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CRYOGENIC SUCTION PUMP MECHANISM FOR COMBINED SALT- AND FROST EXPOSURE

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Abstract

Freezing of water can be explained by the thermodynamic properties of the water due to the influence of temperature, pressure and special effects such as surface tension and salt solution. Gibbs free energy curves for ice and pore liquid containing different concentrations of NaCl (0-6%) are presented. These curves explain the onset of freezing in pores when the energy level for solid ice and pore liquid containing salt are equal. Upon further cooling a non-equilibrium condition develops since the Gibbs function for pure ice is less than the Gibbs function for the liquid. The theory also explains why ice nucleation is developing in the largest pores containing liquid, including air-voids. Below the nucleation temperature, a vacuum with low partial pressure of the water develops around the ice which starts a cryogenic suction pump. For a closed system (i.e. no external liquid) partial pore-drying develops leading to specimen shrinkage. In air-entrained concrete the ice growth may be accommodated within the pore system without structural damage. In the case external liquid is present, such as when the surface contains a salt solution, pore suction attracts surface liquid, and additional ice growth may not be accommodated within the pore system. Thus, a net expansion occurs. Frost expansion due to crystal growth is time-dependent and progresses as long as liquid is available and until thermodynamic equilibrium is re-established at a given temperature.

Keywords: Cryogenic suction; frost expansion; Gibbs-Free energy; salt frost attack;

1. INTRODUCTION

Combined salt and frost attack is a major durability problem in concrete highway pavements in the state of Michigan, USA, where road-salts are used extensively for ice melting purposes. Disintegration of the Portland cement paste has been found to develop rapidly (<10 years) in cases where sub-surface drainage is poor and where concrete frost resistance is reduced due to an inadequate air-void system [1]. The concrete exposure level is more severe if freezing occurs in the presence of a surface liquid as the salt solution remains liquid above the eutectic temperature. Therefore, concrete specifications over time have evolved to include requirements to maximum water-cement ratio (0.45) and target air content (6 % for 25 mm maximum aggregate size) of fresh concrete [2] for severe exposure conditions, i.e. freezing in the presence of a deicer solution. These specifications are based on decades of field service experience and extensive laboratory testing [3].

Several studies have demonstrated that salt frost exposure leads to water uptake [4-7]. Water uptake is a clear indication that the surface region quickly reaches critical saturation levels resulting in frost expansion and surface flaking. Different aspects of the process mechanisms have been proposed which involves the moisture uptake in a diffusion process [5], multi-phase interfaces as in the micro-ice-lens model is based on chemical potential differences between the ice body inside the pores and the pore liquid [8]. Many of these observations have been explained to show that the ice pressure becomes dominant within very few cycles and a cryogenic pump action is active [9].

2. GIBBS FREE ENERGY

Freezing of water can be explained by the thermodynamic properties of the water due to the influence of temperature, pressure and special effects such as surface tension and salt solution. The equilibrium phase of the water is determined by the minimum of the partial Gibbs function (chemical potential) which we can write as

$$g = g_o - \int s\, dT + \int v\, dP + \int \sigma\, dA + RT \ln y$$

where the last expression is written for a liquid (salt-water with $y < 1$) or solid phase ($y = 1$). Evaluating the properties following Lindmark [9] for the specific volume $v_{sat\ T} = 1/\rho$, the isothermal compressibility β_T and the surface tension σ, we can find the Gibbs function for water in larger pores and voids under different conditions.

$$g = g_{sat\ T} + v_{sat\ T}\,(P - P_{sat\ T})\,[1 - \tfrac{1}{2}\,\beta_T\,(P - P_{sat\ T})] + \sigma\,\frac{2\,v}{r} + RT \ln y$$

A special treatment is done for the subcooled liquid, which is not an equilibrium state for pure bulk liquid water, and this was developed by Pátek et al. 2009 [10]. Liquid at $P_o = 100$ kPa was curve fitted as a polynomial in temperature which we then correct for the actual pressure and the presence of a surface tension and salt solution. The surface tension integral is evaluated from a cylindrical geometry neglecting the end effects which explains the variation with radius.

Some examples are shown in Fig 1 for the solid ice and liquid water in a 0%, 3% or 6% salt solution. For a smaller pore size the curves for the liquid shifts downwards whereas it is the opposite for the ice caused by the sign of the surface tension. The curves show that ice in a large pore or void is at equilibrium with pure liquid water in a pore of 30 nm at -4 ^{0}C whereas with 3 and 6% salt solution the temperature is lowered to about -6 ^{0}C and -7 ^{0}C respectively. Ice can also form in the pore but at a lower temperature indicated by the solid curve for ice under the influence of surface tension, for instance pure liquid water can freeze to ice at -7 ^{0}C in the 30 nm pore. As the model for the water does not contain ionic contributions the real equilibrium freezing point is at a slightly smaller temperature and in practice some degree of subcooling is required to form nucleation sites.

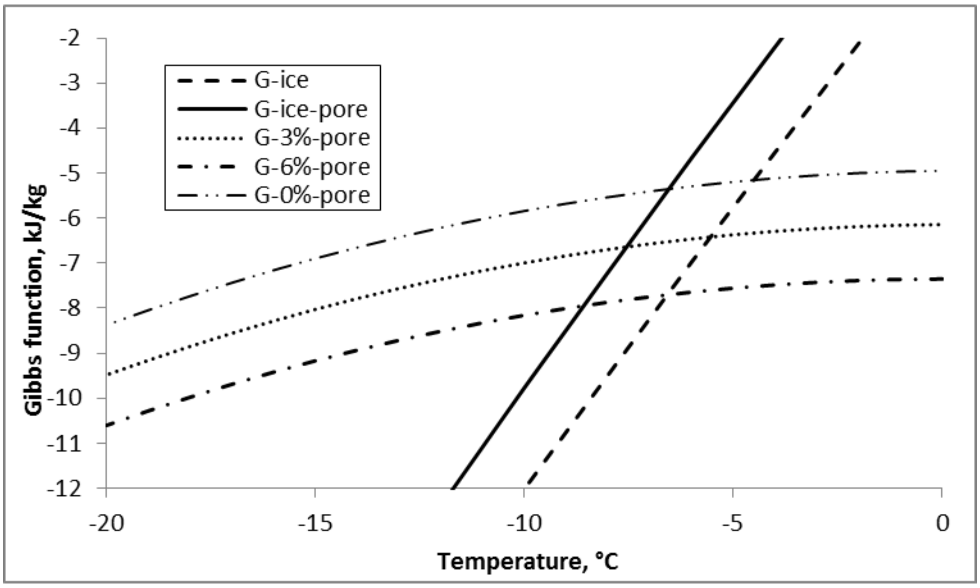


Figure 1: Gibbs functions for solid and liquid water, pore size is 30 nm.

The influence of the pore size is illustrated in Fig 2 where the Gibbs function is shown at a fixed temperature (i.e. isothermal temperature condition) for ice and two liquid solutions located in a pore of radius r. Ice will first form in the larger pores where the Gibbs function curves for liquid and ice are flat corresponding to bulk states at the prevailing pressure. For pore sizes > about 1 μm freezing is not affected by surface tension effects. Thus, there is a tendency for ice-body growth to occur in these larger pores since the Gibbs function is lower. As the Gibbs function for liquid in very small pores (< 10 nm) is much smaller than the value for ice such liquid will not freeze.

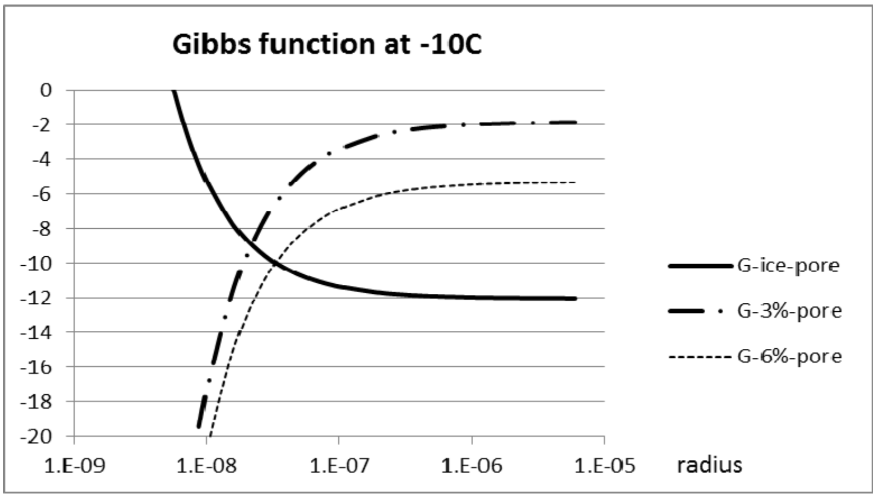


Figure 2: Gibbs function as a function of pore radius for ice and liquid.

3. CRYOGENIC SUCTION PUMP

As the water and concrete is cooled we reach the first occurring of freezing in the larger pores/voids where there is liquid present. As the temperature decreases further we will have additional ice formation at the nucleation sites since now Gibbs function of ice in large pores without surface tension effect is lower than Gibbs function for liquid in large pores, see Fig 1. Also as the temperature decreases the pores shrink and squeezes liquid out into any larger space. Further temperature drop continues this process so water will diffuse towards the ice formation locations due to the difference in Gibbs function. This will empty the pore structure around the voids with ice formation sites. On the surface there is a stronger salt solution liquid available which then goes into the pores where the Gibbs function is smaller. Under the ice formation on the surface the strong salt solution is created as the water has been taken out to form ice thus keeping a liquid available to fill the pores.

This process can continue as long as the temperature drops and this constitutes the cryogenic pump. When the temperature no longer drops the system slowly moves towards thermodynamic equilibrium for the given temperature. Ice can still form until the Gibbs function for the liquid becomes as small as the Gibbs function for ice. Diffusion of water towards the ice happens and diffusion of salt near the ice front towards the less salty liquid locations will also happen. Even at the lowest temperature there will be some amount of liquid left in the smallest pores, see Fig. 2.

The cryogenic pump decreases in rate when the temperature drop stops as the differences in Gibbs function no longer are driven by a lower temperature for the ice. This is evident in the measurements where the temperature is kept steady at -10 ^{0}C and in the standard cycle at -20 ^{0}C. At the time of constant temperature additional ice is formed by transport of water due to the now diminishing difference in Gibbs function and the system moves towards equilibrium. This part of the process slows down in a diffusion like manner where eventually the Gibbs function of the remaining liquid equals the Gibbs function of the ice. Damage happens when some of the voids become filled with ice and the ice front moves further into the pore structure and the pressure in the void increases. For lower temperatures ice can form in smaller pores where otherwise the Gibbs function will be larger. Now there is no release for the pressure in the liquid being pushed by the front of the ice formation. The whole system is sensitive to the pore structure in terms of its distribution of pore volume/size and its connectivity to the surface and between voids. Development is currently underway to simulate the thickness of the scaling in relation to the pore connectivity [11].

4. DILATOMETER RESULTS

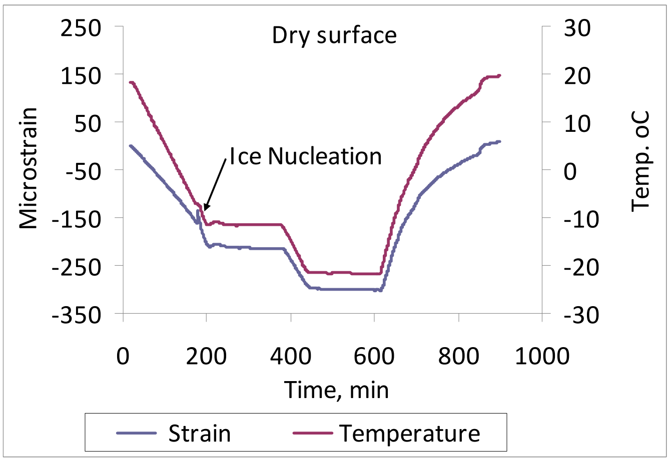
Dilatometry is an effective tool in indentifying frost mechanisms associated damage for different surface liquids (water and salt solution) [12]. In this study the focus was to evaluate the cryogenic suction effect on frost expansion.

Specimen cross section dimensions were approximately 12 mm by 12 mm, and the specimen length was about 90 mm. This geometry ensures that specimen temperature gradients are small during a freeze-thaw test. The specimen is tested in a horizontal position, which allows for including liquid transport from the top surface. This is facilitated using a wetted paper towel. To avoid ice-sheeting effect the towel is cut into small sections and the specimen is then sealed using a plastic foil in order to avoid evaporation during testing.

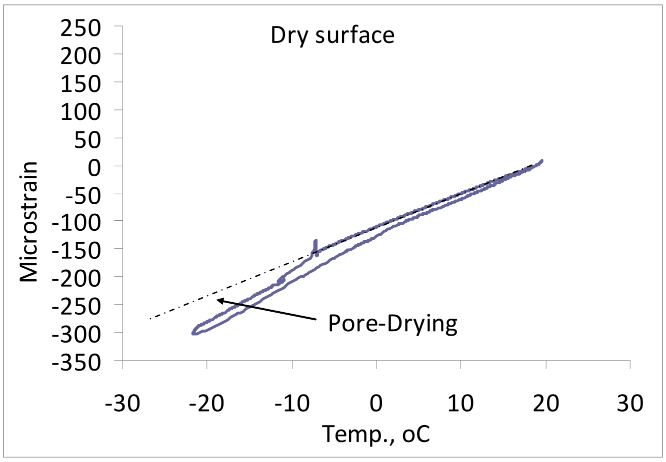
Concrete cylinders (100 mm diameter by 200 mm height) were cast with a water cement ratio of 0.45 and air content ranging from 3% to 8%. Total air and air-void system was measured according to ASTM C457 by linear traverse [13]. Specimens were obtained from the concrete cylinders at the age of 28 days or later, and dried at 50 ^{0}C for 1 week followed by re-saturation until capillary pore water was replenished as determined from water sorption tests. This ensured a high degree of capillary pore saturation prior to freeze-thaw testing.

Three consecutive freeze-thaw cycles were run per specimen for each test condition (i.e. with and without a surface liquid). A freeze-thaw cycle consisted of cooling from 20 ^{0}C to -10 ^{0}C at 10 ^{0}C /hour followed by a 3 hour isothermal condition; then cooling to -20 ^{0}C at 10 ^{0}C /hour followed by another isothermal ramp for 3 hours. The heating cycle was linear at 10 ^{0}C /hour followed by one hour at 20 ^{0}C. During testing a thermocouple was in contact or near contact with the specimen surface.

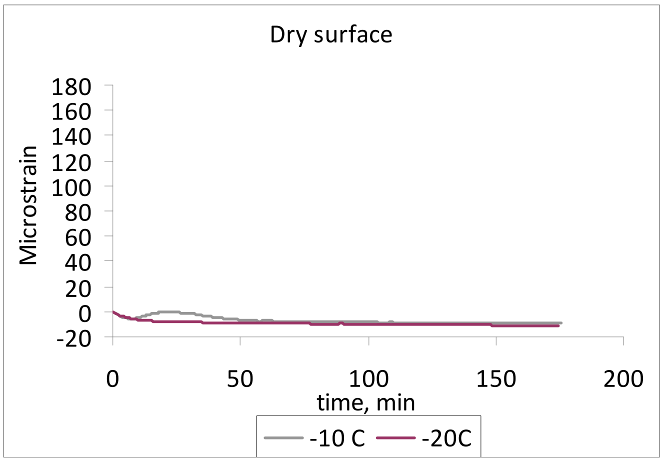
Fig 3 (a-c) illustrate a typical freeze-thaw response for air-entrained concrete (3% air) which is internally saturated without access to additional surface liquid (water or salt solution) during freeze-thaw. In Fig 3a the nucleation temperature is apparent with an abrupt small rise in temperature at about -7 ^{0}C followed by a small expansion due to ice pressure on walls of macropores. As the temperature is lowered the ice pressure is rapidly decreased due to its high thermal expansion coefficient. Additional specimen contraction happens due to the pore drying effect created by ice growth [14]. The ice growth is most likely developing in the air-voids, but is limited by surrounding pores as no additional liquid transport can develop from the surface. Thus no significant ice pressure develops inside the air-voids or macropores and contraction occurs during further cooling. An extreme case of liquid transport resulting in substantial ice growth and pore pressure expansion is the presence of a 3% salt solution on the top surface during a frost cycle. This is seen from Fig 4 (a-c). Once ice nucleation develops and the temperature is lowered the suction pump effect is effective in the liquid transport from the outer surface to the ice front in the larger pores within vicinity of the surface. Ice growth is now only limited by the amount of surface liquid available and the transport properties.



(3a)

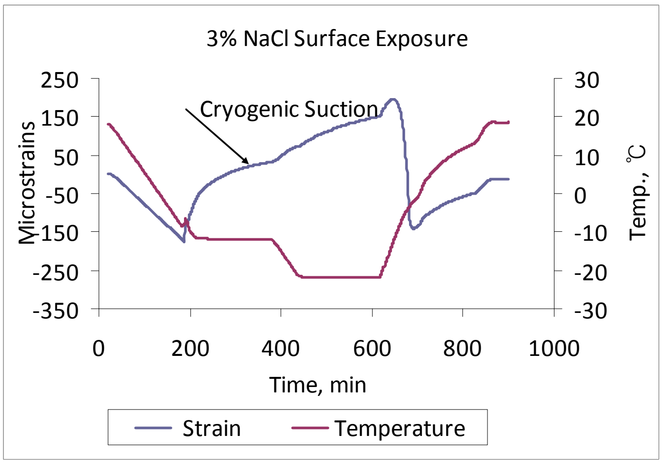


(3b)

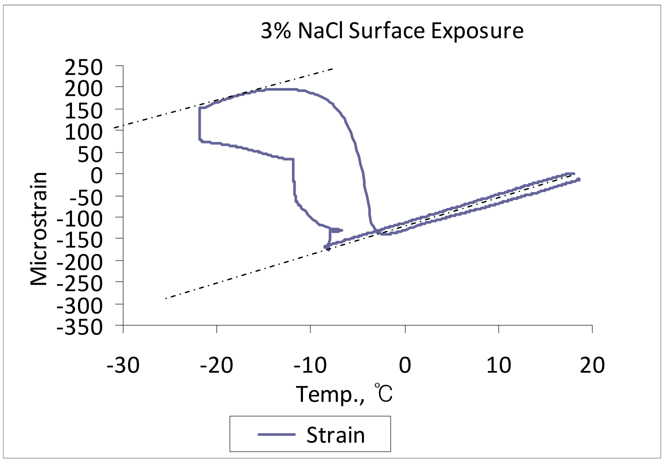


(3c)

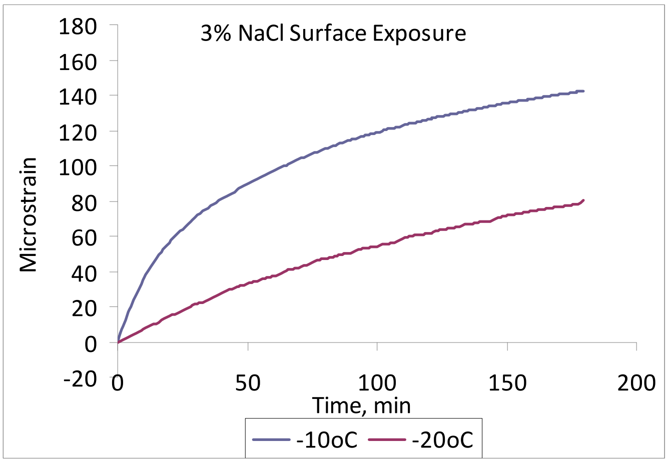
Figure 3: (a) Typical temperature and strain versus time response for air-entrained concrete, and (b) strain versus temperature, and (c) strain versus time at constant temperature.



(4a)



(4b)



(4c)

Figure 4: Typical freeze-thaw results for air-entrained concrete exposed to 3% salt solution on the surface; (a) temperature and strain versus time; (b) strain versus temperature and; (c) strain versus time for isothermal condition.

5. CONCLUSIONS

The cryogenic suction pump is a major factor in salt frost damage. Thermodynamic theory (Gibbs-Free energy) explains why ice attracts liquid. As the temperature is lowered below the nucleation point, transport towards ice from surrounding pores continues as long as liquid is available and the Gibbs function of ice is lower than that of liquid. Cryogenic suction is also present during constant temperature below the nucleation temperature. Therefore, the duration of freezing is an important factor for durability assessment.

Air entrainment provides additional ice-growth buffer capacity without destructive effects from pore wall pressures. While contraction is typical for air-entrained concrete, which is internally saturated, the presence of a surface liquid (3% NaCl solution) during freezing is a severe exposure condition due to cryogenic suction. This renders the air-void system less effective as compared to freezing without a surface liquid.

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