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A NOTE ON ELECTRICAL FREEZING AND SHORTING POTENTIALS

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ABSTRACT

Electrical potentials developed by charge separation during freezing of water and dilute CaCl_2 solutions were studied in the laboratory, using gold-plated copper electrodes placed across the freezing boundary. A sudden increase in the potential occurs when the freezing front reaches an electrode. A shorting potential was observed at the electrodes when the freezing front advanced past the reference electrode. The magnitude of the freezing and shorting potentials is of the order of a few hundred millivolts. This technique can be used to detect and monitor the movement of freeze-thaw boundaries in water and moist soils.

[Key Words: Freezing, Potentials, Electrodes, Interface, Freeze-Thaw Boundary]

Introduction:

An electrical potential develops across a freezing interface in aqueous solutions and moist soils due to charge separation and preferential entrapment of ions in the two different phases (Workman and Reynolds 1950; Parameswaran and Mackay 1996). The magnitude of the potential depends on various factors including the rate of cooling and species and concentration of solute present in the solution or soil. Under normal rates of cooling experienced in nature, the freezing potentials measured are in the range of a few millivolts. Under fast cooling using very cold circulating baths, potentials of several volts

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have been measured (Workman and Reynolds, 1950; Gill and Alfrey, 1952). The wide range of values of freezing potentials observed in solutions by different authors under similar conditions, indicates that the measured potential depends on various factors such as the purity of the solution, the experimental set up, including the type of electrodes and wires used, the connection to the measuring/recording equipment, internal resistance of the recorder, and so forth. Pressure also has an effect on the development of potentials, especially in soils, where frost heaving is commonly observed (Kelsh and Taylor, 1988). The magnitude of the potentials measured by various authors has varied over three orders of magnitude, 100 mV to 230 V (Workman and Reynolds, 1950; Pruppacher, et al., 1968; Cobb and Gross, 1969; Murphy, 1970). In pure water, the values of the freezing potentials measured were between 200 mV and 120 V (Arabadzhi, 1948; Workman and Reynolds, 1950; Gill and Alfrey, 1952; Bayadina, 1960; Murphy, 1970; Korkina, 1975; Parameswaran, 1982).

Fortier et al. (1993), measured the electrical potential developed across a thawing boundary in the active layer of permafrost in Umiujaq in Nunavut, located on the east coast of Hudson Bay, in the Arctic regions of Quebec. They used a reference electrode located deep in the unfrozen ground and the potentials developed on each electrode above that were measured. The potentials measured were interpreted as a combination of freezing potentials, streaming potentials due to water migration and changes in the electrolyte concentration. They concluded that by monitoring these potential differences, changes in temperature, water content and migration and ionic distribution can be studied.

Outcalt and his co-workers (1989, 1990) carried out combined measurements of soil temperature and electric potential in the seasonally freezing top layer of a sandy loam soil at a site in the Botanical Garden in University of Michigan, Ann Arbor. They measured electric potentials of 300 to 700 mV and interpreted the data as the result of thermally induced ionic concentration in the soil. They suggested that secondary effects due to advective flow of water to the freezing front (streaming potential) could also give rise to electric potentials. They concluded that valuable information on the geotechnical conditions of freezing soils (the state and mobility of the soil water) can be gathered by combining thermal and electrical potential measurements.

Past measurements in the laboratory and in the field indicate that the potentials developed during freezing of water and soils containing ionic impurities in solution, are on the order of a few hundred millivolts (Parameswaran, et al., 1982, 1983, 1985, 1996; Burn et al., 1998). Field measurements near the western Arctic coast of Canada include those carried out in the lakes near Inuvik, pingos and at the bottom of a drained lake of the Tuktoyaktuk Peninsula area where permafrost was aggrading. The ionic impurities in these systems consisted mainly of cations: Ca^{++} , Mg^{++} , K^+ and Na^+ and the anion, Cl^- . For example, the drill hole water from Pingo 9 contained 230 – 260 ppm of Ca^{++} , 85-95 ppm Mg^{++} and about 250 ppm Cl^- , besides small amounts of K^+ and Na^+ . The water from the Inuvik lakes contained 16-30 ppm Ca^{++} , 5-8 ppm Mg^{++} , and less than 10 ppm each of Na^+ and K^+ .

These measurements showed a finite potential difference between an electrode located at the freezing interface and a reference electrode in the unfrozen region. These observations indicate the possibility of using this technique to monitor the movement of

freezing/thawing interfaces in the ground. An experimental program was set up to systematically study freezing potentials developed in different solutions and at different freezing rates.

Experimental Set-Up

Fig. 1 shows a schematic diagram of the experimental cell. This consisted of a cylindrical PVC vessel (A) of internal diameter, 146 mm (5.75" nominal), height 368 mm (14.5"), wall thickness 6.3 mm and closed at one end with an aluminum base (B). The cylinder was insulated with Styrofoam rings (C) of thickness 51 mm. The cylinder was placed on a cooling chamber (D) through which a cold fluid (Prestone antifreeze) could be circulated. The cooling plate had inlet and outlet PVC tubes connected to a Haake G cooling bath with a Haake D8 temperature controller. The temperature of the bath could be controlled to $\pm 0.1^{\circ}\text{C}$ accuracy. A Plexiglas rod (E) of diameter 9.5 mm (0.375") and length, 406 mm and containing 6 electrodes in the form of gold-plated copper strips (F), (25 mm X 9.5 mm X 0.8 mm thickness) was placed at the center of the cylinder. The copper strip electrodes were parallel to the base of the cell. The bottom electrode was 10 mm above the bottom of the vessel and the others were positioned at 25 mm intervals. Thermistors (Beta Therm 2.2K3A1A) were also attached at each electrode location. Coaxial cables (G) were soldered to the electrodes and thermistors and connected to an external data logging system (Campbell Scientific Inc. Model CR 10). The time, temperature and electrical potentials were measured by the recorder every 5 minutes and averaged every 15 minutes and the data was stored in a storage module SM192 attached to the CR-10.

The CR-10 data logger has an internal impedance of 200 giga ohms ($2 \times 10^9 \Omega$), sufficiently large to measure even very small potential differences. Resolution of the instrument in the 10 mV scale is $0.33 \mu\text{V}$ and in the 2500 mV range, 0.33 mV. The top electrode used as the reference electrode was connected to the ground terminal of the instrument and the lower five electrodes were connected to the terminals 1 to 5, starting from the bottom electrode upwards.

Experimental Procedure

Experiments were carried out to measure the freezing potentials in the following liquids:

- a) de-ionized water, boiled to remove dissolved gases, in particular, CO_2 ;
- b) de-ionized, boiled water with CaCl_2 at concentrations of 20, 40 and 60 ppm.

CaCl_2 was chosen as a solute for the experiments, as it is one of the main constituents in the field solutions we continue to study. No reliable data for potentials developed during freezing of CaCl_2 solutions are available other than those of Workman and Reynolds (1950).

The PVC cylindrical vessel with the electrode stand positioned in the center was placed on the cooling plate inside an incubator maintained at 4°C . The liquid was poured in the vessel to a height just above the top electrode, and the column was frozen from the bottom upwards. The top electrode remaining in the unfrozen water (until the freezing front reaches the top) was the reference electrode against which the potentials developed in all the other electrodes were measured. The time, temperature and voltage developed at each electrode were scanned every 5 minutes and averaged every 15 minutes and the data stored in the memory module of the data logger

Figure 2 shows the potentials developed at two different electrode locations in de-ionized water. The circulating bath temperature was -10°C . Fig. 2(a) shows a sharp peak F, when the freezing front reached the electrode-3. The absolute magnitude of this freezing potential was about 75 mV, as measured from the beginning to the end of the straight line portion of the jump in voltage (a drop in potential from -50 to -125 mV). As the freezing front advanced to reference electrode-6, a reverse potential (hereafter called the "Shorting Potential" and indicated by "S") of about 100 mV was measured, from the beginning to the end of the straight line portion of the jump (from -25 to $+75$ mV). In Fig. 2(b) similar jumps in the potential are seen on electrode-5, but the two peaks are closer to each other, as electrode-5 was just below electrode-6. The magnitude of the potentials were of the same order as those observed at the electrode location 3.

Figures 3(a) and 3(b) show, the potentials developed in a solution of CaCl_2 in de-ionized water, at -10°C and -15°C , respectively. The pattern is similar to that seen in Fig. 2, but at -15°C , the peaks of freezing and shorting potentials are sharper, meaning, the rise and fall of the potential is steep and not gradual. Figures 4 and 5 show respectively, the temperatures and the potentials developed at each electrode, in an experiment with distilled water, with the circulating bath fluid at -15°C . The initial dip in temperature below 0°C , seen in Fig. 4 (indicated by the arrow, SC), is due to supercooling of the solution, before normal freezing starts. [Note: The occurrence of supercooling was not a regular phenomenon in all experiments. For supercooling to occur, the system has to be in perfectly still condition with no vibration or nucleating agents present in the solution. This experiment probably provided such ideal conditions for supercooling to occur.]

Fig. 5 shows the variation of the potential difference at all electrodes, with respect to the top reference electrode. There is also a gradual increase in the potential difference after the onset of freezing at each electrode, as the temperature at that location drops with the progress of the cooling, until the freezing front touches the top reference electrode (No. 6). At this time the system is completely frozen and both the measuring and reference electrodes are embedded in solid ice, essentially shorting the system. The simultaneous occurrence of the shorting potential at all electrodes at the instant the freezing front touches the top reference electrode, is seen in Figure 5, as indicated by the peaks occurring at “S”, the vertical dashed line at 78 hours.

The data show the following:

- a) As the freezing front touches each electrode, an abrupt change in potential (measured with respect to the top electrode in the unfrozen liquid) occurs due to the freezing potential associated with the phase change. The potentials measured have been ice-negative. This decays as the freezing front passes the particular electrode.
- b) As the freezing front advances beyond the uppermost electrode, the voltage-time curve shows a spike (abrupt change in potential) caused by shorting of the system. The magnitude of this “shorting potential” peak may be of the same order, but of opposite sign, as the first freezing potential observed at that electrode.
- c) Once the entire bath in the cell is completely frozen, the temperature begins to drop at each electrode and a temperature differential is set up between the top electrode and each of the lower electrodes. This temperature differential causes the development of a small potential due to charge separation caused by the temperature gradient, as reported by Latham et al. (1961)

Table 1 shows the maximum values of the freezing potentials and "shorting potentials" observed in each solution in this series of experiments. In general, the freezing potentials are higher with faster rate of cooling using a colder circulating bath. Ionic impurities increase the magnitude of the potentials.

Discussion

The freezing potentials measured in the present experiments were ice-negative and the "shorting potentials" were ice positive. These are potential differences measured between each of the lower electrodes as the freezing front touches that electrode and the reference electrode in the unfrozen liquid, assuming that the environment around this reference electrode remains unchanged. This may not actually be the case, especially in ionic solutions, as there will be solute rejection at the freezing interface and the concentration of the unfrozen liquid may change, although slightly. Attempts have been made by different authors, to use an external ground electrode as the reference electrode (in particular, in field measurements) against which the potentials at all electrodes were measured. Even in such cases, stray currents through the ground as well as diurnal changes in temperature and atmospheric conditions could affect magnitude of the potential difference developed between the electrodes.

The results from the present experiments show the onset of a freezing potential on an electrode located at the freezing boundary and is a definite indication of the arrival of the freezing front at that electrode location. The absolute magnitude of the potential will depend on several factors such as the quality of the solution, physical characteristics of the electrodes, data logger and the connections used, rate of freezing, etc. The important

point is that the present technique using electrodes does indicate the time of arrival of the freezing front at each location and from this, the rate of advance of a freezing boundary can be accurately determined.

A potential difference can also arise due to the thermal gradient within the ice (Latham et al., 1981). This is mainly due to the concentration gradients of H^+ and OH^- ions set up under the temperature gradient. The gradual increase in the measured potential at different electrodes, shown in Fig. 5, is an indication of this. In ionic solutions a concentration gradient of ions could also arise by rejection of solute to the unfrozen water at the freezing boundary and this could also give rise to the gradual rise in potential.

The observation of a "Shorting Potential", as the freezing front advances past the reference electrode, has not been reported before. This shorting potential arises from charge equalization throughout the ice. The shorting potential is observed at all electrodes simultaneously, when the freezing front passes the reference electrode at the top of the column. In Figure 5, the peaks due to the shorting potentials on all electrodes occur at the same time, about 78 hours after the beginning of the experiment.

The freezing and shorting potentials indicate respectively, the onset of freezing and the completion of freezing of a solution below the reference electrode. Since the potential jumps are quite sharp and instantaneous, this could be used as an accurate method to monitor and measure the progress of freezing in a solution.

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Conclusions

1. Electrical potentials are generated due to charge separation and preferential accumulation in the two phases of a freezing solution. This can be noticed as an instantaneous shift in the DC voltage measured between an electrode at the freezing interface and a reference electrode in the unfrozen solution.
2. The magnitude of the freezing potentials are higher at faster rates of cooling produced by a cooler circulating bath.
3. Dilute solutions of CaCl_2 generate higher freezing potentials than pure water, the magnitude of the potential being higher for the higher concentration.
4. A shorting potential is recorded at the instant the freezing front passes the reference electrode. The magnitude of this shorting potential is of the same order as that of the freezing potential.
5. By measuring the freezing and shorting potentials, the progress of freezing can be monitored accurately.

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Table 1. Maximum values of freezing and shorting potentials measured in the present experiments.

Solution	Maximum Freezing Potentials (ice-negative), mV		Maximum Shorting Potentials (ice-positive), mV	
	-10° C	-15° C	-10° C	-15° C
Deionized Water	175	175	100	130
20 ppm CaCl ₂ solution	190	500	130	135
40 ppm CaCl ₂ solution	175	>1500	125	300
60 ppm CaCl ₂ solution	>1700	>5000	120	200

[The symbol ”>” means the values are larger than the scale set in the data logger]

Figure Captions:

Fig. 1. Experimental cell to measure electrical freezing potentials in solutions

Fig. 2. Freezing potentials developed in de-ionized water, with the circulating bath temperature at -10°C . The first negative peak (F) indicates the onset of freezing and the next positive peak (S) denotes the shorting potential.
(a) Electrode 3; (b) Electrode 5.

Fig. 3. Freezing Potentials developed at electrode 3, using a solution of CaCl_2 (20 ppm) in de-ionized water. Circulating bath temperature: (a) -10°C ; (b) -15°C .

Fig. 4. A typical chart showing the variation of the temperature with time, at different Electrodes. The arrow (SC) indicates supercooling

Fig. 5. A typical chart, showing the simultaneous occurrence of shorting potential (S) at all electrode locations.

Figure 1. Experimental cell to measure electrical freezing potentials in solutions.

Figure 2(a). Freezing potentials developed in de-ionized water, with the circulating bath temperature at -10°C , at electrode-3. The first negative peak (F) indicates the onset of freezing and the next positive peak (S) denotes the shorting potential

Figure 2(b). Freezing potentials developed in de-ionized water, with the circulating bath temperature at -10°C , at electrode-5. The first negative peak (F) indicates the onset of freezing and the next positive peak (S) denotes the shorting potential

Figure 3(a). Freezing potentials developed at electrode-3 using a solution of CaCl_2 (20 ppm) in de-ionized water.
Circulating bath temperature: -10°C .

Figure 3(b). Freezing potentials developed at electrode-3 using a solution of CaCl₂ (20 ppm) in de-ionized water. Circulating bath temperature: -15° C.

Figure 4. A typical chart showing the variation of temperature with time at different electrodes.
The arrow (SC) indicates supercooling.

Figure 5. A typical chart showing the simultaneous occurrence of Shorting potential (S) at all electrode locations.