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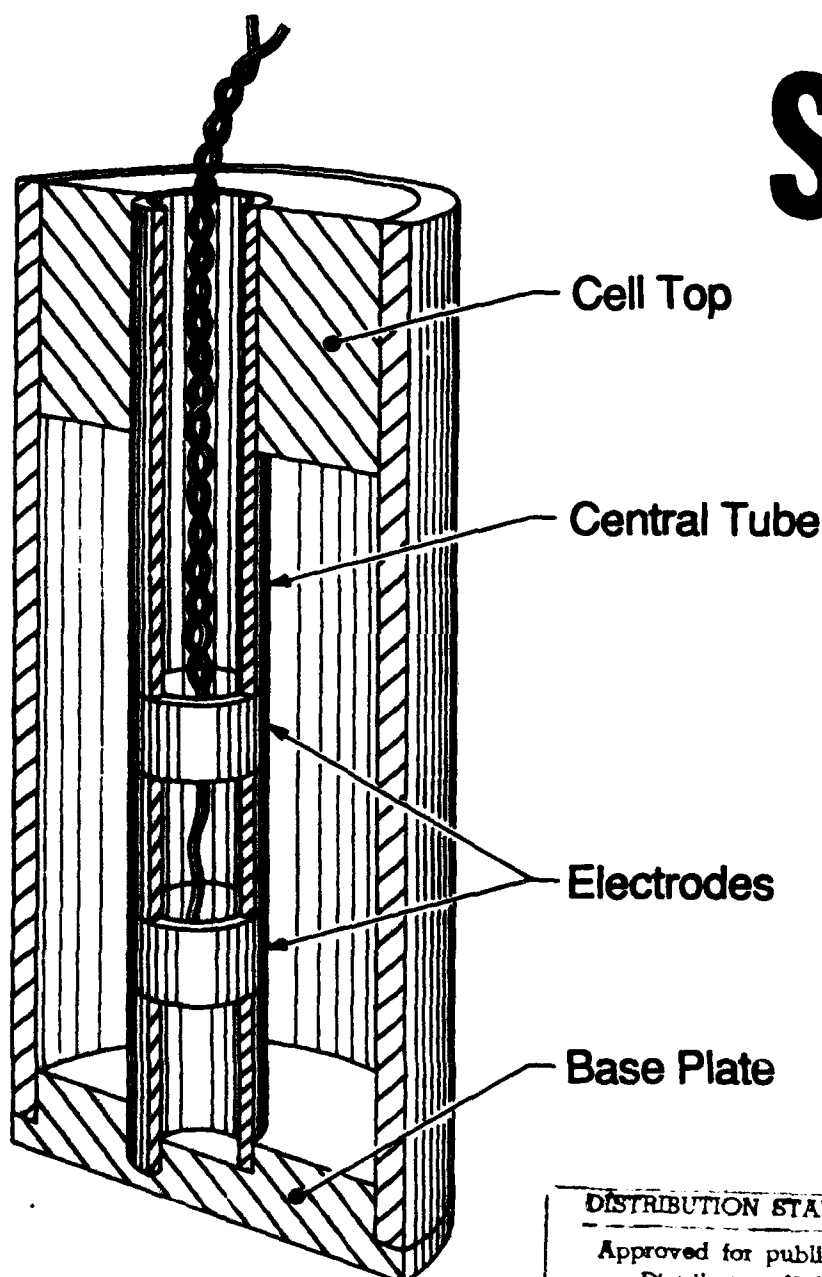
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Measurement and interpretation of electrical freezing potential of soils

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Cover: Test cell used in this study.

CRREL Report 88-10

August 1988



Measurement and interpretation of electrical freezing potential of soils

Dennis J. Kelsh and Susan Taylor

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OFFICE OF THE CHIEF OF ENGINEERS

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PREFACE

This report was prepared by Dennis J. Kelsh, Professor of Chemistry, Gonzaga University, Spokane, Washington, and Susan Taylor, Geologist, Geochemical Sciences Branch, Research Division, U.S. Army Cold Regions Research and Engineering Laboratory. Funding was provided by DA Project 4A161102AT24, *Research in Snow, Ice and Frozen Ground*; Task SS, *Combat Service Support*; Work Unit 020, *Prediction of Chemical Species Transport in Snow and Frozen Ground*; and by the In-house Laboratory Independent Research Program.

The authors thank James Morse, Charles Zue and Richard Guyer for their speedy and insightful assistance in setting up, repairing and programming electrical instruments. Thanks also go to Edward Perkins, who drafted the illustrations, to Donna Harp for typing the manuscript and to Mark Hardenberg for editing the manuscript. This project was conceived by the late Rev. Thomas Hanley, S.J., who is thanked along with Ronald Atkins and Dr. Iskandar Iskandar for initiating the project and obtaining the funds for its realization. This report was technically reviewed by Dr. Kevin O'Neill and Dr. Kazuhiko Itagaki of CRREL who are thanked for the time they took in reviewing the manuscript and for many helpful suggestions.

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Measurement and Interpretation of Electrical Freezing Potential of Soils

DENNIS J. KELSH AND SUSAN TAYLOR

INTRODUCTION

Freezing of moist soil is accompanied by the generation of a transient electrical potential between the frozen and unfrozen regions. While this "freezing potential" (*FP*) has been confirmed by several laboratory investigations, the magnitude, polarity and duration of the potential are dependent on many variables, including the rate of freezing, the nature of the soil, the chemical composition of pore water, and the experimental design chosen to measure the effect. Quantitative disagreements are common, not only between investigators, but within a single study (e.g. Parameswaran, in prep.).

The effect may be of sufficient magnitude and duration to influence such processes as water migration to the freezing front, corrosion of metal objects buried in freezing or thawing ground, etc. Our investigation was undertaken to evaluate the current state of knowledge of *FP*. We critically reviewed the measurements and theories reported in the open literature and conducted laboratory tests to identify the major parameters affecting *FP*. Recommendations are made based on the results.

BACKGROUND

Aqueous solutions

An abrupt change in electrical potential develops between electrodes suspended in dilute aqueous electrolyte solutions when an advancing freezing front engulfs one of the electrodes. This potential, first reported by Workman and Reynolds (1950) and later studied by others (Korkina 1965, LeFebvre 1967, Drost-Hansen 1970, Murphy 1970, Gross 1975), can be of considerable magnitude (hundreds of volts) and either of positive or negative polarity relative to the unfrozen electrode. The effect is generally attributed to the degree to which various ions are excluded from the ice structure, and is sensitive to the nature and concentra-

tions of dissolved ions and gases in the water (Gross 1967, 1971, 1972, 1973; Gross et al. 1975a and b). The freezing rate, temperature gradient and the presence of species that can discharge or neutralize the electrical double layer at the ice/water interface are also important parameters. The phenomenon has been of considerable interest because of its relevance to electrical storms in the atmosphere.

The reproducibility of laboratory results has been poor, and even the polarity at the interface has been disputed by investigators who were presumably working on identical systems. Gross and his colleagues (1975, 1977) have demonstrated the sensitivity of the results to trace amounts of ammonia (NH_3) or carbon dioxide (CO_2), or both, in the laboratory air. Their results, obtained under controlled atmospheric conditions and at a constant rate of freezing, would appear to be among the most reliable of those reported. Of considerable interest to theoreticians is Gross and McKee's (1972) finding that carefully purified distilled water exhibits no freezing potential. This is in sharp contrast to the substantial potentials observed by others. A zero freezing potential for pure water would seem to invalidate theories (e.g., Murphy 1970) that suggest that long dendritic chains of oriented water dipoles at the ice/water interface are major contributors to the freezing potential.

Moist soils

When water-saturated or partially saturated soils are frozen, electrical potentials are observed, but their magnitudes are considerably smaller than those for aqueous solutions. Gravels exhibit potentials comparable to those observed with dilute electrolyte solutions, but sands and clays produce potentials of less than 1 V. The polarity of the frozen soil may be either positive or negative, depending on such things as the soil type and the contacting electrolyte solutions, freezing rate, etc. Widely variant results are again commonplace and

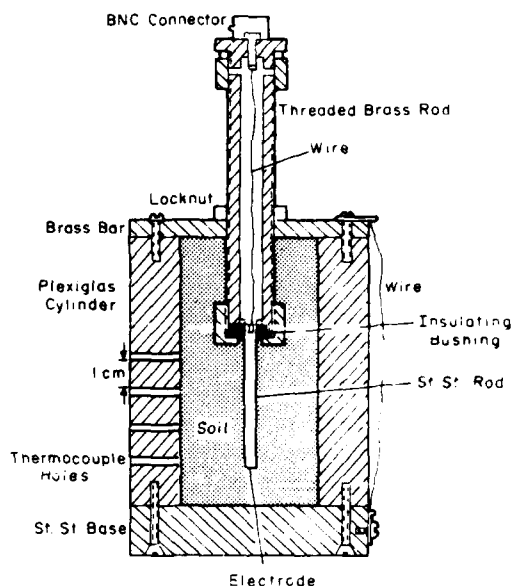


Figure 1. Cross section of the cell used for studying freezing potentials in soils by Hanley and Rao (1980).

researchers did not consider the effects of atmospheric contaminants (although the ready availability of ions from the clay would seemingly make atmospheric contamination a negligible problem). Freezing rates are not always kept constant and their effects depend on the system being studied. For example, Yarkin (1974) reports that large freezing potentials for soils require very slow freezing rates, whereas Parameswaran (in prep.) states that the highest freezing potentials for "pure water" are obtained with fast freezing.

Designing a cell that is capable of giving unambiguous measurements of freezing potential (FP)

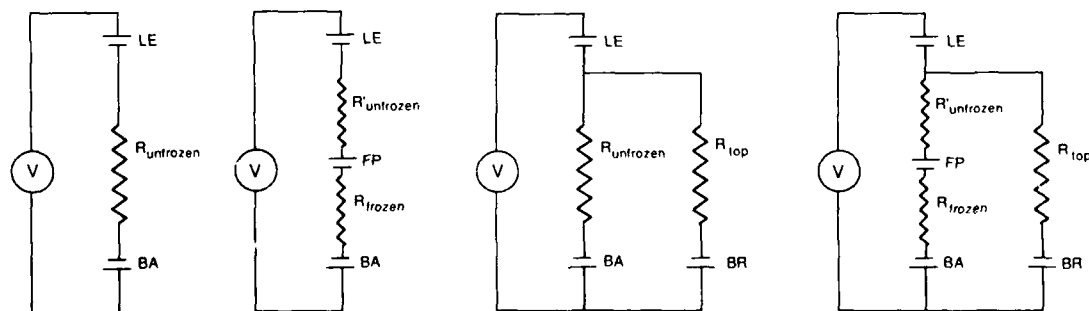
is not a trivial problem. Analysis of the design used by Hanley and Rao (1980) reveals some of the difficulties.

The soil-filled cell shown schematically in Figure 1 was frozen from the base upwards, and the electrical potential (V) between the stainless steel base (BA) and their "lower electrode" (LE) was monitored over time. Changes in this potential that occurred as the soil froze were ascribed to freezing potential (FP). The electrical circuit corresponding to their interpretation is shown in Figure 2a.

In addition to the complications encountered in nearly all cell designs, such as a volume expansion accompanying freezing, ice lens formation, etc., one feature of the Hanley and Rao cell is open to criticism. The wire connecting the brass superstructure (BR) to the base (BA) introduces two alterations to the equivalent circuit. These alterations are shown in Figure 2b.

1. A contact potential difference will exist between the brass (BR) and stainless steel (BA) electrodes by virtue of their different compositions. This potential is shown on the diagram as originating at the brass electrode. If this potential remains constant for the duration of the test, it will not affect the FP because FP is the *change* in potential (V) that accompanies soil freezing. However, freezing the base electrode BA should alter the contact potential between it and the brass electrode BR , and thereby contribute to the change in V . Thus, the total change in V could not be attributed to FP alone.

2. If soil makes electrical contact with the brass superstructure BR , an alternative path for current flow between LE and BA is created. The significance of this path depends on the magnitude of the soil resistance R_{top} , between LE and BR . Be-



a. Equivalent circuit inferred by Hanley and Rao.

b. Equivalent circuit including alternative current path through the brass superstructure (BR).

Figure 2. Circuit used by Hanley and Rao (1980).

fore any of the soil freezes, R_{top} is probably much larger than $R_{unfrozen}$ owing to the greater distance between *LE* and *BR* than between *LE* and *BA*. However, when soil begins freezing, R_{frozen} exceeds $R_{unfrozen}$, and R_{top} may become comparable in magnitude to the sum of R_{frozen} and $R_{unfrozen}$. A relatively large current will then pass through R_{top} , thereby affecting the measured value of V . Again we see that the change in V cannot be fully attributable to a potential *FP* at the frozen/unfrozen soil boundary.

All experimenters face the problem of finding an electrometer of sufficiently high input impedance such that electrical potential can be measured without drawing a significant amount of current. If input impedance is ever comparable to or smaller than the cell resistance, the current flow through the measuring circuit will actually change the potential between the electrodes, thereby giving a false indication of the potential that existed between electrodes prior to switching on the electrometer.

We are aware of only one field study of freezing potentials (Parameswaran and MacKay 1983). Results are confusing and difficult to rationalize, e.g., a periodic variation of electrical potential with depth into the frozen soil, but a potential difference of some 200 to 400 mV is consistently observed across the freezing front.

MATERIALS AND METHODS

Two soil materials were used for our electrical potential measurements. We selected clean quartz sand because it did not heave during freezing and its grain size could be altered. A kaolinite clay purchased from Wards Scientific was the second material used. We chose kaolinite because it shows marked volume expansion and ice lens formation during freezing and has a low cation exchange capacity (Deer et al. 1966).

We prepared the sand-water mixtures by weighing the dry sand and adding variable amounts of deionized, filtered water (Millipore water system). The wet sand was well stirred using an aluminum spatula. The clay-water slurries were similarly prepared.

The experimental cell used for freezing the sand or clay was a Plexiglas cylinder (17 cm high, with 6.5-cm id and 7.0-cm od) fitted with a 1.5-cm-thick, o-ring sealed, Plexiglas base (see Fig. 3). A 4.5-cm-thick Plexiglas "piston" that could move up or down a central Plexiglas tube served as the

top. The central Plexiglas tube (1.2-cm od, 0.5-cm id) was fitted with copper bands mounted flush with the outside diameter of the tube. Leads were soldered onto the inner surface of the copper bands and the wires, which ran up the center of the tube, were connected to a BNC. An electrometer, built in the CRREL electronics shop, was used to measure the potential. A Texas Instruments TL 082 operational amplifier (input impedance = $10^{12}\Omega$) was the key component of the electrometer. The circuit diagram is shown in Figure 4. The output signal from the electrometer was continuously displayed on a Hewlett-Packard 7100B strip chart recorder and, every 10 minutes, on a Kaye Instruments Digistrip III, which gave a digital readout. Copper-constantan thermocouples taped to the outside of the test cell were connected directly to the Digistrip III. A TechTran 817 Data Cassette translated the Digistrip III signal to computer-readable data.

To obtain an insulated environment for freezing the test cylinders, a 40-cm-high Styrofoam box was constructed to totally enclose a 60- by 60-cm aluminum cold plate. The insulating box was constructed with 5-cm-thick Styrofoam sheets; sections were glued together using RTV silicon seal-

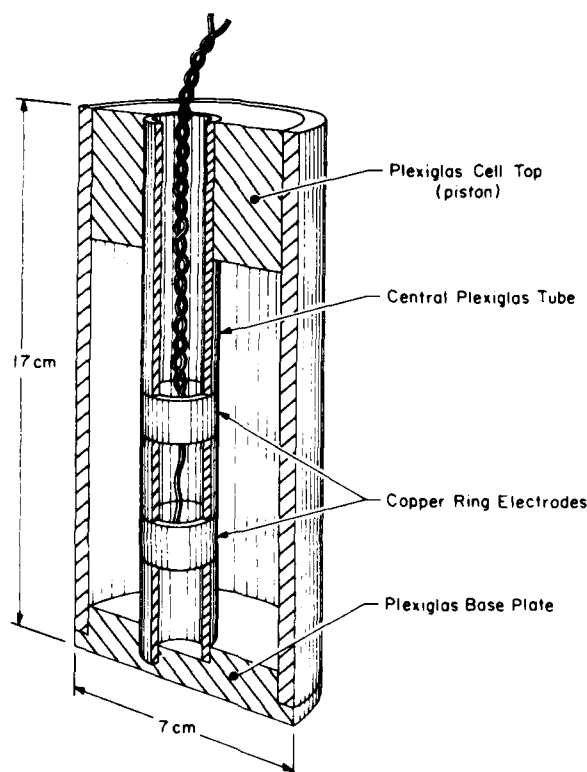
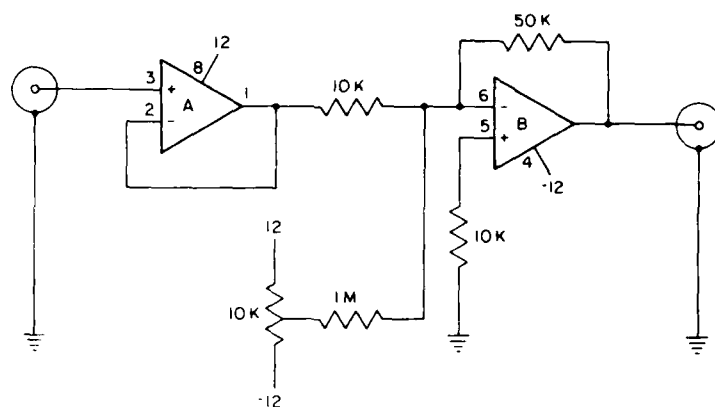
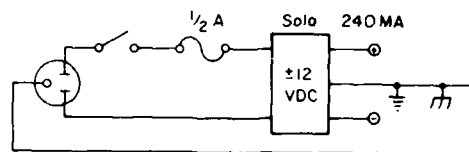


Figure 3. Experimental cell design used in this study.



a. Electrometer circuit.



b. Power supply circuit.

Figure 4. Circuits used in experimental cell.

ant and then taped. That portion of the cold plate surface not being used was covered with Styrofoam and the empty space remaining in the box was filled with Styrofoam packing material.

A NESLAB Endocal refrigerated circulating bath provided ethylene glycol at -30°C to the cold plate. This corresponded to a plate temperature of -15 to -20°C . At these temperatures the material in the cell completely froze in 1 to 2 days. The rate of freezing was not constant, being higher at the base of the cell, which was adjacent to the cooling plate, than at the top of the cell.

In addition to freezing the clay or sand, the effects of pressure on the electrical potential of unfrozen sand and clay were studied. The test cell was filled with material and placed on a California Bearing Ratio unit made by Soiltest of Evanston, Illinois. Pressure was applied to the soil when the piston top of the cylinder was forced against a proving ring. Only approximate pressures were obtained with this system as the proving ring was calibrated for higher pressures than those used. The potentials were measured with the same setup described previously.

EXPERIMENTAL FINDINGS

Our main result was finding that transient changes in electrical potential of about 100 mV

were produced when pressure was discontinuously increased on an unfrozen, undersaturated sand (15% H_2O by weight) or saturated sand (see Fig. 5). Smaller potentials, less than 50 mV, were produced in 60% kaolinite/40% water slurries. The increase in pressure produced closer packing of the soil particles, thereby increasing the soil-electrode contact. The magnitude and sign of the potential are thought to depend upon the extent of frictional movement of soil over an electrode surface. Although the pressure measurements were made using unfrozen samples, one process that accompanies the freezing of soil is a volumetric expansion (when water changes to ice) and a concomitant increase in pressure. By inference, these pressure increases may therefore be the cause of the transient freezing potentials.

We made most measurements of electrical freezing potential using 80-mesh (200- μm) quartz sand because neither the sign nor the magnitude of the potential were reproducible when kaolinite slurries were frozen. Freezing the distilled water contained in a saturated slurry of 80-mesh quartz sand produced freezing potentials that were all positive relative to the unfrozen electrode, but whose values were not reproducible (see Fig. 6). The freezing potentials obtained from experiments run using clay-sized quartz sand saturated with distilled water and 80-mesh sand saturated with tap water were negative relative to the unfrozen electrode

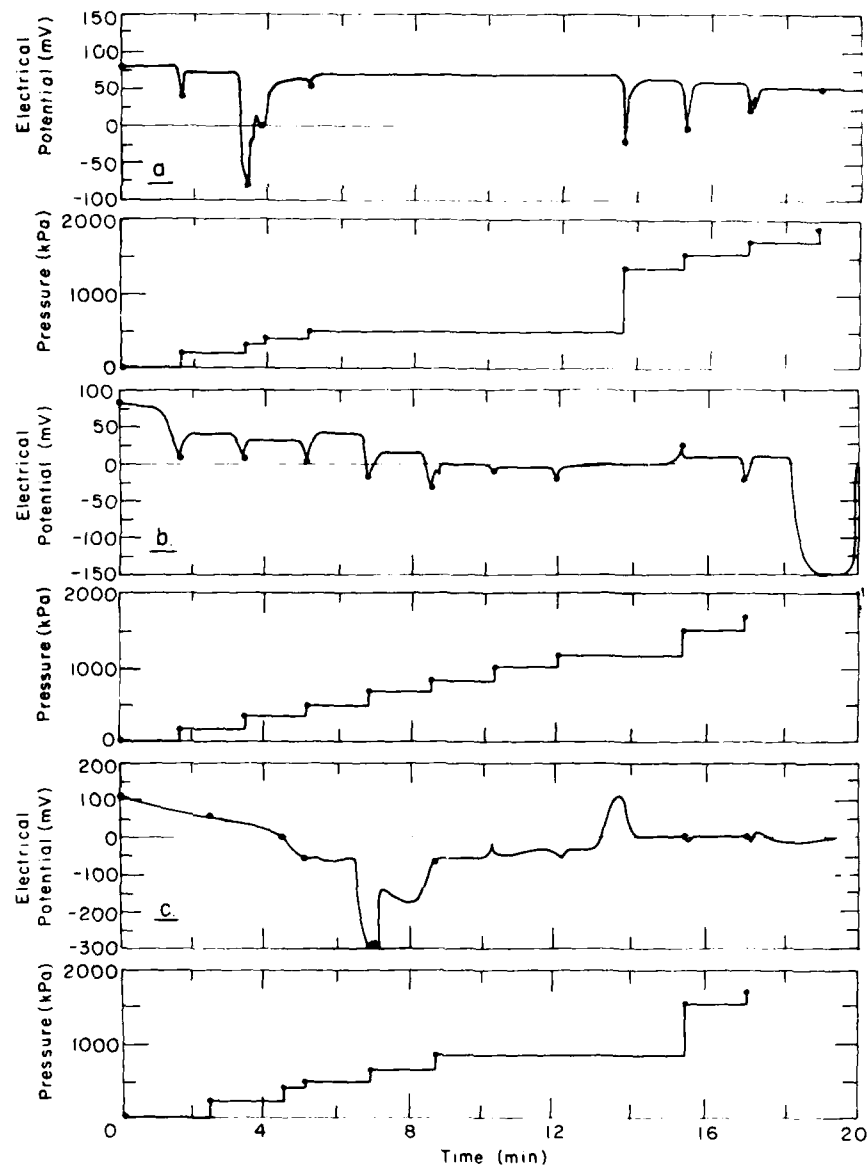


Figure 5. Electrical potential versus applied pressure for water-saturated quartz sand (a and b) and unsaturated quartz sand (c).

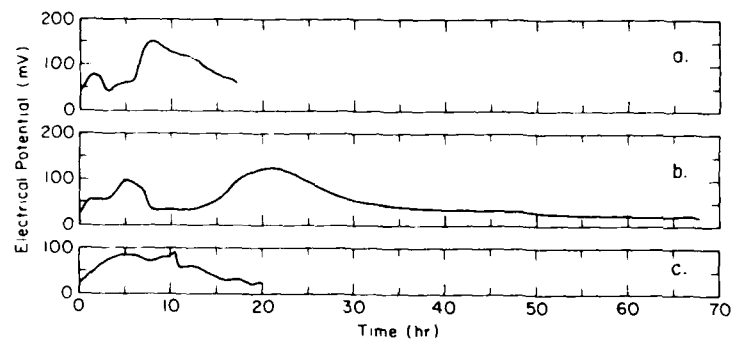


Figure 6. Freezing potential measured on 80-mesh quartz sand saturated with distilled water.

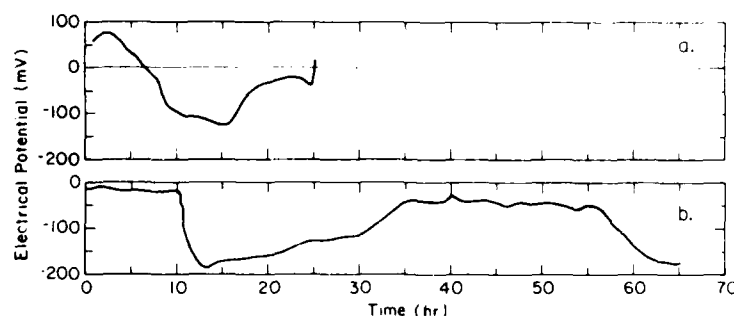


Figure 7. Freezing potential measured on clay-sized quartz sand (400 mesh) saturated with distilled water (a) and 80-mesh quartz sand saturated with tap water (b).

(Fig. 7). Time did not permit the systematic study of the effects of particle size on the magnitude and polarity of the potential. The excursions seen in the potential cannot usually be correlated to the freezing-in of the electrodes.

Every effort was made to maintain constant experimental conditions, i.e., degree of soil compaction, same cold plate temperature, etc., but identical conditions were not always achieved. For example, using an identical experimental setup, we found that one of the sand-filled cells took twice as long to freeze as all the others (see Fig. 6b). We think that a layer of ice between the cold plate and the cell was responsible for the slow rate of freezing of this particular cell.

Our work indicates that soils should be uniformly consolidated by applying external pressure to the cell contents before making freezing potential measurements. If a soil is not fully consolidated prior to freezing, erratic potential measure-

ments can arise by changes in soil-electrode contact, even when the electrodes are immovably fixed in position. Even after the soil is fully consolidated, voltage excursions can occur as pressure increases. It may therefore be impossible to separate this pressure-induced potential from other sources of freezing potential. Discussion of soil packing has been notably absent in papers devoted to freezing potential measurements.

EXPERIMENTAL PROBLEMS

Our original experimental design, which was based on Yarkin's (1973) design, proved unsatisfactory (Fig. 8a). The platinum electrodes deformed easily under differential settling of the clay and sand, and were severely deformed during frost heaving of the clay. Changes in the electrical potential of the same magnitude as reported from ex-

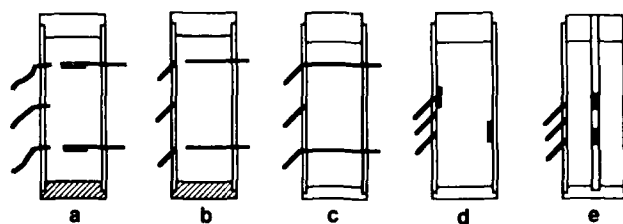


Figure 8. Modifications in cell design and problems experienced with each design.

- Platinum electrodes deformed; thermocouples could not be adequately insulated.
- Stainless steel electrodes would move; aluminum baseplate created stray electrical currents.
- Stainless steel electrodes subjected to bending.
- Copper electrodes detaching from side of cell.
- Electrodes have a significant thickness relative to the freezing front; soils probably froze radially as well as horizontally.

perimental results (100 mV) were associated with the movement of these electrodes. To minimize electrode deformation, the second group of experiments was run using 3-mm stainless steel rods as electrodes. Difficulties with movement of the rod electrodes necessitated supporting the rods from holes on opposite sides of the cylinder (Fig. 8c). During freezing, the stainless steel rod electrodes tended to split the soil plug, thereby reducing soil-electrode contact. To obtain better soil-electrode contact, 2-cm² sections of copper piping were glued to the inside of the Plexiglas cylinder and were soldered to two leads going to the electrometer (Fig. 8d). These electrodes were found to loosen during freezing. Our final design (described in the *Materials and Methods* section) enabled us to compact the sample (to ensure good soil-electrode contact) and keep the electrodes firmly in place (Fig. 8e).

Two characteristics of the final cell design make it less than perfect. First of all, the electrodes have a significant thickness vis-a-vis the freezing front and therefore do not give an instantaneous response when the advancing front first contacts the electrode. Secondly, the soils froze much more rapidly with this cell design than with the previous cells tried, apparently because the central tube acted as a heat sink. The freezing probably occurred radially outward from the central tube. To minimize this effect, the central Plexiglas tube should be constructed from some thermally insulating material with a low coefficient of thermal expansion. Epoxy-impregnated cardboard or wood might be satisfactory materials.

To obtain maximum heat conduction between cell contents and the freezing plate, a cylindrical plug of aluminum was originally chosen to serve as the base of the cell (see Fig. 8a and b). This plug was later replaced with a Plexiglas plug fitted with an o-ring seal because the aluminum surface in contact with the soil was visibly corroding during the experimental runs. This indicated that oxidation-reduction processes were occurring at one or both electrode probes, and these processes, if changed by freezing, would give rise to a difference in electrode potential, which could incorrectly be interpreted as a freezing potential.

Metal-to-metal contact between the cell base and the grounded freezing plate also introduced an unwanted ground loop into the measuring circuit, further compounding our difficulties. Good electrical grounding would presumably remove such problems, but we found it difficult to completely eliminate ground loops and other sources of potential difference from our electrical system.

ELECTRICAL POTENTIAL AND RELATED PHENOMENA

Is the freezing potential that is sensed by a pair of buried electrodes really a measure of the relative electrical environments of frozen vs unfrozen soil, or is it merely an artifact of the measuring process? When soil freezes, two things happen at the electrode/soil interface that can influence the measured potential.

1. Ions in solution are excluded from the ice phase, and in most cases, positive ions are excluded to a greater extent than negative ions. The effect on the electrode contacting the frozen soil is to make it sense a more positive potential in the remaining unfrozen water. The negatively charged solid ice would presumably counterbalance this effect. However, because electrical resistance is higher across the ice/electrode boundary than across the unfrozen water/electrode interface, the electrode senses a more positive potential than it did before freezing.

2. Water from the unfrozen region migrates to the freezing front because of the magnitude of the thermal gradient, and the concentration gradient in the unfrozen water. (Ion concentrations will be higher in liquid existing in the frozen soil because of the ion exclusion from ice during freezing.) Migration of water to the freezing zone will change the potential sensed by the electrode in the frozen soil (because ion concentrations in the newly arrived water will differ from those in the "old" unfrozen water in the frozen zone). This electro-kinetic effect would take place gradually rather than abruptly, and could account for much of the drift in electrical potential observed during the freezing process.

When the upper electrode is also frozen in soil, a second change in potential is reported (Yarkin 1974). Ion exclusion effects noted in point 1 above are now presumably the same for the two electrodes (although the amount of unfrozen water present will diminish with temperature, and therefore the two electrodes are not sensing identical environments so long as the lower electrode is at a lower temperature). Location of ice lenses and their continuous growth will determine whether electro-kinetic effects contribute as before. Potential drift will continue until the two electrodes both come to a steady-state condition.

We now return to our question regarding the significance of a potential measured between two electrodes. These electrodes are sensitive to the electrical resistance at the soil/electrode interface.

They respond more to the cation-rich liquid in both the frozen and unfrozen zones than to the anion-rich but more resistive solid phases of ice and soil. Measured potential differences therefore indicate the relative ion concentrations of the liquids in contact with the two respective electrodes. Such concentration differences are ordinarily associated with nonequilibrium conditions, and we might expect that there should be ion and solvent migration to equalize electrolyte concentrations throughout the liquid in the system. Such reasoning ignores the presence of excess negative ions in the solid particles. Just as it is possible for ion concentrations to equilibrate at different levels as one moves away from a charged surface (Gouy-Chapman diffuse double layer) or for ion concentrations to stabilize at different levels on two sides of a semi-permeable membrane (Donnan equilibrium), so also can ion concentrations differ in frozen and unfrozen soil. The electrical potential sensed by two electrodes will therefore not necessarily indicate a driving force for ion movement through soil when the electrodes are no longer there. Electrochemical reactions, hydraulic flow, or similar phenomena would be required to stimulate electrolyte movement.

Water migration

Movement of water through soil under the influence of an electric field is a well-known phenomenon (electro-osmosis); the effect has been used to dewater slurries of finely divided solids (Kelsh and Sprute 1986). The influence of freezing potential on water migration is not known; thermal gradients at a freezing front will, under most circumstances, constitute the dominant driving force for water's migration to the ice zone, and electro-osmosis will be very slow when the electrical potential is as small as a fraction of a volt. Water migration caused by pressure differences (reverse osmosis), and unknown solute concentration gradients between unfrozen water in the frozen zone and the unfrozen soil will also complicate the analysis of the extent of electro-osmosis. Significant transfer of water through frozen soil has been induced by an external electric field of 1 V/cm (Hoekstra and Chamberlain 1964), but freezing potentials may be too small to stimulate electro-osmosis in a freezing soil.

Corrosion

Hanley (1985) has suggested that the corrosivity of a sludge or soil should be affected by freezing, and has measured (by electrochemical inference)

up to twofold increases in corrosion rate in the unfrozen region when prepared clay slurries are frozen. Ion exclusion from the ice, and the consequent increase in ion concentration in the remaining frozen water, are presumably responsible. No correlations between freezing potentials and corrosivity increases were found, but further research was planned by Hanley to obtain more conclusive results.

We are of the opinion that freezing potential, a transient (nonequilibrium) phenomenon whose measurement is difficult to reproduce and which is influenced by so many difficult to control conditions (freezing rate, trace impurities, soil consolidation, etc.), is unlikely to be correlated with anything as simple as corrosivity inferred from potentiostat measurements. Freezing may indeed influence corrosion rates, not just by increasing ion concentrations in the unfrozen regions, but by creating nonhomogeneous surface boundaries between buried metal and soil, which lead to localized anodic and cathodic areas on the metal. The pitting corrosion that results from such heterogeneities is the most important source of metal failure. Such pitting would not be expected to correlate with "corrosivity" as measured by a potentiostat, much less with freezing potential.

CONCLUSION

In summary, experimental results indicate that freezing potential depends in complex ways on so many different variables that it is hard to sort out their individual effects. It therefore makes the interpretation of freezing potentials very problematical, and the use of freezing potential as a predictive variable for corrosivity, water migration, or other physical properties of freezing soils will be fraught with uncertainties. It is true that the freezing of soil will influence water migration, metal corrosion, etc., but we simply believe that freezing potential is not a useful measure of such effects.

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