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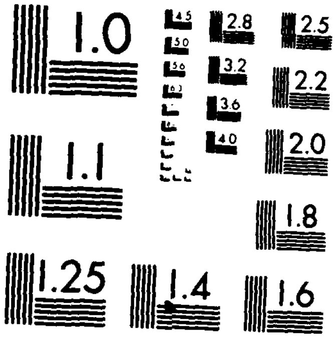

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Natural electrical potentials that arise when soils freeze

I.G. Yarkin

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Samples of sand, kaolin, bentonite, and loam were frozen from the top downward in cylinders 10 to 12 cm high and 7 cm in diameter. During the freezing process electrical potentials of up to 300 mV were measured between platinum electrodes placed near the ends of the samples. The mechanism that gives rise to these potentials and the effect of soil type and fineness, moisture content, and moisture migration are discussed.

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PREFACE

This report is a translation of a paper by I.G. Yarkin of the Scientific Research Institute of Foundations and Underground Structures (NIIOSP) in Moscow, U.S.S.R. The paper was translated by Thomas O'D. Hanley, S.J., Professor of Physics, Campion College, University of Regina, Regina, Saskatchewan, Canada. Funding for the translation was provided by DA Project 4A161102AT24: Research in Snow, Ice and Frozen Ground; Mission Area: Combat Support; Work Unit 001: Environmental Constraints on Frozen Terrain.

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Dr. Joseph Oliphant and Cheng Guodong performed technical reviews of the translation.

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ILLUSTRATIONS

NATURAL ELECTRICAL POTENTIALS THAT ARISE WHEN SOILS FREEZE

I.G. Yarkin

The frost heave of soils, which results from the migration of water toward a freezing front, significantly complicates building construction, and in a number of cases it gives rise to inadmissible and even damaging deformation of buildings. In a complex of problems related to the frost heave of soils, a question arises about the forces that give rise to the migration of water toward a freezing front. Among the investigators there are differences of opinion about the nature of these forces. A majority of them hold that these forces basically involve electric and electromagnetic interactions at the molecular level.

Among the electrical phenomena accompanying freezing processes is the appearance of differences of electrical potential between different parts of a system of freezing soil. This phenomenon was noted by A.R. Jumikis during freezing of "glacial outwash material" (Jumikis 1958). He measured potentials of the order of 120 mV. Later V.P. Borovitskiy (1969) measured electrical potential differences in freezing specimens of sand and clay. He measured potentials up to 29 mV in clays and up to 195 mV in sandy samples. In all cases the frozen portion of the sample was charged negatively relative to the unfrozen portion. During thawing of the samples the sign of the potential reversed. The experimental data about the electrical potentials that appear in freezing soils are currently limited only to the works of these authors, who presented conflicting mechanisms for this effect. A.R. Jumikis reasoned that the electrical potentials that appear during the freezing of the soils made their appearance secondarily, and are produced by a "thermal potential" (a temperature gradient). V.P. Borovitskiy (1969) attributes electrical potential differences to a streaming potential that results from the migration of contained moisture toward the freezing front.

In any event, the measured electrical potential difference is a result of several physicochemical processes, of which one or a few can be of primary importance, depending on the composition of the soil and the conditions of freezing. Therefore, to ascertain the role played by a physicochemical process under different conditions of freezing of soils, one ought to study the influence of different factors on the magnitude and dynamics of natural electrical potentials in the freezing processes -- factors of the mineralogical composition and fineness of the soils (the type of soil), the wetness, and the rate of freezing.

EXPERIMENTAL METHOD

In the course of experiments on the freezing of soils (directed downwards from above) we determined the difference of electrical potentials between platinum electrodes at different depths in the samples. We also measured the temperature and determined the distribution of moisture along the height of the samples after freezing.

For our experiments we used soils of different types: fine-grained Lyubertsij quartz sand, finely ground (powdered) sand, fine-grained near-Moscow loam, Glukhov kaolin, and bentonite. We prepared the samples in the form of cylinders with a height of 10 to 12 cm and a diameter of 7 cm. Having sifted the soil through a sieve with 1-mm openings, we wetted it to the needed moistness and packed it into cylinders with a plastic tamper. At 2 to 2.5 cm from the upper and lower ends of the sample, we laid two electrodes in the form of platinum mesh.

The samples were placed in an ultrathermostat* and frozen in a refrigerated room at a suitable temperature. The potential difference was measured with a type LPU-01 potentiometer, modified from a pH meter into an electronic millivoltmeter with large input impedance. Simultaneously the difference of potentials was recorded by a KBT-12 autowriter connected with the potentiometer. The precision of the measurements was ± 2 mV. With copper-constantan thermocouples we measured the temperature in the sample with the aid of a type PPTV-1 potentiometer and a type M-195 galvanometer.

The results of the experiments, presented as figures, give evidence of a change of potential difference with time in the process of freezing. The lower electrode was used as the measuring electrode, and therefore in the figures the sign of the potential corresponds to the sign of the potential

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*Translator's note: Apparently a thermostatically controlled chamber.

of the lower electrode, which most of the time was found in the non-freezing part of the sample.

Before the portion of the samples between the electrodes began to freeze, a potential difference was noted, which depended on a dissimilarity of the electrodes (non-identical amounts of components in the metal from which they were prepared, contamination of the surface, and so on). In the figures all curves were displaced relative to the coordinate axes by the amount of this initial difference, so that all curves begin from the axis of the abscissa.

After final freezing of the sample between the electrodes, there remains a remnant of the difference of potentials. This potential difference disappears if the electrodes are shorted momentarily and does not recover its initial value. Apparently the remanent potential difference reveals a charge accumulated on the electrodes before the final moment of freezing of the sample. Therefore this remanent potential difference is changeable and depends on chance causes. In the analysis of the curves that describe the dynamics of the difference of potentials in the process of freezing, only those portions are examined that correspond to a stable potential difference; sections of the curves that correspond to change of the remanent potential difference after the final freezing of the sample are not examined.

CHANGE OF POTENTIAL DIFFERENCE DURING FREEZING OF SANDY SOILS

The most typical dependence for sandy soils is presented in Figure 1, which shows the results of experiments on freezing sand and powdered sand at a temperature of -16° to -18°C.

In the graphs it is possible to distinguish three regions:

1. A first region, corresponding to the first period of freezing, from the moment of the beginning of crystallization to the moment of freezing-in of the upper electrode. In this section the lines of the graphs drop downward and go through a minimum that corresponds to the moment of freezing-in of the upper electrode. The upper electrode is charged positively relative to the lower.

2. A second region, corresponding to the freezing of the sample from the upper to the lower electrode. The lines of the graphs rise upward and then go through a maximum that corresponds to the moment of freezing-in

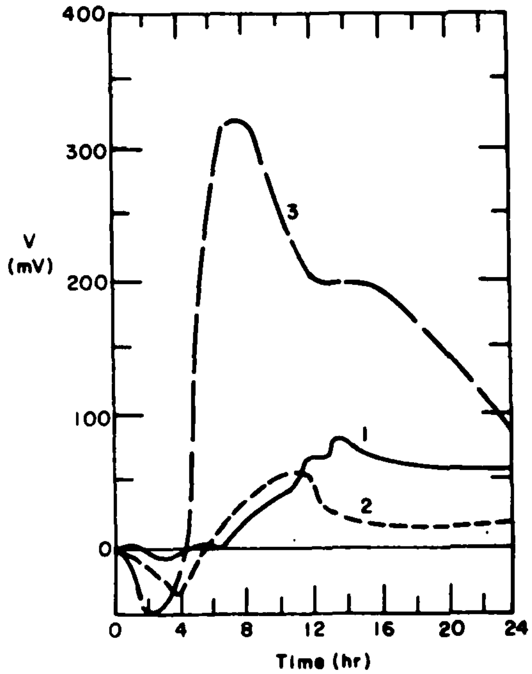

Figure 1. Change of electrical potential difference during freezing of samples of sandy soils (1 - sand with 20% moisture content; 2, 3 - powdered sand with moisture content 19.8 and 22.7%).

of the lower electrode. The upper electrode gains a negative charge relative to the lower, and the lower is charged positively relative to the upper.

3. A third region, corresponding to the final freezing of the sample to the bottom and to a leveling out of negative temperature of the frozen sample in its entire volume. The lines of the graphs drop downward, i.e. the positive charge of the lower electrode relative to the upper is reduced. The difference of potential is reduced at first, but subsequently acquires some constant remanent value. In the graph presented in Figure 1 one can analyze how the potential difference in freezing samples depends on their moisture content and fineness. By comparing curves 2 and 3 in Figure 1, obtained for powdered sand, one can see that the maximum value of the electrical potential difference increases with increasing initial wetness of the samples. For instance, for moisture contents of 19.8% and 22.7%, the maximum potential differences were 52 and 325 mV, respectively.

At the same time, however, comparison of curves 1 and 2 of this figure shows that the maximum potential difference for sand (86 mV) is greater than that for powdered sand (52 mV) for identical moisture contents and conditions of freezing.

Thus the magnitude of the difference of potentials in sandy soils depends on the wetness and the particle size. With increasing wetness the potential difference increases; with increasing fineness (the transition from sand to powdered sand), other things being equal, it is reduced.

For freezing samples of sand and powdered sand, frost heave was not observed. Analysis of the wetness of the samples after freezing did not show any noticeable migration of water in the profile of the frozen samples, in comparison with the distribution of moisture before the beginning of freezing. Analysis of the curves shown in Figure 1 makes it possible to picture how the electric charge was distributed along the profile of the freezing samples of sand and powdered sand. The relative charge of the upper and lower electrodes, which appears after the upper electrode has frozen in, indicates that the freezing portion is charged negatively relative to the unfrozen portion. But the presence of a maximum and a minimum in the curves confirms that a surplus of positive charges moves together with the freezing boundary in the region of phase transitions immediately adjacent to the freezing front. This surplus of charges creates its own kind of potential barrier before the freezing front, relative to which both the unfrozen and frozen portions of the sample are charged negatively. Such a barrier must hinder the migration of moisture toward the freezing front, just as water in soil is transferred from a positive pole to a negative.

The height of the potential barrier in relation to the unfrozen portion of the sample is determined by the minimum point of the curve, but in relation to the freezing portion of the sample, it is determined by the maximum value. For instance, in the experiment with sand (see Fig. 1, curve 1) the free energy difference of the potential barrier* in relation to the unfrozen portion is 34 mV, but in relation to the frozen portion, 86 mV. The difference of potential between the frozen and unfrozen portions is equal in value to the difference of the potential at the maximum minus the height of the potential barrier over the unfrozen portion of the sample, i.e. 52 mV.

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*Translator's note: ΔG, the difference of free energy from the bottom to the top of the barrier.

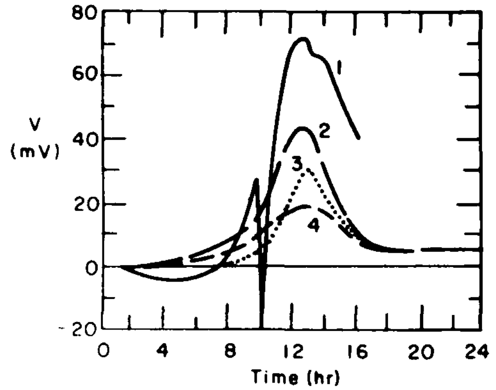

Figure 2. Change of electrical potential difference during the process of freezing sand with different spacings between the electrodes (1: 20 mm; 2: 10 mm; 3: 5 mm; 4: 2.5 mm).

In order to analyze how the distribution of charges** changes near the very boundary of freezing, a series of experiments was undertaken. In the experiments electrodes were placed in the middle of the sample. The space between them was varied from 2.5 to 20 mm. Samples were frozen with the air temperature at −7°C. The results of these experiments are presented in Figure 2; in it are shown only those portions of the curves that corresponded to the freezing front moving across the electrodes. In the interval the potential difference increased to a maximal value and then fell to zero. Before and after the interval, when the freezing front was moving between the electrodes, the potential difference was zero. From this it follows that the principal drop of potentials is confined to the width of the region near the boundary of the phase transitions.

The dependence of the maximal difference of potentials on the distance between the electrodes is presented in Figure 3. As the distance is changed from 2.5 to 10 mm the maximal potential difference increases linearly. This linear dependence is violated with removal of the electrodes from each other to a distance of 20 mm, and the magnitude of the potential difference is approximated by values that were obtained in the experiments in which the electrodes were placed near the ends of the sample. Consequently the width of the region in which the sharp change of electrical potential difference begins ought to be commensurable with a distance of 20 mm.

**The dependence between the magnitude of the electrical charge and the difference of the electrical potentials is determined by the relation $V = q/C$, where V is the electrical potential difference, q is the magnitude of the electrical charge, and C is the electrical capacitance of the system (Koshkin and Shirkevich 1962).

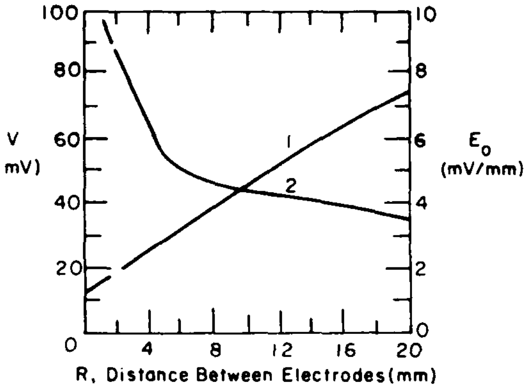

Figure 3. Variation of the difference (curve 1) and the gradient of electrical potentials (curve 2) with change of spacing between the electrodes.

At very small spacing between the electrodes the potential difference will approach zero, and the line of the graphs ought to intersect the origin of the coordinate axes. However, when line 1 of Figure 3 is extended, it intersects the ordinate axis at a point corresponding to a value V_o of the potential difference. This indicates that the drop in potential is greater in the region adjacent to the freezing boundary (the width of which is less than 2.5 mm) than at some distance from the freezing boundary. Apparently such a quick drop in potential occurs within a very narrow region and can be regarded as a potential jump. The potential drop V_o can be determined either graphically or analytically from the relation

$$V = V_o + E_o \ell, \qquad (1)$$

where V = the potential difference between the electrodes

V_o = the drop in potential at the phase boundary

E_o = a constant corresponding to the magnitude of the potential gradient (or to the rate of increase of the potential difference in the linear part of curve 1 in Figure 3)

ℓ = the distance between the electrodes.

A solution gives the following values for the constants of this equation: V_o = 11.67 mV; E_o = 3.33 mV/mm.

In this way three regions of change of potential can be distinguished near the freezing boundary: a jump, a region of linear change, and a region of smooth, slower growth (or decrease) of the potential difference. The jump occurs in a very narrow width of the sample and can have to do with its phase boundary. The regions of linear and of slower change of potential occupy a breadth of more than 10 mm and can be found in either the frozen or the unfrozen portion of the soil.

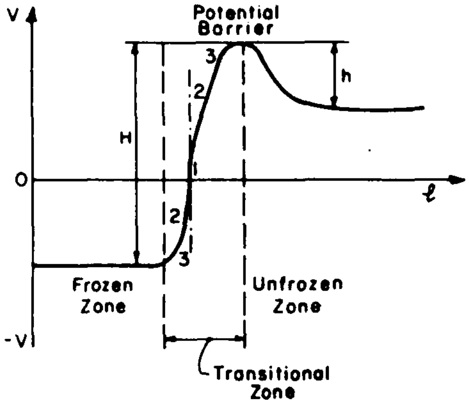

Figure 4. Schematic diagram of the electric charge distribution along the profile of a sample of freezing sand. (1, 2, 3 - regions of potential jump, linear, and nonlinear change in potential. H and h are the heights of the potential barrier in the frozen zone and the non-frozen zone respectively; the dash-dot line marks the freezing boundary.)

Curve 2 in Figure 3 reflects the dependence of the potential gradient on the distance between the electrodes. With reduction of distance, the potential gradient rapidly increases according to a curvilinear law. A distance of 20 mm between the electrodes corresponds to a potential gradient of 3.6 mV/mm, and a distance of 2.5 mm corresponds to a potential gradient of 8 mV/mm. In the region of the jump of potentials, the potential gradient must tend to infinity.

The distribution of charges in freezing sand can be presented in the following form (Fig. 4):

1. The frozen portion of the sample is negatively charged, and the unfrozen portion is positive.

2. In front of the freezing front of the sample is a potential barrier of positive charges, the free energy difference of which is larger with respect to the frozen portion than to the unfrozen portion.

3. At the phase boundary occurs a potential jump, which makes up a small portion of the total potential drop in the region adjacent to the phase boundary transition.

4. The principal change in magnitude occurs in a narrow region near the phase boundary division. The magnitude of the potential beside the boundary division at first changes rapidly to a linear dependence, and then the drop of potential slows down. The electrical charges are distributed over some distance from the phase boundary, and these form a so-called volume charge, a portion of which can be found in the ice. The other portion is distributed in front of the freezing front in the unfrozen soil.

CHANGE OF POTENTIAL DIFFERENCE IN FREEZING CLAY SOILS

For samples from clay soils - kaolin, bentonite, and loam - the electrical potential difference was found to be dissimilar in its dependence on moisture, fineness, and condition of freezing. If the samples froze quickly or if their moisture content was insufficiently great, the electrical potential changed almost as it did in samples of freezing sand, i.e. the frozen portion of the sample was charged negatively relative to the unfrozen portion, and a maximum corresponding to the moment of freezing-in of the upper electrode appeared on the curve of potential difference vs time of freezing.

With slower freezing and higher moisture content of the samples, the opposite change of potential difference with time was observed. The unfrozen portion of the sample gained a negative charge, and a minimum of the curve corresponded to the moment of freezing-in of the lower electrode. In the figures that follow, we shall call "curves of the first kind" those characteristic of sands and fast-frozen clays with little moisture. The curves for moist and fast-frozen clay samples we shall call "curves of the second kind."

Bentonite

Bentonite is the most finely divided and least frost-heaving of the clay soils investigated here. Experiments in freezing were conducted on samples of natural bentonite and on a sample prepared from a fraction with particle size of less than 0.001 mm. The results of these experiments are presented in Figure 5.

The samples were frozen at -16° and -18°C. The moisture content of the samples from natural bentonite was 76.3, 100, 127.8, and 155.8% (curves 1, 2, 3, 4 in Fig. 5). The moisture content of the sample of particles <0.001 mm was 118.8% (curve 5 in Fig. 5).

For samples of 76.3% moisture content and for samples of the fraction <0.001 mm, the characteristic curve was of the first kind; for others the curve was of the second kind. With increase of the moisture content of natural bentonite samples, the maximum potential difference is reduced at first, changes its polarity, and then begins quickly to increase. In Figure 6 is shown the dependence of the maximum potential difference on the moisture content in samples from natural bentonite, and the result of a

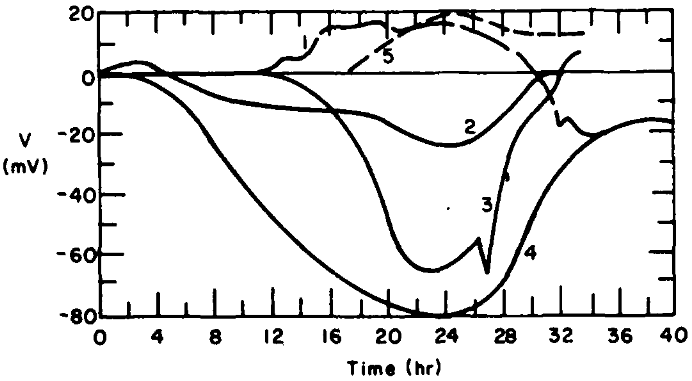

Figure 5. Change in electrical potential difference during freezing of samples of bentonite with different moisture contents (1, 2, 3, 4 - samples of natural bentonite with moisture contents 76.3, 100, 127.8, and 155.8% respectively; 5 - sample of bentonite of fraction < 0.001 mm and moisture content 118.8%).

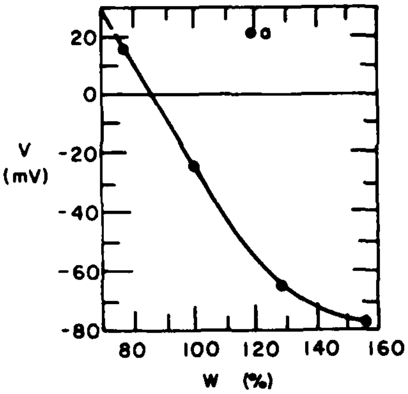

Figure 6. Dependence of maximum electrical potential difference on the moisture content of freezing samples of bentonite (a - result of tests with bentonite of particle size < 0.001 mm).

test with bentonite of the fraction <0.001 mm (point a). The dependence of the maximum potential difference on moisture content is nearly linear. At a moisture content above 127.8% the linear dependence is violated. The zero value of the maximum freezing potential corresponds to a moisture content of 86%.

The point obtained for a sample of the fraction <0.001 mm does not lie on the curve for samples from natural bentonite and falls in the region of curves of the first kind. The points for natural bentonite with the same moisture content fall in the region of curves of the second kind. Consequently an increase of fineness enlarges the region in which curves of the first kind occur.

In summary, the maximum potential difference for bentonite depends on its moisture content and fineness. At increased moisture content not only the maximum potential difference is changed, but also the relative charges of the upper and lower electrodes; i.e. dependencies of the first kind are replaced by dependencies of the second kind.

Kaolin

Kaolin is the soil with the greatest frost heave. With regard to fineness it occupies an intermediate position between bentonite and loam. Some experiments were conducted at different moisture contents and different temperatures of freezing with kaolin and kaolinitic clay, in which the average grain size was larger than usual. For kaolin the dependence of the maximum potential difference on moisture and fineness is similar to that for bentonite.

Figure 7 shows curves for three samples of kaolin. The samples had approximately the same moisture content (40-41%), but were frozen under different conditions. The first sample (curve 1) was frozen without moisture migration from below at a temperature of -14° to -15°C. The second and third samples (curves 2 and 3) were frozen with moisture migration from below and across the wick at the same temperature of -7°C, and the third sample was frozen at a higher temperature in an ultrathermostat. The first sample took approximately 20 hr to freeze through, the second 70 hr, and the third 150 hr. The rate of freezing of the first sample was approximately equal to 5 mm/hr, of the second 1.5 mm/hr, and of the third 0.6 mm/hr.

In Figure 7 one can see how the maximum potential difference is influenced by the rate of freezing. With reduction of the rate of freezing, the maximum freezing potential is reduced at first, attains zero, and then begins to increase. At this time the relative charge of the upper and lower

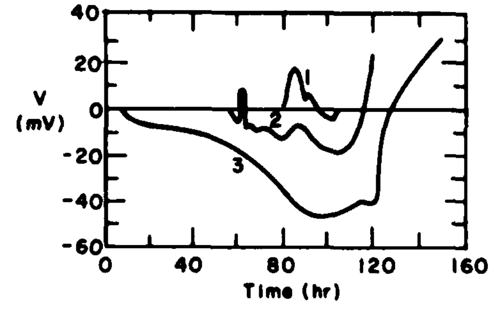

Figure 7. Change in electrical potential difference during the freezing of samples of kaolin at different rates of freezing (1, 2, 3 - freezing rates of 5, 4 and 0.6 mm/hr, respectively).

electrodes is changed to the opposite. The dependence of the electrical potential's magnitude on the rate of freezing is analogous to a similar dependence on the moisture content.

During freezing, moisture migrated over the height of the sample, and frost heave occurred. In the first sample moisture migration was insignificant, and the heave of the soil was not observable. In the second sample a significant migration of moisture was revealed. In the upper region of the sample many icy layers were formed, the heaving of the soil reaching 14 mm. In the upper portion of the third sample the moisture content, in comparison with its initial value, increased by 3 times (122.4%), in the center region by 2.5 times (79.7%), and in the lower region of the sample the moisture content was reduced to 38%. The frost heave of the third sample was about 25 mm.

In summary, the experiments on kaolin showed that the change in potential difference depends not only on moisture content and fineness but also on the rate of freezing. In very moist soil the maximum freezing potential increases with increased amount of moisture migration and with the magnitude of the frost heave.

Loam

In its degree of heaving, loam occupies an intermediate position between kaolin and bentonite; in its fineness, it is intermediate between clay and sandy soils. For loam the typical regularity resembles that for clayey soils. However, these dependencies were not as clearly expressed as for bentonite and kaolin. The time curves for loam, reflecting the change in potential difference in the process of freezing, also have certain specific features (Fig. 8).

Curve 1 reflects an unevenness in the freezing process. Great vertical and sloping ice veins, which intersected the electrodes at different moments of time, were formed in the sample. The potential difference changed in jumps; these were observed at the moment when a line of veins intersected an electrode. Curve 2 reflects the process of slow and steady freezing of a sample. At the beginning of freezing, a peak was directed upward that corresponds to the moment of freezing-in of the upper electrode. At the conclusion of this process, a peak was directed downward, corresponding to the moment of freezing-in of the lower electrode.

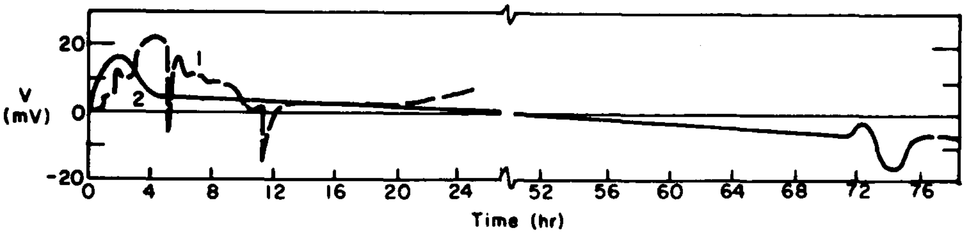

Figure 8. Change in electrical potential difference during freezing of samples of loam (1 - rapid freezing of a sample with a moisture content of 20% at air temperature -18°C; 2 - slow freezing of a sample with a moisture content of 20% at temperature -7°C).

In the first sample, the upper electrode was charged negatively for most of the time. Consequently the distribution of charge was typically the same as during the freezing of sandy soils.

In the second sample, the sign of the charge changed during the process of freezing of the sample. Nevertheless, for a long period of time the potential difference was near the zero value, and the upper and lower electrodes were at nearly the same potential. Only at the time of freezing-in of the upper and lower electrodes was there a sharp change in the value of the charge.

During freezing of a sample very little moisture migration was observed along the profile of either sample, and heaving was not noted.

Summary of results for clay soils

Typically, 1) the curves were of two types, reflecting the dynamics of the potential difference during freezing; 2) the value of the potential difference depended on the moisture content, the fineness, and the rate of freezing; and 3) there was an interdependence between the value of the potential difference, the migration of moisture, and the heaving of the soil on freezing.

In samples that, on freezing, yielded curves of the second kind, the charge of frozen and unfrozen portions was directly opposite; the frozen portion was charged positively with respect to the unfrozen. Apparently an abundance of negative charges is formed ahead of the freezing front, indicated by a small peak and maximum on the curve near the beginning of the experiment, corresponding to the moment of freezing-in of the upper electrode (cf. Fig. 7 and 8, curve 2). For a molecule of water migrating toward the freezing front, a surplus of negative ions introduces by itself a potential well, and therefore such a distribution of charges intensifies migration. If the curve shown in Figure 4 is reversed relative to the horizontal axis, this will represent the distribution of charges in the profile of such samples.

ANALYSIS OF RESULTS

If the results of measurement of a difference of electrical potential, adduced above, are compared with the results of observations on the change of moisture and the frost heave of experimental samples, one can note a common regularity. Curves of the first kind were obtained in the case when samples froze without noticeable migration of moisture (in freezing sands and quickly frozen clay), but curves of the second kind appeared with samples in which moisture migration and frost heave occurred (in slowly frozen kaolin). Curves of the second kind were obtained likewise in samples of bentonite.

We note that there are gradual transitions between curves of the first and second kind (cf. Fig. 5, 6, and 7). By changing the moistness or the rate of freezing, curves of either the first or the second type can be obtained in samples of one and the same kind of soil. For all different types of curves the changes of electrical potential difference correspond to a different distribution of electric charges in the profile of the sample. For instance, the surplus of positive or negative charges found ahead of the freezing front may either hinder (curve of the first kind) or help the migration of moisture toward the freezing front (curve of the second kind). This explains how a difference of electrical potential arises under the influence of physico-chemical processes, by which some of these processes are reinforced under diverse conditions of freezing, but others are reduced.

Oxidation-reduction processes give rise to redox potentials. Different proportions in the metal of the electrodes lead to the formation of galvanic potentials. On contact with different media, contact potentials and Workman-Reynolds potentials appear (Workman and Reynolds 1950), but in the unfrozen portion of the soil a gradient of electrical interphase potential appears, which by the data of the investigations (Tyutyunov 1961) is shown as the initial cause of the moisture migration and soil heave. Under the influence of the movement of moisture a streaming potential appears (Zhukov et al. 1956).

In experiments on freezing conducted at NIIOSP, we made use of pure soils, not containing easily oxidized components. Therefore the role of oxidation-reduction processes must not be great. Attention was given to the value for the initial difference of potential, which arose as a result of the dissimilarity of the metal of the electrodes; this value was subtracted from the value after each test was stopped.

Contact potentials make their appearance in the boundary of the phases during the freezing of the water and of dilute water solutions (of the order of 10^{-3}N and less) and during crystallization of other substances, for instance, paraffin. A contact potential difference is found as a result of a change of phases by charged particles (electronic or ionic) by preferential adsorption of ions of one sign or as a result of orientational adsorption of polar molecules by a surface at a division of phases (Antropov 1969).

During the crystallization of pure substances, not including mixtures, a contact potential difference is not great and is measured in millivolts or tenths of millivolts. E. Gill (1953), V.I. Arabadzhi (1948, 1956), F. Heinmets (1962), and others have studied contact potentials that appear during the freezing of water and of solutions of salts. F. Heinmets (1962) has shown a linear dependence of the value of contact potentials on the logarithm of the concentration of HCl and NaOH. In solutions, contact potentials make their appearance when the solid and liquid phases are in balance, i.e. when the solid phase does not increase at the expense of the liquid. When such equilibrium is absent, freezing potentials or Workman-Reynolds potentials appear at the boundary between the phases. Workman-Reynolds potentials occasionally attain tens or even hundreds of volts.

Much labor has been devoted to the study of contact potentials and Workman-Reynolds potentials in freezing dilute aqueous solutions. The results of the investigations show a dependence of the signs and values of the potentials on the chemical composition of the solutions, their concentration, and the rate of freezing (Bayandina 1960, Workman and Reynolds 1950). In particular, research has determined the optimal concentration of the solutions and the rate of freezing at which the difference of potentials between the solid and liquid phases is greatest. At very low rates of freezing in pure distilled water, the potential difference between the solid and liquid phases approaches zero. The majority of the researchers explain this by the selective separation of ions in the solution and a selective adsorption of one of them by the solid phase (ice).

In our experiments contact potentials and Workman-Reynolds potentials appeared during the freezing of samples of sand and powdered sand. This indicates the nature of the change of potential difference and the distribution of electric charges in the profile of the sample. A potential barrier from a surplus of positive charges is found ahead of the freezing front as a result of the selective separation of ions of opposite sign at the boundary of the division of phases. The mechanism of the appearance of contact potentials enables us also to explain other dynamic peculiarities of the electrical potential difference in sandy samples. For instance, the dependence of the value of the potential difference on the fineness of the soil can be explained. With an increase of fineness of the soil there is a reduction in the size of the ice crystals that arise in the spaces between the mineral grains, and the randomness in orientation is increased. With increase of the latter, the potential difference is decreased (Konnova 1965, Korkina 1965).

With an increase of moisture content, the size of the ice crystals in ths spaces between the grains increases and the randomness of arrangement is decreased. Therefore the difference of electrical potentials also increases with the increase of moistness of the samples. But the processes of formation of the potential difference in freezing solutions and in freezing sandy soils have substantial dissimilarities. For instance, researchers studying freezing solutions (e.g. Workman and Reynolds 1950) did not observe a minimum of the potential difference at the moment of freezing-in of the upper electrode, and for freezing soils the values of the potential difference were low compared to those for freezing solutions.

The former dissimilarity is explained by the fact that, for the freezing of aqueous solutions, all investigators have used as one of the electrodes the metal bottom of the container in which the freezing was produced. Since the soil froze from the bottom, the beginning of freezing coincided with the moment of the formation of ice on one of the electrodes — the bottom of the container. In our experiments the electrodes were at a depth of 1-2 cm from the ends of the sample. Therefore the freezing front reached the upper electrode at a certain time after the beginning of crystallization, thanks to which a minimum value was produced in the curve of potential difference vs time.

For the low value of the potential difference in freezing solutions we give two explanations. First, it could be caused by the amount of mineralization of the solution in the pores themselves, and this mineralization could differ significantly from the value causing a maximal value of the potential. Secondly, it could be caused by the structure of the ice which, in contrast with the ice in a solution, does not form dense uninterrupted frozen grains but consists of separate crystals, confined between the mineral grains and having random orientation. The latter disturbs the uniformity of the electromagnetic field at the freezing boundary.

In clay soils, besides contact potentials that give rise to polarization of the interface of the solid and liquid phases, there can also be gradients of interfacial electrical potential and streaming potentials. Experimentally a certain electrical potential difference makes its appearance as a result of the simultaneous action of these potentials.

An understanding of the gradient of an interfacial electrical potential was proposed by I.A. Tyutyunov (1961, 1963). The potential difference that can be formed at the boundary of the phases he names the "interfacial potential." During equilibrium of the included phases the electrical potentials at the boundary between the phases balance themselves out. A gradient of interphase potential appears as a result of exchange-adsorption processes at the surface of the mineral skeleton of the stock.

These exchange-adsorption processes begin during the freezing of soils as a result of the change in the surface energy of the particles and the change of the concentration and chemical composition of the solution in the pores. We shall now examine which conditions give rise to exchange-adsorption processes.

The unit surface free energy of the particles increases as the temperature drops, since the entropy of the surface is thereby reduced (Tyutyunov and Nersesova 1963):

$$\sigma = U_s - TS, \tag{2}$$

where σ = the unit surface free energy

U_s = the total surface energy

T = the absolute temperature

S = the entropy.

Change in the surface energy occurs as a result of a change in the surface density of the adsorbed components during their transfer from the solution to the surface of the mineral skeleton. The latter exchange some of their chemical potential, expending part of their own free energy in the bond with the surface of the particle. The relation between the magnitude of the surface energy and the excess density of the adsorbed components is expressed by Gibbs' fundamental equation (Tyutyunov and Nersesova 1963):

$$\frac{d\sigma}{d\mu} = -\Gamma, \tag{3}$$

where μ is the chemical potential of the component and Γ is the density excess of the component.

If the component with chemical potential μ is an ion, bearing a charge α_n, then in being transferred to the surface of the mineral particle, this ion will change the magnitude of the interphase surface potential by a certain value dV:

$$d\mu = \alpha_n \, dV. \tag{4}$$

From eq 3 and 4 we obtain

$$d\sigma = -\Gamma\alpha_n \, dV, \tag{5}$$

or

$$-\frac{d\sigma}{dV} = \Gamma\alpha_n = E \tag{6}$$

where E is the electrical capacitance per unit area at constant potential.

This equation can be written in the following form:

$$dV = -\frac{d\sigma}{E}. \tag{7}$$

If we assume that in a certain interval ΔV the capacitance changes negligibly, then by integrating eq 7 we obtain

$$V = V_o - \sigma/E. \tag{8}$$

Since in soils the surface of the particles is charged negatively with respect to the pore solution, the magnitude V_o has a negative value. Therefore with increasing σ the negative potential of the surface will increase. As σ increases with a reduction of temperature, the interphase potential V likewise will increase with a reduction of temperature. At the freezing front, where the temperature is 0°C, V will be greater (in absolute value) than in the unfrozen zone.

Thus a gradient of electrical potential arises whose magnitude is

$$\eta = dV/d\ell, \qquad (9)$$

where η is the potential gradient and ℓ the distance over which the exchange-adsorption processes take place.

Thanks to this gradient in the unfrozen part of the soil there appears an electromagnetic field that, in relation to the film of water, has an electromotive force directed toward the side of the freezing front. Under the influence of this force, the film of water is shifted on the surface of the stock, and the thickness of the electrical double layer at the freezing front increases.

The gradient of interphase potential at the surface of the mineral skeleton of the stock disappears at the beginning of crystallization.

Ice is formed at the place where the interphase potential of the surface, and consequently the thickness of the aqueous film, is small. After the formation of ice and of a freezing front, a gradient of interphase potential in the unfrozen portion of the system preserves its own original polarity and causes movement of moisture toward the freezing front. As a result of the interphase potential gradient, the region of unfrozen soil situated directly ahead of the freezing front always has a negative charge. Thus the distribution of electrical charges in the unfrozen portion of the sample is produced in the first place by the interphase potential gradient.

The formation of the charge in the frozen portion of the system relative to the unfrozen region arises in the following manner. The charge at the surface of the growing crystal is influenced by the surface charge of the mineral skeleton of the stock. This influence is made possible through the film of water situated between the ice and the mineral part. The thinner the film, the more significant is the influence of the mineral skeleton.

The charge at the surface of the ice relative to the charge of the mineral skeleton is equal to the drop of the electrical potential at the film of water confined between the surface of the particle and the crystal of ice. If the surface of the mineral skeleton is charged negatively, the surface of the ice has a positive charge relative to the skeleton of the stock. These changes become smaller as the film of water between them becomes thinner. If there is little or no migration of moisture during the freezing of the soil, the crystals of ice continue to grow as a consequence of crystallization of the combined portion of the water, and the thickness of the film is reduced. The influence of the mineral skeleton on the polarization of the ice surface increases. The magnitude of the positive charges at the surface of the ice (relative to the surface of the mineral skeleton) is reduced.

The charge of the surface of the ice can become negative relative to the unfrozen portion of the soil. In this case the frozen part of the sample is charged negatively with respect to the unfrozen part, and the change of electrical potential in the profile of the frozen sample rises monotonously. The differences of electrical potentials in the process of freezing yield curves of the first kind.

If moisture migrates strongly in a freezing sample, then the thickness of the film is invariably restored owing to the influx of new portions of water. The magnitude of the positive charge on the surface of the ice relative to the surface of the mineral skeleton increases. The frozen portion of the sample acquires a positive charge relative to the unfrozen portion. In this case a "potential well" is formed in front of the freezing front from the surplus of negative charges, and so the polarity of the gradient of interphase potential in the unfrozen portion of the soil is not changed. Measurement of the electrical potential difference yields curves of the second kind.

Thus the relative charge of the frozen and unfrozen portions is set up by the first layer of the polarized surface of the growing crystals of ice under the influence of the charge on the surface of the mineral skeleton of the stock and the compensating influence of the migration of water toward the freezing front. The compensation of the surplus surface charge of the migrating film of water can be regarded as a result of the appearance of streaming potentials with a polarity opposite to the polarity of the interphase potential gradient, giving rise to the migration of water. Therefore one can say that the distribution of electrical charges in freezing clay soils depends on the degree of polarization of the surface of the growing crystals of ice, the gradient of interphase potential, and the magnitude of the streaming potentials. The value of this last effect is always less than the value of the initial potentials, which give rise to the migration of water. Moreover these processes, which also give rise to contact potentials and Workman-Reynolds potentials, can also exert an influence on the polarization of the crystals of ice. But the role of those processes in samples of clay is reduced, since in them free (unbound) water, in contact with which the aforementioned processes arise, is practically absent.

One ought to note that, independently of the sign of the relative charge of the frozen and unfrozen portions of the system, the polarity of the electromagnetic field in the unfrozen portion of the samples remains one and the same and coincides with the direction of the migration of moisture toward the freezing front, since that polarity depended on the direction of the gradient of the interphase electrical potential.

Thus the electromotive force, which gives rise to the migration of moisture and the frost heave of soils, operates in both the first and the second case, although in the first case (when there is no migration of moisture) it can be even larger than in the second, since the potential gradient which occurs is not compensated by a streaming potential. The absence of migration in the first case is explained by the necessity of a set of conditions, such as necessary supplies of moisture, or a sufficient length of time during which the water is moved toward the freezing front. If the lengths of time are small and inadequate, the rate of freezing can exceed the rate of streaming of the moisture. In that case ice will not accumulate in the freezing region even in the presence of a large electromagnetic force.

In summary, curves of the first kind are obtained with low-moisture samples and rapid freezing. The migration of moisture is limited. With increased moisture and reduced speed of freezing, more favorable conditions for migration of moisture are set up, and therefore the distribution of electrical charges in the samples is modified; measurement of the electrical potential difference yields curves of the second kind.

Such transitions from curves of the first kind to curves of the second kind are observed in experiments with bentonite and kaolin (see Fig. 5 and 7). The same also occurs during measurement of the fineness of samples (see the results of experiments with natural bentonite and bentonite of the fraction <0.001 mm). In experiments with kaolin, the correlation of the value of the electrical potential difference, the migration of water, and frost heave is explained by the mechanism of the formation of a difference of potentials in freezing clay soils. Of smaller significance is the difference of electrical potentials establisned in loams in comparison with kaolin and bentonite, caused by the smaller specific surface of the mineral skeleton. On the other hand, in experiments on bentonite the specific surface of the mineral skeleton is very great, and all processes which give rise to the appearance of an electrical potential difference develop strongly. Although bentonite is recognized as a non-frost-heaving soil, all of the conditions typical for an electrical potential difference, even those linked with an insignificant migration of moisture, have been expressed in it very clearly.

CONCLUSIONS

1. The magnitude and dynamics of the electrical potential differences that arise in freezing soils vary under different conditions of freezing and depend on the type of soil, its fineness, its moisture content, and the rate of freezing.

2. In sandy soils, which freeze without noticeable redistribution of moisture, an electrical potential difference arises as a result of the appearance of contact potentials and Workman-Reynolds potentials at the phase boundary. In this process there is a distribution of electric charges over the profile of the freezing samples, which results in a potential barrier formed ahead of the freezing front. This barrier inhibits the flow of moisture toward the freezing front.

3. In freezing clay soils, the electrical potential difference arises as a result of the simultaneous action of several physico-chemical processes. The following play a principal role: the electrical interphase potential gradient that causes moisture migration, the polarization processes at the surface of the growing ice crystals, and the streaming potentials.

4. The dynamics of the electrical potential difference in freezing clay soils depends on the intensity of the migration process. If moisture migration is impeded, the electrical potential difference during freezing will change in the same way as in sandy samples (a curve of the first kind will result). If migration of moisture occurs strongly, the electrical potential difference varies differently (a curve of the second kind will result).

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