



Wet pavement anti-icing – A physical mechanism



Alex Klein-Paste*, Johan Wählin¹

Department of Civil and Transport Engineering, Norwegian University of Science and Technology, Høgskoleringen 7A, 7491 Trondheim, Norway

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ABSTRACT

Anti-icing of wet pavements is often explained by the fact that anti-icing chemicals (for example sodium chloride) depress the freezing point of water. It appears however that the required concentration predicted by freezing point depression can be unrealistically high. Recently it has been suggested that anti-icing chemicals weaken the ice that forms when a wet pavement freezes and that it allows traffic itself to destroy the ice. It provides an alternative physical mechanism for anti-icing of wet pavements. This article describes the physical basis of this mechanism and proposes a single parameter (equilibrium brine fraction) to predict if the ice is sufficiently weakened. Existing laboratory and field data are re-analyzed to determine a value for the minimum brine fraction, which is used to calculate the theoretically minimum chemical concentration needed to ensure sufficient tire-pavement friction. Microscopic observations of the freezing process are also given. The results of the analysis provide a conservative estimate of the minimum brine fraction $F_{b,min} = 0.4$. This brine fraction criterion implies that 60% less salt is needed compared to the concentration predicted by the freezing point depression theory. The predicted theoretical minimum salt concentration should not be confused with actual application rates. Actual application rates have to account for a large number of practical issues like chemical losses during spreading, dilution and temperature drop, uncertainties about weather forecasts, and the cycle time of the plow/salting truck (time).

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1. Introduction

The freezing of water on pavement surfaces can cause slippery driving conditions and impair safe and efficient travel. A common countermeasure to prevent this from happening is to apply chemicals. Highway maintenance engineers refer to this practice as “anti-icing” (Ketchem et al., 1996; Minsk, 1998). The term anti-icing also includes weakening of the adhesive bond between snow and the pavement (Penn and Meyerson, 1993) but this paper focuses exclusively on wet pavements subjected to freezing temperatures.

Typical anti-icing chemicals are chloride-based salts like sodium chloride (NaCl), calcium chloride (CaCl₂) and magnesium chloride (MgCl₂) or organic salts like calcium magnesium acetate (CMA), and potassium formate (KCOOH). The chemicals can be spread from salting trucks on the road surface as dry (solid) granulate, dissolved in water (brine application), or a combination of both (prewetted granulate). Brine can also be applied with stationary systems (Ye et al., 2013). Focus on traffic safety together with demands for environmentally and economically responsible winter maintenance requires that practitioners have to optimize their spreading rates and spreading frequencies. To do this safely and efficiently there is a need for a proper understanding of the physical mechanism behind anti-icing.

Anti-icing of wet pavements is often explained by freezing point depression. In fact, many textbooks on physical chemistry illustrate freezing point depression by the example of road anti-icing. In essence, freezing point depression is a colligative property of an ideal solution, meaning that it depends on the concentration of dissolved particles, and not on their chemical composition (Atkins and de Paula, 2002). However, at higher concentrations (>0.5 m) and for non-ideal solutions the chemical composition of the particles starts to play a role (Fullerton et al., 1994). The freezing point depression of road anti-icing chemicals is therefore often determined experimentally (ASTM, 2003) and the results are presented in a phase diagram. The phase diagram for sodium chloride (NaCl) in water is illustrated in Fig. 1. The freezing curve gives the freezing temperature as function of the chemical concentration.

It appears however that the required concentration predicted by freezing curves can be unrealistically high. Murakuni (1997) reported that the Japan highway Public Corporation (JH) uses application rates that do not necessarily correspond to the freezing curve. Recently, Haavasoja et al. (2012) collected field data and concluded that only about 3% NaCl is enough to keep friction at acceptable levels of about 0.5 (friction coefficient) even at temperatures down to -20°C . In other words, less salt is used in practice, compared to the salt amount predicted by the freezing curve.

Haavasoja et al. (2012) explained the low levels of salt needed by the fact that the presence of salt makes the ice structure softer. They noted during sample collection that the soft salty ice tended to break into small ice particles which do not pack under the tire. Independently, the present authors investigated in laboratory experiments the same

* Corresponding author. Tel.: +47 73 59 46 13; fax: +47 73 59 70 21.

E-mail addresses: alex.klein-paste@ntnu.no (A. Klein-Paste), johan.wahlin@ntnu.no (J. Wählin).

¹ Tel.: +47 73 59 47 27.

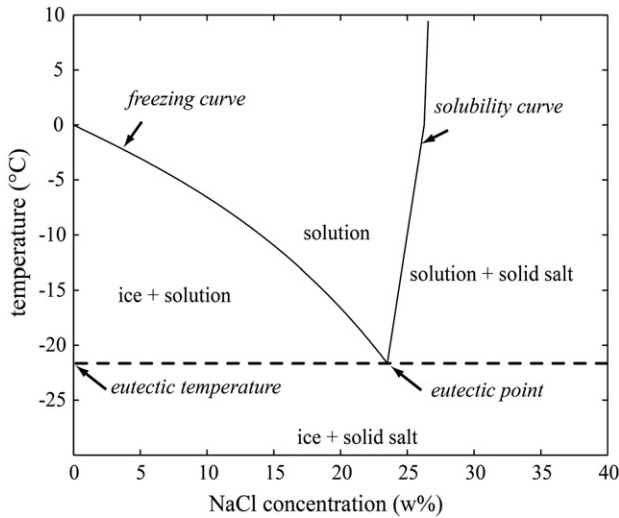


Fig. 1. The phase diagram of NaCl in water.

hypothesis that salt weakens the ice that forms when a wet pavement freezes (Klein-Paste and Wählin, 2011; Wählin and Klein-Paste, 2011). From these laboratory and field studies, it has become apparent that anti-icing of wet pavement does not only rely on freezing point depression. The notion that anti-icing chemicals weaken the ice provides an alternative physical mechanism for anti-icing of wet pavements, and gives thereby new insights in how anti-icing chemicals work.

In this article we describe the physical basis of this mechanism, propose a single parameter (equilibrium brine fraction) that can be used to calculate a theoretically minimum chemical concentration and re-analyze existing laboratory and field data to determine a value for the minimum brine fraction to ensure sufficient tire-pavement friction.

2. Proposed mechanism

The freezing of water containing a solute is fundamentally different from the freezing of pure water. Water freezes when it has reached its freezing point T_f and heat is withdrawn. In pure water, the freezing can start at $T_f = 0^\circ$ and all the water can freeze at this temperature. This means that once the freezing point is reached, the rate of freezing is solely governed by the rate of heat loss. But this situation changes when foreign molecules are dissolved in the water.

Since most solutes are not accepted in the ice lattice, they will remain in solution (brine) until the eutectic point is reached (Hobbs, 1974). During sea ice formation, there is usually a large liquid bulk present to which a part of the salt is expelled. Hence the bulk salinity of sea ice is lower than the bulk salinity of sea water (Nakawo and Sinha, 1981; Weeks, 2010). The salt that is present in the ice is trapped into brine pockets within the ice. On pavements, the water films are very thin (typically less than 0.5 mm) meaning that there is no large liquid bulk phase to which anti-icing chemicals can be expelled. The result is that the chemical concentration in the (remaining) liquid water phase quickly rises once freezing has initiated. A higher chemical concentration in the remaining liquid means a lower freezing point. Hence, the freezing point of the remaining liquid changes during the freezing process (Turunen, 1997). Anti-icing chemicals thus retard the freezing process by stretching the freezing over a temperature range, rather than solidification at a single temperature.

The presence of solutes (anti-icing chemicals) also affects the microstructure of the ice that forms. In aquatic solutions the crystals grow dendritic with solution of higher concentration entrapped between the dendrites (Ayel et al., 2006). Also in sea ice, the inclusion of brine

pockets (which increases the porosity of the material) greatly affects the microstructure (Sinha, 1977) and thereby the mechanical properties of ice. For example, the flexural strength of sea ice decreases with increasing brine volume (Timco and O'Brien, 1994), and the fracture toughness decreases with increasing porosity (Schulson and Duval, 2009). When tires roll or brake on a pavement, they exert both compressive and shear forces. Also free-rolling tires induce shear forces because the circular tire tread is forced to comply with the flat pavement, a process known as micro slip (Moore, 1975). With sufficient anti-icing chemical present, the ice will be too weak to withstand the exposed traffic loading and disintegrate into small pieces. This allows the tire to reach the underlying pavement texture and create friction mainly by hysteresis and mechanical interlocking (Clark, 1971).

The proposed mechanism for wet pavement anti-icing can therefore be summarized as follows:

- (1) Anti-icing chemicals change the microstructure of the ice that forms during freezing.
- (2) Anti-icing chemicals thereby weaken the ice.
- (3) The ice will disintegrate into small pieces under the exposed traffic loading.
- (4) The re-exposed pavement texture provides sufficient friction.

Whether the ice film fails or remains intact will depend on: 1) the microstructure of the formed ice, 2) the properties of the pavement and 3) the magnitude of the loading. Therefore there are a range of parameters that may influence this "point of failure", for example the chemical concentration, pavement temperature, freezing time, level of super cooling prior to freezing, pavement type (concrete or asphalt), pavement texture, tire pressure, axle loading, vehicle speed and traffic volume. It will be very difficult and of little practical value to include all these parameters into a model to predict if the ice will fail or not. It is more useful to estimate this with a limited number of parameters and ensure that this estimate is sufficiently conservative. This means that the ice should always fail, irrespective of the variability in all the parameters that are not accounted for.

A useful parameter is the fraction of water that remains unfrozen; the equilibrium brine fraction F_b . At a given temperature and chemical concentration, F_b can be calculated from the phase diagram of the used anti-icing chemical using the lever rule given in Eq. (1):

$$F_b(T) = \frac{c}{c_f(T)} \quad (1)$$

where c is initial concentration of the solute in the water film prior to freezing, and c_f the concentration where equilibrium is reached. The function $c_f(T)$ is given by the freezing curve (the liquidus) in the phase diagram.

The question is how large should F_b be in order to predict with sufficient confidence that the ice will fail and that sufficient friction can be generated. Once this minimum brine fraction $F_{b,min}$ has been determined it is possible to calculate the theoretically minimum salt concentration c_{min} using Eq. (2):

$$c_{min} = F_{b,min} c_f(T_p), \quad (2)$$

where T_p is the pavement temperature.

3. Experiments and method

3.1. Summary of previous studies

3.1.1. Laboratory experiments

Laboratory experiments have been carried out to explore the proposed mechanism and study the weakening of thin ice films with anti-icing chemicals (Klein-Paste and Wählin, 2011; Wählin and Klein-

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