamics that this available energy is given by

$$\Delta F = \frac{L(T_0 - T_x)}{T_0} \tag{2}$$

The freezing of 1 cc of water at 1 C of supercooling provides sufficient energy to lift 12.5 kg a distance of 1 cm. Taber (2) recognized that it was supercooling, as distinct

from freezing point depression, that provided the energy for heave. As can be seen from Eq. 2, if freezing takes place at $T_0$ (which need not be 0 C) there is no energy available for heave.

The temperature, $T_x$, at the ice front will remain constant as long as the heat flux at the ice front is constant; that is, the slopes at points A and B in Figure 3 are the same. Formation of ice at a supercooled temperature induces a pressure deficiency at the ice front, which in turn produces flow of water to the ice front and the water that flows is frozen into ice. Both the water flow and the latent heat of fusion are supplying heat; therefore, two additional terms must be added to the heat supply. The amount of flow, Q, is a function of the pressure gradient and the permeability (which is also a function of pressure). The amount of water going to ice, and hence L, is a function of Q. It has already been shown how at any point the temperature tends to become lower with time; therefore, in order to maintain a constant heat flux at the ice front, the heat supply must also increase with time. The additional heat from Q and L will temporarily keep the heat flux constant.

A silt soil with a permeability of $10^{-5}$ cm per sec can supply enough water to give heave of about 1 mm per hr, which is a very reasonable heave rate. This water flow, as previously discussed, results from the pressure deficiency at the ice front. The water reaches the ice front through the water film that exists between the ice and the soil surface as shown in Figure 1. The film of 2 or 3 molecules provides a ready passage for water molecules along the soil surface to the ice front and at the same time can withstand the large normal stresses developed during heave. This two-dimensional liquid concept was suggested by Taber (2) as a means of water transport.

It has already been mentioned how the larger a crystal becomes the faster it tends to grow. Quite obviously the larger the ice crystal becomes, the more water is required to increase its size uniformly. With time, the water demands of the growing ice crystal are increasing rapidly and at the same time the ability of the silt soil to supply water, in order to keep the temperature at the ice front from decreasing, is diminishing. Thus, the water demand and water supply are working at cross purposes, which produces the inevitable decrease of the temperature at the ice front. When this happens, the demand for water by the ice crystal is further increased and the ability of the silt to supply water is further decreased because of the increased negative pressure in the water, which lowers the freezing point of the water present at the ice front, and which decreases the permeability, still further decreasing the ability of the soil to adequately supply water to the ice front. Obviously, this whole process soon "snowballs."

Ice formation need not actually cease, but the rate of formation is greatly reduced. A freezing temperature now penetrates into the unfrozen soil ahead of the ice front and water continues to flow slowly to the ice front, further reducing the available water in advance of the ice front. Ice does not form at a small distance ahead of the existing ice front because there are no nuclei present and in order to start ice formation the temperature must now be lowered to the nucleation temperature.

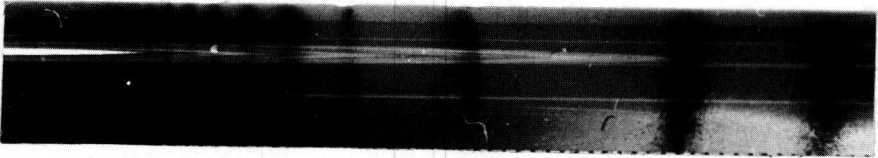The nucleation temperature, $T_N$, is decreased in the region ahead of the ice front



Figure 4. Gradients of actual temperature and nucleation temperature with time.
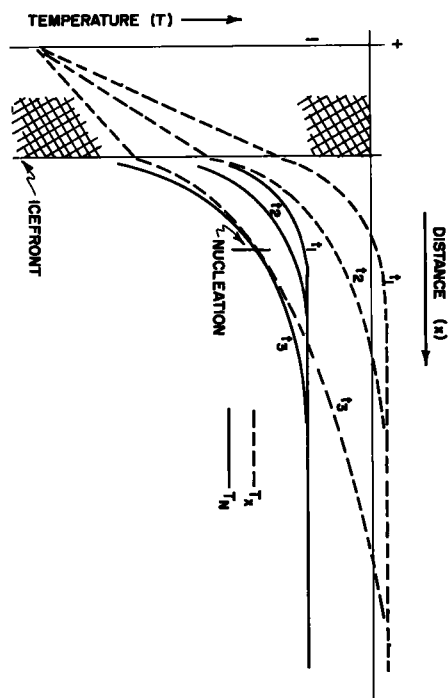
## SOIL–WATER

**Approximate Scale :–**
**Soil Water 1:1**
**Ag—CrO$_4$  2:1**



## Ag — CrO$_4$

Figure 5.  Rhythmic banding in a water-soil and a $Ag^+$ - $CrO_4^=$ system.  (Soil water photo courtesy of the Arctic Construction and Frost Effects Laboratory, Corps  of  Engineers, New England Division.)

because the negative pressure in the water will consolidate the soil and/or lower the degree of saturation.  Both of these effects would greatly lower the nucleation temperature because they have in effect decreased the maximum distance that water molecules can be from an interface.  As shown by Hosler and Hosler (10), for pore sizes likely to be found in a silt a small decrease in the distance to an interface solid-liquid or liquid-gas appreciably lowers $T_N$.  The envisioned changes in actual temperature, $T_x$, and nucleation temperature $T_N$, within the soil mass are shown in Figure 4, where time is a variable.  These temperature curves illustrate how ice is nucleated a considerable distance ahead of an existing ice front.  Right at the ice front $T_N$ ceases to exist because ice already exists; therefore, the $T_N$ curves in Figure 4 are started an infinitesimal distance from the existing ice front.

When $T_x = T_N$, ice formation occurs very rapidly.  This situation impedes further growth of the existing ice lens, accelerates the depletion of available water to the left of the new ice lens, and the instantaneous addition of the latent heat of fusion temporarily slows the advance of the thermal gradient.

Before growth of the new ice lens proceeds back to the previous lens, the available water in the region between the two lenses is reduced to where $T_0 < T_x$ ; therefore, continued growth of the new lens must obtain water from farther down in the soil (to the right in the model).  The cycle is now complete.

With the passage of time the thermal gradients become less steep, as do the water pressure gradient and the $T_N$ gradient, which means that the distance between lenses increases, as well as the thickness of the lenses.

To recapitulate briefly, the proposed theory assumes a general unsteady heat flow condition.  When ice is forming at a supercooled temperature, it is possible for a silt
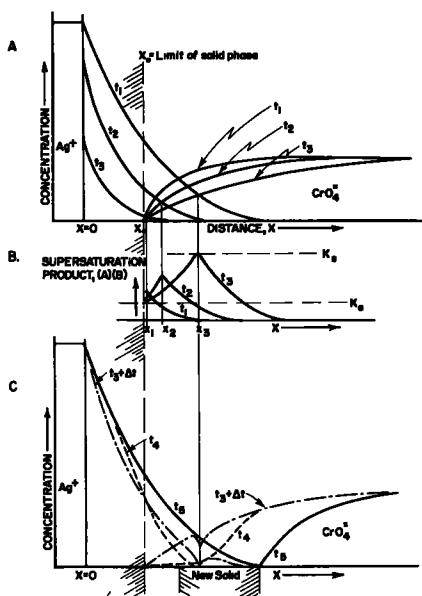
Figure 6. Effect of time on concentration gradients and on the supersaturation product for a $Ag^+$-$CrO_4^=$ Liesegang system.

to provide adequate water to the ice front in order that the heat flux at the ice front can be temporarily constant. Without supercooling there can be no extensive heave because there is no energy available to raise the overburden and draw water to the ice front. In time, the ability of the silt to supply water decreases because the permeability decreases. The decreased permeability arises from the increased negative pressure in the water ahead of the ice front, which results from the fact that continued heat extraction freezes all available water at the ice front, which in turn increases the negative water pressure. The slowdown of water supply decreases the amount of water being converted to ice, and thus the heat of fusion per unit time; therefore, the rate of heat extraction exceeds the rate of heat supply and the temperature decreases. Ice nucleates when the actual temperature is lowered to the nucleation temperature. This takes place at some distance from an existing ice front, because the nucleation temperature is lowered tremendously as the negative water pressure increases.

## FREEZING SAND AND CLAY SOILS

When the heat sink is brought into contact with a sand soil, freezing begins. The volume of water that can instantaneously freeze is large enough that the temperature is raised to very near the freezing point, $T_0$; therefore, there can be no heave, as shown by Eq. 2. For the usual rates of freezing the maximum heave rate of a silt is 1 mm per hr. The saturated permeability of a sand is at least an order of magnitude larger than this maximum water requirement. Such a high flow rate prevents a pressure deficiency from developing at the ice front, and because the freezing takes place at $T_0$, there is no supercooling to trigger the development of a pressure gradient. Ice propagates through the largest pore constrictions fairly easily because (a) no pressure gradient exists to produce flow and (b) the pore above the constriction is filled solid with ice. Therefore, in order for ice to continue it advances via the largest pore constrictions. Water in the smaller pores gradually freezes as the temperature is lowered.

If the freezing rate is greatly increased, so that the initial instantaneous latent heat of fusion does not raise the temperature to $T_0$, a large pressure gradient quickly develops and, as shown in Figure 2, the permeability of the sand drops to a low value. There is now such a small volume of water being converted to ice that the temperature quickly drops to such a low value that at any infinitesimal distance ahead of the ice front the actual temperature is as low as the nucleation temperature; therefore, the water that is present is converted to ice.

When the heat sink is brought into contact with a clay soil, freezing of the soil water begins. The volume of water that can be instantaneously frozen is so small that the latent heat of fusion per unit time is very small; therefore, the temperature within the clay drops quickly. The permeability of the clay is so low that for normal freezing rates the clay cannot supply water fast enough for Q and L to materially contribute to the total heat supply; that is, Q and $L \approx 0$. Accordingly, the temperature continues to drop and the water initially present in the clay at a particular distance converts to ice as the temperature is lowered. This situation is very similar to the case of the unsaturated sand.

If in a clay the freezing rate is greatly reduced, to the point that the rate of water

supply, which depends on the permeability, and the accompanying latent heat of fusion can temporarily match the rate of heat extraction, the clay will heave by the same mechanism as described for the silt because (a) the change in permeability of a clay is gradual at modest negative pressures in the water, and (b) the clay has an electrical double layer so that there will be a two-dimensional liquid film between the soil particle and the ice through which water can reach the ice front.

In conclusion, rhythmic ice banding requires that the components (heat extraction and heat supply) comprising the general unsteady heat flow have a ratio that can vary within certain fairly narrow limits. Further, the rate of change of heat supply with time must be slow. A reliable numerical value for the optimum ratio of heat extraction to heat supply can not be determined at present because no data are available. Nevertheless, it is felt that, at usual freezing rates encountered in nature, silt soils are near this optimum ratio. In sand the permeability is such that with time the rate of heat supply either potentially can exceed the rate of heat extraction, or rapidly can fall to nearly zero. For a clay, at the usual freezing rate, the rate of heat extraction is much greater than the rate of heat supply because the rate of water flow and the accompanying heat of fusion are much less in a clay than in a silt. However, by greatly reducing the rate of freezing a clay system can satisy both conditions for rhythmic ice banding: (1) the proper ratio of heat extraction to heat supply, and (2) a gradual change in the rate of heat supply with time.

From the foregoing discussion of the different soil types, it is apparent that some of the conditions necessary for rhythmic ice banding are found in all soil-water systems; namely, (1) a nucleation temperature appreciably lower than the temperature required for freezing the most easily frozen soil water, and (2) an unsteady heat flow condition. The additional stipulation required for rhythmic ice banding and the resultant heave is that the permeability of the soil be such that a steady state heat flow condition can be maintained temporarily. There is no fixed permeability that will give rhythmic ice banding, because the permeability required depends upon (a) the rate of freezing, (b) the moisture content and depth to the water table, and (c) the amount of supercooling at which this temporary steady heat flow is established.

## LIESEGANG RINGS

Periodic precipitation of a solid within a liquid occurs in systems other than freezing soils, and has been extensively studied. Liesegang ring formation is such a system, which occurs when two solutions diffuse into one another and react to form an insoluble product. A classic illustration is the formation of red silver chromate bands, $Ag_2CrO_4$, within a gel containing a low concentration of potassium chromate, $K_2CrO_4$, and a higher concentration of silver nitrate, $AgNO_3$, diffusing into the gel. This is shown in Figure 5.

First, an analogy is built between the diffusion process of Liesegang rings, mass transfer, and the heat transfer of the freezing soil. The analogous components between a freezing soil and a silver nitrate-potassium chromate Liesegang system are indicated in Table 1, along with various conventions and symbols used herein. A necessary, but not a sufficient condition, for rhythmic banding is that $[Ag^+] >> [CrO_4^-]$; that is, A>>B.

The reaction of silver ions (A) with chromate ions (B) forms silver chromate (AB), which has a solubility product $K_0 = [Ag]^2 [CrO_4]$. However, to start precipitation the product (AB) must exceed the supersaturation product $K_s$. Once precipitation starts it will continue as long as the supply of A and the supply of B are adequate to maintain (AB)>$K_0$.

The supply of silver and chromate at any point are given by Fick's law for each component:

$$\frac{\partial [Ag]}{\partial t} = -D_{Ag} \frac{\partial^2 [Ag]}{\partial x^2}$$

and

$$\frac{\partial [CrO_4]}{\partial t} = -D_{CrO_4} \frac{\partial^2 [CrO_4]}{\partial x^2}$$

Because the diffusion constants for silver and chromate ions are about equal $(D_{Ag} \approx D_{CrO_4})$ and the silver ion concentration, $[Ag]$, is larger than the chromate ion concentration, $[CrO_4]$, it is clear that the rate of supply of silver ions at any point exceeds the rate of supply of chromate ions at the same point, with the result that the

TABLE 1

ANALOGOUS COMPONENTS BETWEEN LIESEGANG RING
AND SOIL-WATER SYSTEMS

|  | Liesegang<br>(AgNO₃ - K₂CrO₄) | Soil |
|---|---|---|
| Reactant A | Silver ion concentration, $[Ag^+]$, decreases in +x direction. Source reservoir at x = O | Heat extraction, by heat sink at x = O. |
| Reactant B | Chromate ion concentration $[CrO_4^=]$, decreases in -x direction. Sources:<br>a. CrO₄ present in gel<br>b. diffusion of CrO₄⁻ from reservoir at large x | Heat supplied by —<br>a. Soil and water present in soil<br>b. Water flow to ice front<br>c. Heat of fusion |
| Reaction product | Silver chromate, Ag₂CrO₄ | Ice |
| Reaction by-product | Potassium nitrate, KNO₃ | Heat of fusion |
| Reaction begins: | When $[Ag]^2 [CrO_4]^{>>} = K_S$, the supersaturation product. | At nucleation temperature, $T_N$, which is a function of temperature, tension in the water, and proximity of an interface. |
| Reaction stops: | When $[Ag]^2 [CrO_4] = K_0$, the solubility product | At normal freezing point, $T_0$, or when tension in the water at ice front increases to where A advances beyond ice front. |
|  | $K_S > K_0$ | $/T_N/ > /T_0/$ |

rate of precipitation is controlled by the rate of supply of chromate ions. From the conditions just stated, it is also evident that, at any point, the amount of silver ions is going to increase with time and likewise at this same point the amount of chromate ions will decrease. (See Figure 6A, which is exactly analogous to the condition shown in Figure 3.) Therefore, with time, the demand for chromate ions at the precipitation zone increases while the rate of supply decreases, which produces the inevitable; the product (AB) becomes less than $K_0$ and precipitation virtually stops. At the same time silver ions advance into the region beyond the precipitation zone. In the region free of solid phase nothing will happen until the product (AB) = $K_S$. If, however, as is the case here, A > B and $D_A \approx D_B$ the rate of increase of A exceeds the rate of decrease of B, then the product (AB) will increase with time and become equal to $K_S$. Figure 6B illustrates the change in (AB) as a function of distance with time as a parameter. This technique was used by Ostwald (12) to explain Liesegang rings. Without going into the

equations, Figure 6A indicates why (AB) first reaches $K_S$ at some distance from the existing solid phase. Obviously, a new band of solid phase begins to form when (AB) = $K_S$ . Solid phase formation depletes the supply of A and B at this point; therefore, there is established a steep concentration gradient at the point where this second precipitation began. Transport of A and B into this zone takes place from both directions (see Figure 6C).

The situation shown in Figure 6C for time $t_3 + \Delta t$ impedes further growth at the first zone, accelerates depletion of B to the left of the new zone, and retards build-up of A to the right of the new zone. Before the growth of the new zone proceeds back to the first zone of solid phase, the concentration of B in the region $x_0$ to $x_3$ is so low that the product (AB) is less than $K_0$ ; therefore, continued growth of this new zone must be to the right. With time, conditions similar to those initially present will be established and still another zone further to the right will develop.

The time required to reach $K_S$ to the right of an existing zone, and the displacement x at which it occurs, depends on the concentration gradients of A and B. Because the concentration gradients of both A and B decrease with time, it takes longer for A to build up, hence each succeeding band is thicker and there is an increased distance between bands   Furthermore, if the rate of supply of A equals the rate of supply of B, a continuous solid phase will build up. If the rate of supply of A>>> rate of supply of B, then as A advances beyond existing solid phase, the product (AB) is always greater than $K_S$ and again continuous solid phase is produced, but in reduced quantity.

To summarize the conditions for Liesegang ring formation:

1. The initial concentration of A is several times greater than the initial concentration of B.

2. The supersaturation product, $K_S$ , must exceed by an appreciable amount the solubility product, $K_0$ , before precipitation begins.

3. The transport, diffusion, of A and of B to the zone of precipitation remains an unsteady state process throughout the period of ring formation.

The close analogy between the rhythmic periodicity of Liesegang rings and ice banding in soil systems is self-evident. Miller ([13]) has brought to the author's attention a brief note that appeared in the Russian literature in 1937. By use of Taber's data, Simiakin and Mikhalev ([8]) showed that the distance between successive ice fronts could be expressed by an equation of identical form to that used to express the distance between successive precipitation zones in a Liesegang ring system. Therefore, they concluded that "the process of formation of periodic ice streaks is absolutely analogous to the formation of Liesegang's rings."

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