Electrical freezing potentials and the migration of moisture and ions in freezing soils

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In continuation of work previously reported on freezing potentials, this paper reports voltages measured at a constant freezing rate (interface advancing at 2.8×10^{-4} cm/s) and amounts of electric charge required to neutralize the displacement of charge produced by freezing, in sludges consisting of silica, kaolin, and bentonite. For the freezing potential, a model is proposed which takes into account the diffusion of cations in the unfrozen portion of the sample, the separation of ions at the freezing front, and the migration of moisture and ions towards the freezing front. Results calculated from this model are compared with experimental values of the potential. In connection with the measurements of electric charge, in the order of 1 to 100μ Coul., a model is discussed based on the electrical double layer which forms at the surface of a mineral surrounded by water. Further studies should aid understanding of water migration and corrosion in freezing soils.

Faisant suite aux travaux déjà signalés concernant les potentiels de gel, la présente étude signale les tensions mesurées pour des vitesses d'engel constantes (progression de l'interface à $2,8 \times 10^{-4}$ cm/s) et la charge nécessaire pour équilibrer le déplacement de charge produit par l'engel dans des boues composées de silice, de kaolin et de bentonite. On propose, pour le potentiel de gel, un modèle tenant compte de la diffusion de cations dans la partie non gelée de l'échantillon, de la séparation des ions au front de gel et de la migration de l'humidité et des ions vers le front de gel: les résultats calculés à l'aide de ce modèle sont comparés aux valeurs expérimentales du potentiel. On mesure la charge électrique en fonction de la couche électrique double qui se forme à la surface d'un minéral entouré d'eau. On soutient que la poursuite de ces recherches devrait permettre d'approfondir nos connaissances sur la migration de l'eau et la corrosion dans les sols soumis au gel.

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Introduction

Electrical voltages in freezing soil systems have been observed by several investigators. Jumikis (1958) reported measuring potentials of 40 to 120 mV during freezing in samples of glacial outwash soil. Korkina (1965) studied the effect in kaolin and gumbrine (a montmorillic clay) in the course of a study of freezing potentials in ionic solutions. The present investigators (Hanley and Rao 1980; Rao and Hanley 1980) have described their studies conducted with Regina clay, which is a natural clay predominantly bentonite–kaolinite, and their more recent studies[1] conducted with pure clay minerals kaolin and bentonite and their mixtures with silica.

Conclusions from the previous studies can be summarized as follows:

1. Freezing potentials arise principally because at the freezing front cations are preferentially rejected from the frozen region into the unfrozen portion. The unfrozen portion, however, includes the unfrozen water within the frozen region behind the freezing front, and so an electrometer sees the frozen region as positive with respect to the unfrozen region of the sample.

2. Both the freezing potentials and the migration of moisture are dependent on the ions present in the wet soil. As the soil freezes, moisture migrates toward the freezing front along with dissolved ions.

3. The magnitude of the freezing potential is further enhanced by the presence of unfrozen water in the frozen region. The potential continues to increase in magnitude as long as there is a significant amount of unfrozen water content in the frozen region.

4. The presence of one dominant species of ion in the soil increases the amount of water which migrates toward the freezing front, but the effect of ionic content on the freezing potential depends both on the soil type and on the ionic species present and cannot be summed up in a simple statement.

5. Although the freezing potential must have some electro-osmotic effect on the migration of water, it is not yet possible to assess the magnitude of this effect. Development of a model for freezing potential will probably aid in estimating its electro-osmotic effect.

6. As cations gather preferentially just ahead of the freezing front and in the unfrozen channels of the

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[1]Hanley, T.O'D. and Rao, S.R. 1980. Freezing potential studies in wet clay systems. Paper presented Heat Transfer Div. Amer. Soc. Mech. Eng. Winter Ann. Meet. Nov. 16–21, Chicago.

frozen region of the sample, these sites serve as electron sinks. Electron sinks facilitate de-electronation and corrosion of any metallic objects present in the soil.

Purpose of the Present Work

Statements about the freezing potentials, moisture migration, and ionic concentrations will be more useful when they can be expressed in equations. In an effort to develop quantitative relationships which belong to suitable models for these effects, the authors have carried out two types of experiments. They have recorded freezing potentials which occur when the freezing front advances at a constant rate. They have also measured the charge required to neutralize the electrical effects of the freezing process by tests in which the sludge was frozen by cooling the cell on a thermo-electric cold plate as described in a previous paper (Hanley and Rao 1980). Models which result from these studies are reported in the present paper.

General Experimental Details

The bentonite, kaolin, and silica used in these experiments were of commercially available laboratory grade. The particles in the kaolin and bentonite were of colloidal dimensions, and the silica was − 240 mesh. The preparation of sludges of known composition and their treatment with a chosen electrolyte (KCl, $CaCl_2$, or $FeCl_3$) have been described in previous papers (Hanley and Rao 1980; Rao and Hanley 1980). In each case the resulting sludge was aged for three to four weeks.

After freezing was terminated, the concentration of ions at chosen positions in the sample was measured by atomic absorption, using the standard procedure of leaching with 0.1 N hydrochloric acid.

The cell used for all of these experiments (Hanley and Rao 1980) was constructed of a hollow cylinder of acrylic plastic 75 mm high, 38 mm inside diameter, with its wall 13 mm thick. The base of the cell is a plate of stainless steel, which also serves as a lower electrode for voltage measurements, the upper electrode being the lower end of an insulated rod of stainless steel inserted into the sample from above. Four thermistors are inserted through the wall of the cell to measure the temperature of the sample at distances of 1, 2, 3, and 4 cm above the base, and a fifth thermistor is inserted down through the sample to measure the temperature of the soil at the bottom of the sample. A digital multimeter was used to measure the resistances of the thermistors. Voltages or currents at the electrodes were measured by an electrometer with

FET input and with its output connected to a digital multimeter and a chart recorder.

I. Freezing Potentials at Constant Growth Rates

Experimental Details

In order to achieve a constant rate of advance of the freezing front, the cell was suspended by a suitable length of piano wire which passed over a pulley and was attached to a constant speed motor with adjustable speed. By this arrangement the cell was lowered at constant speed into an alcohol bath maintained at − 14°C in a top-loading freezer. In the experiments reported below, the cell was lowered at a rate such that the temperatures at the thermistors indicated that the freezing interface advanced at a constant rate $R = 0.0028$ mm/s, and that the sample cooled at the rate of 0.074 deg/min.

For experiments at constant freezing rates it was found useful to measure moisture contents before and after freezing. The moisture content before freezing was known from measurements made when the sludge was prepared. After freezing had been terminated, the frozen and unfrozen portions of the samples were separated, and the portions were weighed. Then the portions were dried in an oven and weighed again to find the weight of water which they had contained after freezing. In one series of tests, freezing was allowed to proceed for one, two, four, and six minutes after the first formation of a freezing front, and in each case the average moisture content in the frozen and unfrozen portions was ascertained as described above.

Theory

Although a satisfactory model for the freezing potentials has not yet been achieved, the following is proposed as a first approximation for constant freezing rates.

As soon as freezing has begun at the base of the sample, the rate of change of the concentration C of cations in a thin layer of frozen sludge near the freezing front is controlled by three factors, namely, the diffusion of the cations forward ahead of the interface, the advance of the interface at rate R with its resulting rejection of dissolved ions, and the migration of ions toward the freezing front along with migrating moisture. As a result an equation can be written as follows:

$$[1] \quad D\frac{\partial^2 C}{\partial x^2} + R\frac{\partial C}{\partial x} - \frac{M}{\rho A}\frac{\partial C}{\partial x} = \frac{\partial C}{\partial t}.$$

In this equation, D is the coefficient of diffusion for cations in the liquid sludge, x is distance from the

base of the cell, R is the rate of advance of the interface, and t is time measured from the end of the rapid drop in potential which accompanies the initial formation of the freezing front. With M representing the mass of moisture migrating per unit time toward the freezing point, ρ the density of water, and A the cross-sectional area of the freezing cell, the quantity $M/\rho A$ can be considered as the rate of change of a thickness of the sludge sample which contains one gram of water. This third term in equation 1 is preceded by a negative sign because the migration of moisture toward the interface depletes the moisture content in the remainder of the unfrozen sludge.

The potential difference ΔV which is measured by the voltmeter is the difference between the potential of the upper electrode in contact with the liquid sludge and the cell base below the freezing front. As the freezing front moves forward, some cations are rejected into the unfrozen region, but some cations remain in the unfrozen water of the frozen region, constituting a path of relatively low resistance between the freezing interface and the base of the cell. Since the electrometer draws negligible current, there is negligible drop in potential between the interface and the base of the cell. In the region ahead of the freezing front, the cation concentration decreases rapidly to the value of the cationic concentration in the bulk of the unfrozen sludge. As a result the observed voltage can be expressed by the equation

[2] $\Delta V = V_\ell - V_s$

where V_ℓ is the potential in the bulk of the liquid sludge and at the upper electrode, and V_s is the potential in the frozen solid, both just behind the interface and at the base of the cell.

The electrical potential at a given point is directly proportional to the charge and hence to the ionic concentration at that point. Thus, the concentration C in equation 1 can be replaced by the product of the voltage and a proportionality constant which can be divided out of the equation, leaving

[3] $D \dfrac{\partial^2 Vs}{\partial x^2} + R \dfrac{\partial Vs}{\partial x} - \dfrac{M}{\rho A} \dfrac{\partial Vs}{\partial x} = \dfrac{\partial Vs}{\partial t}$.

With the exception of the third term, representing moisture migration in the sludge, equation 3 is similar to the equation used by Gross (1968) to describe solute redistribution while an aqueous solution is frozen unidirectionally. Following Gross, a solution can be used that was developed for suitable boundary conditions by Pohl (1954); with the added term for moisture migration, the solution may be expressed as follows:

[4] $V = k + (1 - k)\{ 1 - \exp[-B(R - NM)x]\}$;

here $V = V_s(x)/V_\ell$, k is the coefficient of cation distribution, B is $(1 - k)k/D$, and $N = 1/\rho A$.

For two values of the potential, V_1 and V_2, measured when the freezing front is at positions x_1 and x_2, equation 4 yields the difference

[5] $V_1 - V_2 = (1 - k) \times$
$\{ \exp[-B(R\text{-}NM)x_2] - \exp[-B(R\text{-}NM)x_1] \}$.

From equation 2, $V_1 = (V_\ell - \Delta V_1)/V_\ell$ and $V_2 = (V_\ell - \Delta V_2)/V_\ell$; moreover when R is constant (constant freezing rate), x can be replaced by $x = Rt$. This equation then relates two measured potential differences at two times, t_1 and t_2, thus:

[6] $\Delta V_2 = \Delta V_1 + V_\ell (1 - k) \times$
$\{\exp[-BR(R\text{-}NM)t_2] - \exp[-BR(R\text{-}NM)t_1]\}$.

During the initial formation of the freezing front the upper electrode changes rapidly to a negative potential with respect to the base of the cell; it reaches a minimum potential and then begins to rise slowly. With $t = 0$ at the time when the voltage of the upper electrode reaches its minimum value, equation 6 applies to the time interval during which the voltage is rising during the four to five minutes following the formation of the freezing front. Experimentally the authors found that it is during this time that most of the moisture migration in the sample occurs. As moisture migration dies away, the potential begins to decrease once again; for this later portion of the voltage curve the migration factor M in equation 6 vanishes, and the equation becomes reduced to

[7] $\Delta V_2 = \Delta V_1 + V_\ell (1 - k) \times$
$\{\exp[-BR^2t_2] - \exp[-BR^2t_1]\}$.

Results and Discussion

For experiments performed at a constant growth rate $R = 2.8 \times 10^{-4}$ cm/s, equations 6 and 7 were examined using $N = 1/(\rho A) = 8.817 \times 10^{-2}$ cm/g and $D = 5.86 \times 10^{-5}$ cm²/s, the diffusion coefficient for H^+ ions. V_ℓ, the potential in the liquid sludge far from the freezing front, was measured by a standard Ag–AgCl electrode as described in a previous paper (Rao and Hanley 1980). The value of the distribution coefficient k for H^+ ions was determined by recording the pH of the sludge at a layer just ahead of the interface and at a layer just below the interface. The rate of moisture migration M, measured experimentally as described above under the heading "experimental details", was found to be constant for silica during the first eight minutes after the measured voltage began to rise, but varied with time for kaolin and bentonite. Values for k, V_ℓ, the initial voltage ΔV_1 at time $t_1 = 0$, the time t_m when the measured voltage attained its maximum value after the formation of the

interface, and values or approximate functions for M are shown in Table 1.

The dependence of M on time is troublesome, raising questions about the validity of equation 6. However, values were substituted into the equations and are displayed in Figure 1 for comparison with the measured values of voltage. Equation 6 was used up to the time t_m, and thereafter equation 7 was used. The calculated values correspond reasonably well with the measured values for all three types of sludge, and this correspondence seems to indicate that the model from which equations 6 and 7 were derived is acceptable as a first approximation for freezing at a constant rate.

The model may also be applicable to experiments done by freezing on a cold plate, in which the freezing rate decreases with time from an initial rate of advance which is usually quite fast. In that case the factor $(R - NM)$ of equation 4 is positive, whereas in results at constant freezing rate reported above, $(R - NM)$ was negative. This fits with the fact that, in cold plate experiments such as those reported earlier (see Footnote 1), the voltage continued to decrease after its initial fast drop.

TABLE 1. Values for quantities used in equations 6 and 7

		Silica	Kaolin	Bentonite
k		1.175	1.349	1.318
V_ℓ	(volt)	0.200	0.022	0.025
ΔV_1	(volt)	0.016	0.013	0.051
t_m	(minutes)	8	6	4
M	(g/s)	0.010	$0.0537\,e^{-0.186t}$	$0.0603\,e^{-0.371t}$

II. Charge Measurements

Experimental Details

For experiments designed to measure the charge required to neutralize the electrical effects in the sample as it freezes, the cell containing the soil sample was placed on a thermoelectric plate precooled to $-15°C$, and readings were recorded until the sample had frozen up to a point above the upper electrode. Current was measured by a feedback-type picoammeter configuration which incorporated a bucking voltage adjusted so that initially (at room temperature) the output of the picoammeter was zero. As the sample was cooled, the output of the picoammeter was recorded by the chart recorder, and subsequently the charge transfer was calculated by integrating the current over a suitable time interval, using the trapezoidal rule.

Theory

As a freezing front develops and advances in the sample of clay sludge, water-borne ions migrate toward the frozen zone. This gives rise to an electrical double layer with positive charge in the frozen region opposed by the diffuse layer of anions in the liquid sludge. The configuration can be represented by a parallel plate capacitor. A reasonably similar model for mineral systems has been used by de Bruyn and Agar (1962) for the electrical double layer at a surface of clay mineral surrounded by water. Adapting their model to the situation found near a freezing front, we can interpret their Gouy-Chapman equation 19 as follows:

$$[8] \qquad Q = A(2\,\varepsilon\,kT)^{1/2}\,n_o^{1/2}\sinh\,(z\,e_o\,V/2kT),$$

where Q represents the total charge transfer during freezing, A is the cross-sectional area of the cell, ε is the dielectric constant of the medium, k is Boltzmann's constant, T is the Kelvin temperature, n_o is the concentration (ions per cm^3) of cations of valence z far from the freezing interface, e_o is the electronic charge, and V is the observed freezing potential.

Results and Discussion

For several combinations of soil material and cationic content, Table 2 compares voltages measured in freezing potential experiments with charge transfer both as measured and as calculated from equation 1. Two values of freezing potential are shown. As was described earlier (see Footnote 1), for some sludges the rapid drop in potential observed immediately after freezing began was followed by a further, slower decrease in potential; these potential differences are referred to as the *fast drop* and the *total drop* respectively (see Table 2). Both of these values were used for calculating the charge Q.

Table 2 shows good agreement between the experimental values of charge and the values calculated from the fast drop in potential. Good agreement for twelve different varieties of sludge leads the authors to infer that the electrical double layer model described for the interface between a mineral and water also holds good for frozen clay systems. It should be noted that the period of fast potential drop is the stage during which the surface charge is created. As they suggested (see Footnote 1), a further drop in the electrical potential which is observed in certain cases is caused by the slow diffusion of cations away from the freezing front in the frozen region. This migration does not alter the surface charge which is continually being built up at the ice–water interface. This indirectly supports the authors' view that the continued drop in electrical potential observed with certain systems is due to the presence of a significant amount of unfrozen water in the frozen zone.

TABLE 2. Measured freezing potentials and experimental and calculated values of electrical charge

Clay system	Ion	Freezing potential (mV)		Charge (microCoulombs)		
		Initial "Fast drop" (A)	Total drop (B)	Experimental	Calculated	
					from (A)	from (B)
Kaolin	K$^+$	36.7	76.1	1.98	2.16	6.31
Kaolin + SiO$_2$	K$^+$	3.1	90.2	3.04	3.96	184.13
Bentonite	K$^+$	11.2	39.8	0.27	0.22	0.85
Bentonite + SiO$_2$	K$^+$	11.3	17.8	0.32	0.33	0.52
Kaolin	Ca^{++}	16.3	53.5	0.83	0.71	4.15
Kaolin + SiO$_2$	Ca^{++}	28.5	113.0	0.54	0.50	14.92
Bentonite	Ca^{++}	47.3	73.1	1.71	1.93	5.63
Bentonite + SiO$_2$	Ca^{++}	9.4	150.6	0.30	0.34	159.72
Kaolin	Fe^{+++}	9.2	20.8	0.50	0.49	1.34
Kaolin + SiO$_2$	Fe^{+++}	8.3	8.3	1.54	1.14	1.14
Bentonite	Fe^{+++}	11.3	11.3	2.60	3.18	3.18
Bentonite + SiO$_2$	Fe^{+++}	13.4	13.4	2.45	2.52	2.52

Implications for Corrosion

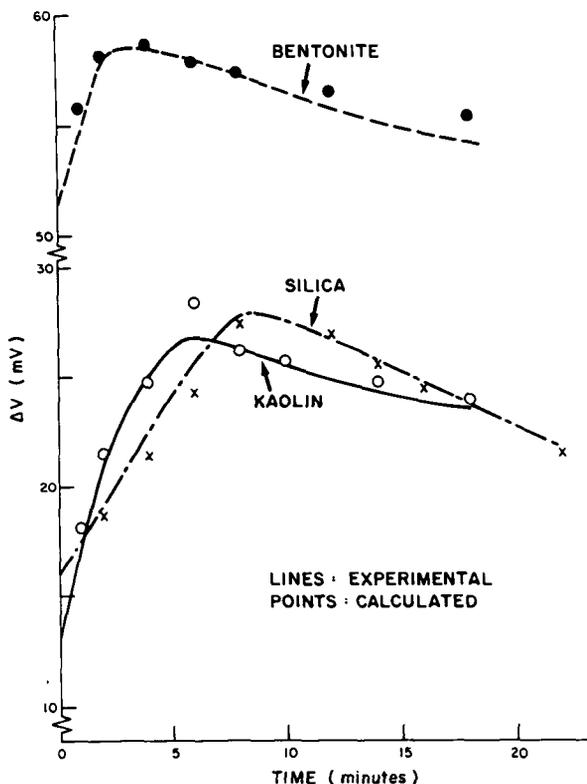It is now clear that, at least for the types of soils studied up to the present, the frozen zone is electrically positive with respect to the unfrozen sludge. The frozen portion of the soil would thus serve as an electron sink, facilitating the de-electronation of any metallic object placed in the soil. This must affect the corrosion of metallic objects buried underground when the wet soil on the top freezes in winter. It is well known that cathodic protection is used, for example, along buried portions of the hot-oil Alyeska pipeline. The situation is somewhat different with buried gas pipelines carrying chilled gas. In this case the cold pipeline freezes the soil around it, and any lesions which might occur in the pipeline wrapping will leave the line in contact with an electron sink. This link with corrosion is being kept in mind as studies of the freezing potential effect continue.
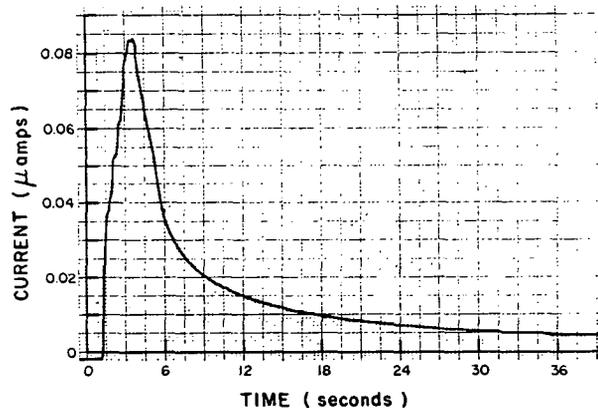

FIGURE 1. Measured voltage compared to calculated values (see text).

FIGURE 2. Portion of the chart record for current *versus* time, for a typical current run. Freezing began at the time when current began to rise.

Conclusions

In this paper the authors proposed a model for the electrical effects which accompany freezing in clay sludges, a model based on the migration of water and of ions, and on an electrical double layer at the freezing interface. It appears likely that the study of these effects will contribute to the understanding of moisture migration and of corrosion in freezing soils.

Acknowledgements

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