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**FROST ACTION IN CEMENT IN THE  
PRESENCE OF DE-ICERS**

by  
G. G. Litvan

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FROST ACTION IN CEMENT IN THE PRESENCE OF DE-ICERS

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ABSTRACT

Cement samples impregnated with water and with 5, 9, 13, 18 and 26 per cent NaCl solutions have been subjected to temperature cycles between +5 and -70 °C and changes in their dimensions and heat content determined. The results are consistent with the theory proposed by the author for frost action in the absence of chemicals (J. Am. Ceram. Soc. 55, p. 38-42, 1972) and with the findings of a study of phase transitions of NaCl solutions adsorbed in porous glass (J. Colloid and Interface Science, 45, 154-169, 1973). These observations can be explained by the fact that solution contained in the pores, when cooled below the bulk freezing point, remains in a liquid-like state. This condition gives rise to instability, which is eliminated by mass transfer. If the process cannot proceed at a required rate, mechanical damage occurs. The well-known aggravating effect of dissolved chemicals is due, primarily, to the increased degree of saturation they promote.

Des échantillons de ciment imprégnés d'eau et de solutions de NaCl de 5, 9, 13, 18 et 26 pour cent sont exposés à des cycles de température de +5 à -70 °C et l'on détermine leurs changements de dimensions et leur teneur calorifique. Les résultats sont en accord avec la théorie proposée par l'auteur relativement à l'action du gel en l'absence de produits chimiques (J. Amer. Ceram. Soc. 55, 38-42, 1972) et avec les résultats d'une étude des transformations de phases de solutions de NaCl adsorbées dans du verre poreux (J. Colloid and Interface Science, 45, 154-169, 1973). Ces observations s'expliquent par le fait que la solution présente dans les pores reste comme à l'état liquide lorsqu'elle est refroidie sous le point de congélation en bloc. Il en résulte une instabilité qu'élimine le transfert de masse. Si le procédé ne peut pas avancer à la vitesse requise, il se produit une détérioration mécanique. L'effet aggravant des produits chimiques dissouts est dû surtout au degré accru de saturation qu'ils entraînent.

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Deterioration of concrete as a result of frost action in the presence of de-icing salts has become a serious problem in the last decade, a problem that can only become increasingly grave as the use of these chemicals becomes more widespread. This point is illustrated by the fact that in 1966-67 highway authorities deployed 6.3 million tons of sodium chloride in the U.S.A. but estimate that the amount to be applied in 1975 will exceed 11 million tons (1). Of particular concern is the extremely short lifespan of bridge decks.

Several theories have been advanced regarding the effect of de-icers (2,3), but none is capable of accounting for all the observations and, more importantly, none has made it possible to develop a practical method of protection against salt scaling. Little guidance can therefore be offered the practitioner in his attempts to minimize damage from frost action in the presence of de-icers, in contrast with the case of frost action in their absence. Although no agreement concerning the mechanism appears to have been reached, air entrainment has proved most effective in providing frost durability, and is known and used to great advantage. Thus, further investigation of the salt scaling phenomenon is well warranted.

#### Experimental

Five-year-old hydrated cement paste having a water-cement ratio of 0.5 was used in the tests. Rectangles (20 by 6 mm) 1.27 mm thick were cut from cylindrical (32 mm diam) stock material with a precision diamond saw, care being taken to maintain complete saturation of the specimens during preparation and testing.

Conditioning consisted of keeping the samples immersed in an NaCl solution of known concentration in deaerated glass cells for at least 120 days. At the end of this period changes in dimensions and heat content (DTA) were simultaneously determined during temperature cycles controlled automatically at 0.33 °C/min. The range extended from +5 to -70 °C. A detailed description of the experimental apparatus has been given previously (4).

#### Results

Changes in dimensions and heat content of samples impregnated with 0, 5, 9, 13, 18 and 26 per cent aqueous NaCl solutions during the temperature cycle are shown in Figures 1 and 2. The most important characteristics exhibited by the curves will be summarized.

#### Cooling

1. When the samples contained water, anomalous changes occurred at approximately -8 °C. When they were impregnated with salt solution, the sharp DTA peak and length anomaly shifted to lower temperatures. The absolute value of the temperature and the magnitude of the area under the peak are functions of concentration. With the saturated salt solution the peak is not observable. It should be noted that the extension curves for 5 and 9 per cent concentrations are plotted on a 5x smaller scale and for this reason the anomalies are not apparent in the vicinity of -14 °C.
2. Subsequent to the first length anomaly considerable expansion took place, particularly at low salt concentrations. With a 5 per cent solution the paste expanded 0.5 per cent compared to 0.08 per cent in water and 0.01 per cent in a 26 per cent solution.
3. The DTA curves indicate a second exothermic heat effect at approximately -25 °C, the magnitude of which is a function of salt concentration.

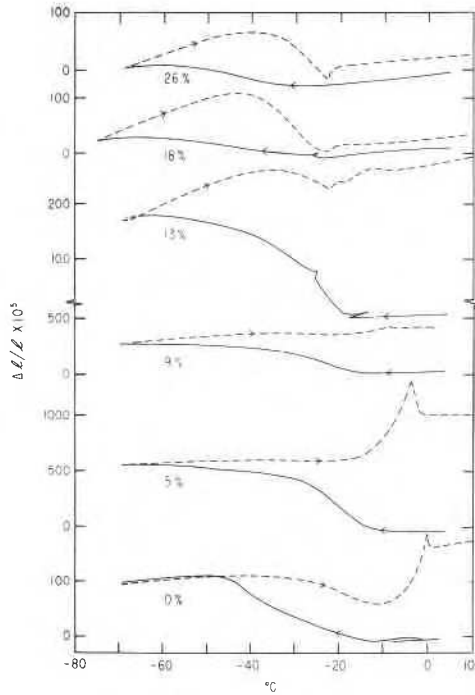


FIG. 1

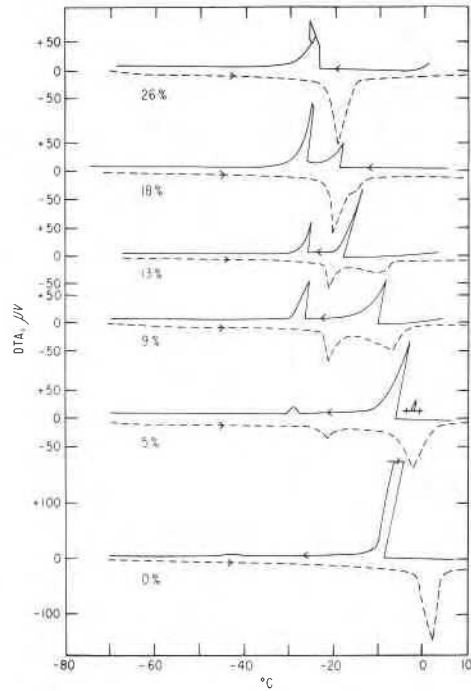


FIG. 2

Fractional length changes of 0.5 water-cement ratio cement pastes impregnated with NaCl solutions (concentrations as indicated) during temperature cycles.

Differential thermogram of 0.5 water-cement ratio cement pastes impregnated with NaCl solutions (concentrations as indicated) in temperature cycle.

4. Below  $-25^{\circ}\text{C}$  no discontinuous heat effect is detectable in the salt-impregnated specimens, although they expanded uninterruptedly until cooling was terminated at  $-70^{\circ}\text{C}$ .

#### Warming

1. Significant expansion of the 13, 18 and 26 per cent systems without any abrupt change in heat content is observable between  $-70$  and  $-40^{\circ}\text{C}$ .
2. On warming to higher temperatures the 13, 18 and 26 per cent samples contract, reaching a minimum length at  $-21^{\circ}\text{C}$ . At this temperature an endothermic heat effect is observable for all five salt-containing samples; magnitude is directly proportional to concentration.
3. Another endothermic peak, together with a length anomaly, occurred at temperatures that approached  $0^{\circ}\text{C}$  as the salt content decreased.
4. Every sample suffered permanent increase in length as a result of processes taking place during the temperature cycle.

#### Discussion

The results will be considered in the light of the previously proposed mechanism of frost action (4-7), now summarized briefly. Water adsorbed in the pores of a solid is unable to crystallize without redistribu-

G. G. Litvan

tion and the vapour pressure of the unfrozen adsorbate,  $p_l^0$ , is similar to that of supercooled water (8). Thus, when a fully saturated solid is cooled to below 0 °C a portion of the adsorbed water becomes unstable because  $p_l^0$  is greater than  $p_s^0$ , the vapour pressure of crystalline ice, which unavoidably forms in the surroundings. Thermodynamic equilibrium is restored by partial desorption, which thus reduces the vapour pressure of the liquid remaining in the pores. On reaching the external surface after nucleation, the desorbed liquid crystallizes. Because the difference between  $p_l^0$  and  $p_s^0$  increases with descending temperature, the water, during cooling, becomes unstable in smaller and smaller capillaries and migrates towards the external surface.

Mechanical failure occurs when desiccation cannot proceed in an orderly fashion; the rate of water transport out of the pores is significantly less than is required by the conditions. Such a situation usually arises if permeability is low and porosity, the degree of saturation, and the cooling rate are high (5, 7).

According to this concept the exothermic heat effects occurring below 0 °C in Figure 2 can be attributed to freezing of desorbed liquid on the external surface. Because the freezing point of the solutions and the temperatures at which they become unstable in the pores decreases with increasing solute concentration, the concentration dependence of the temperature of the DTA peak is to be expected. The fact that, with the exception of the pure water and saturated salt cases, the thermograms exhibit two peaks is also understandable. As this freezing process takes place on the external surface, the phase rules of bulk two component systems apply. The first exothermic peak indicates the initiation of the freezing process, when pure ice commences to form; the second, temperature invariant, at -22 °C, is due to freezing of the solution of eutectic composition.

One consequence of this freezing mechanism is a blocking effect in dilute solutions. If the salt concentration of the exuded liquid is low, in accordance with the freezing curve of the phase diagram, a large fraction of the water component crystallizes at the end of the capillary channels leading to the external surface. Subsequent flow from the interior is thus impeded, resulting in the creation of highly non-equilibrium conditions and extremely large expansions such as those obtained with the 5 and 9 per cent solutions in the present experiments. This behaviour is consistent with the findings of Verbeck and Klieger (9) who stated that a relatively low salt concentration of de-icer salts produces more surface scaling than higher concentrations or pure water. In the latter case the situation is alleviated by the lower degree of saturation, as will be discussed.

Although no heat effect is observable with salt-containing specimens, in the temperature region below -25 °C expansion continues. This phenomenon is consistent with the theory that predicts the formation of an amorphous, glassy solid if desorption of the liquid to the degree required by equilibrium conditions cannot take place.

The endothermic peaks of the thermograms obtained on warming are due to melting on the external surfaces of the eutectic mixture and the ice crystals, respectively. The temperature at which they occurred agrees well with the melting point of bulk solutions of corresponding concentrations. As freezing can only take place on the surface after the solution has migrated to the outer surface, its freezing point is lower than its melting point.

A unique feature of samples impregnated with a highly concentrated salt solution is the rather large ( $100 \times 10^{-5} \frac{\Delta L}{L}$ ) expansion they suffer between -70 and -40 °C. Cement samples saturated with pure water expand less

than  $10 \times 10^{-5} \frac{\Delta l}{l}$  in this region. In previous work on salt impregnated porous glass (10) it was concluded that the stresses developed during cooling often fail to result in expansion because the highly viscous, essentially solidified, adsorbate renders the whole system rigid, at the same time preventing mass redistribution. On warming, as the viscosity of the glassy solid gradually decreases, this restrictive effect is eliminated and the built-up stresses manifest themselves.

#### Conclusions

The major conclusion of the present investigation is that the low temperature behaviour of two component adsorbates in porous solids is explicable by the previously proposed theory (4) if the colligative properties of solutions are considered.

Dissolving any substance in a pure liquid such as water results in a lowering of the vapour pressure of the solvent. The first important consequence of this fact is that, for a given value of relative humidity, the degree of saturation of a porous body is higher if it contains a soluble substance. It has been pointed out (10) that at 100 per cent relative humidity a porous body saturated with a 26 per cent NaCl solution is exposed to an effective relative pressure of 1.33 or, conversely, that the porous adsorbent will become completely saturated with saturated NaCl solution at 77 per cent relative humidity. The detrimental effect of high degree of saturation on frost resistance is well known (5).

Another consequence of the decreased vapour pressure of the solutions is that the freezing point is lower than that of the pure solvent. From the frost action point of view this is significant. The redistribution process commences at lower temperatures, at which the viscosity of the solution may be quite high and at which crystals of the pure solvent may already have formed on the external surface. Thus, flow of the pure liquid is impeded and frost resistance further diminished.

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## G. G. Litvan

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