SODIUM CHLORIDE DIHYDRATE – A POTENTIAL CAUSE OF SLIPPERY ACCIDENTS

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Abstract

From a thermodynamic point of view, it can be expected that sodium chloride dihydrate (hydrohalite, $NaCl{\cdot}2H_2O$) will form on winter roads under certain conditions at temperatures below 0.1°C. In order to elucidate whether or not the formation of hydrohalite on the pavement can explain the phenomenon of ice appearing to be resistant to road salt, a comparative study has been made on a number of different surfaces measuring the friction index. The friction measurements were performed with a Portable Skid-Resistance Tester. Discontinuous surfaces consisting of small islands of hydrohalite was classified as potentially slippery surfaces. It is therefore possible that the formation of hydrohalite contributes to accidents on slippery roads.

Introduction

On January 23rd 1996 three slippery road accidents occurred in Copenhagen County within a period of less than three hours. It was observed that the pavement in general was dry, but that the friction level was reduced in some parts of the road. The County noticed the existence of a dry and rather hard surface (described as glazing) that did not melt by contact with the palm on these parts of the road. Subsequent additional salting (dry road salt, sodium chloride) and gritting did not restore the friction level between road and tire. Similar observations have been reported from other Danish counties. Under certain weather conditions (low temperature and low relative humidity) the effect of the applied dry salt is reduced. The salt agglomerates to a slippery and crystalline mass.

The phase diagram for the NaCl - H_2O-system

The phase diagram for the binary system NaCl-H_2O is shown in Fig. 1. Each circle represents an experimentally determined temperature and composition at which a sodium chloride solution is in equilibrium with one or more solid phases. These experimental data were retrieved from the IVC-SEP Electrolyte Data Bank (2001). Three solid phases can exist

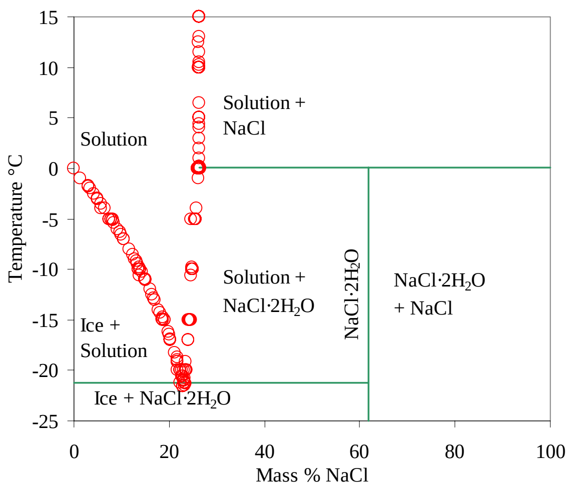

Figure 1: Phase diagram for the NaCl-H_2O system. $NaCl{\cdot}2H_2O$ is identical to hydrohalite (sodium chloride dihydrate)

in this system (ice, hydrohalite ($NaCl \cdot 2H_2O$), and anhydrous salt (NaCl)). At concentrations between 0 and 23.2 mass % NaCl, ice is the only solid phase that can be formed. At concentrations higher than 23.2 mass % NaCl either hydrohalite or anhydrous NaCl can form. Hydrohalite is stable at temperatures below 0.1°C and is the only form of sodium chloride that can be in equilibrium with a solution of NaCl at temperatures below 0.1°C. If the composition and the temperature of an aqueous NaCl solution is known, it is possible to determine from the phase diagram in Fig. 1 which phases are in equilibrium with each other.

Consequently there are indications from thermodynamics that the crystalline mass observed on the winter roads could be hydrohalite. Hydrohalite is often unnoticed due to its superficial resemblance to ice, and one of the main objects of this investigation was to examine whether hydrohalite on the pavement presents a risk for the traffic. A comparative study was performed on the level of friction on a number of different surfaces (e.g. ice and hydrohalite).

Experimental

The friction measurements were made with a portable skid-resistance tester according to a procedure based on the instructions given by the Road Research Laboratory (Road Note no. 27, 1960). The portable skid-resistance tester was rented from the Danish Road Directorates department in Roskilde. The results obtained by the portable skid-resistance tester are friction indices, and should not be taken as coefficients of friction. However, the friction index is a relative measure for the coefficient of friction. Fig. 2 shows a photo of the experimental set-up. The apparatus was fixed on a stainless steel frame and placed in a cooling chamber (WTI Binder model MK720, operated in constant temperature mode). The temperature level was –10°C. The frame was fixed on the chamber walls. The samples were set in a holder in the frame.

Normally the portable skid-resistance tester is used to measure the friction level at a single point

Figure 2: Experimental set-up for the friction measurements.

on the road. The apparatus measures the frictional resistance between a rubber slider (mounted on the end of a pendulum arm) and the road surface. In order to operate the apparatus in the laboratory modifications were made. Besides the metal frame for fixing and levelling the apparatus, a piston (released by compressed air) was installed on the apparatus in order to operate its release mechanism without opening the cooling chamber (and thereby disturb the temperature level). A window with a small hole (diameter 15 cm) covered with a movable piece of rubber, replaced the original window in the cooling chamber making it possible for the operator to catch the pendulum arm on the return swing.

The sodium chloride supplied by Copenhagen County had a water content of 2.8 mass %. The content of anticaking agent ($Na_4Fe(CN)_6$) was approximately 100 ppm. The mean size of the salt grains (d50) was 380 μm. Distilled water was used to prepare the salt solutions and to make surfaces of ice. Road samples (diameter 15 cm, type SMA (Stone Mastic Asphalt)) representing the pavement on the highway were supplied by the county.

Results And Discussion

A comparative study of the friction level on different surfaces has been performed. The friction indices (FI) were evaluated according to the following classification:

- A friction index above 65 indicates that the friction level between road and tire is good.
- A friction index below 45 indicates potential slippery sites.

This categorization is based on suggested minimum values of skid-resistance (Road Research Laboratory, 1960).

The results of the friction index measurements are listed in table 1. The friction indices of dry and wet ice at –10°C were determined to be 20.4 and 17.7 respectively. Measurements on a dry road sample (SMA, Stone Mastic Asphalt) gave a friction index of 94.4 and after wetting the surface with distilled water, the friction index was 60.2 at 20°C. Friction indices of pavement samples covered with ice varied between the value for pure ice and that for pavement, depending on the amount of water applied to make the ice.

In the first experiments with salt, hydrohalite was grown from a sodium chloride solution (saturated at 25°C) in a small glass container. After drying the crystals they were distributed on the road sample and stored for 16 hours at –10°C. Similar experiments were performed with prolonged storing time (30 hours). The friction indices are listed in table 1 as SMA+hydrohalite, SMA+hydrohalite (a), SMA+hydrohalite (b). The friction indices ranged from 55.6 to 58.0. Consequently these surfaces were found not to be potential slippery surfaces. However, in relation to the slippery road accidents these surfaces do not seem to be representative.

In order to reflect the assumed road conditions related to the slippery accidents, hydrohalite was grown randomly directly on the road sample. The hydrohalite surfaces SMA+hydrohalite (c-f) in table 1 were made by distributing sodium chloride on the road sample and subsequent addition of saturated/unsaturated sodium chloride solution. The hydrohalite surfaces SMA+hydrohalite (g-i) in table 1 were made in a similar manner, but the sodium chloride solution was substituted by distilled water.

SMA+hydrohalite (c) was prepared by addition of saturated sodium chloride solution to the road sample partly covered with road salt. This system was stored at –10°C overnight (around 14 hours). The next day the road sample was covered with a hard, greyish surface consisting of minor islands of hydrohalite. Fig. 3 shows a photo of the sample denoted SMA+ hydrohalite (c). The friction index was measured to 45.4, and after one hour to 46.2. This friction index is comparable to that of SMA+Ice and can be categorized as potentially slippery.

Sample SMA+hydrohalite (e) was prepared by adding unsaturated salt solution to a road sample partly covered with road salt. The pavement sample was placed for 16 hours at –10°C and became covered with islands of hydrohalite. The friction index was measured to 49.4 and it did not change much by turning the sample horizontally 90° (f).

Table 1. Friction Indices (FI) for various surfaces.

Sample	FI	Remarks
Ice	20.4	-10°C, Dry
Ice	17.7	-10°C, Wet
SMA	94.4	20°C, Dry
SMA	60.2	20°C, Wet
SMA + Ice	45.0	-10°C
SMA + Ice	66.0	-10°C
SMA+hydrohalite	58.0	-10°C, Crystals grown in a glass container and placed on a pavement sample for 16 hours
SMA+hydrohalite (a)	56.4	Same, after 17 hours
SMA+hydrohalite (b)	55.6	-10°C, Crystals grown in a glass container and placed on a pavement sample for 30 hours
SMA+hydrohalite (c)	45.4	-10°C, Crystals grown randomly from salt and saturated salt solution on a pavement sample for 14 hours
SMA+hydrohalite (d)	46.2	Same, after 15 hours
SMA+hydrohalite (e)	49.4	-10°C, Crystals grown randomly from salt and an unsaturated salt solution on a pavement sample for 14 hours
SMA+hydrohalite (f)	50.2	Sample (e), turned 90°
SMA+hydrohalite (g)	67.0	-10°C, Crystals grown from salt and distilled water on a pavement sample for 20 hours
SMA+hydrohalite (h)	66.8	Sample (g) turned 90°. Measurement performed 30 minutes after (g)
SMA+hydrohalite (i)	68.4	Sample (h) turned 90°
SMA+hydrohalite (j)	66.4	-10°C, 100 g salt and 100 mL 20 mass % salt solution
SMA+hydrohalite (k)	59.2	-10°C, 50 g salt and 100 mL 20 mass % salt solution
SMA+hydrohalite (l)	65.0	-10°C, 25 g salt and 100 mL 20 mass t% salt solution
SMA+hydrohalite (m)	68.2	-10°C, 10 g salt and 100 mL 20 mass % salt solution
SMA+hydrohalite (n)	65.4	-10°C, Composition corresponding to $NaCl \cdot 2H_2O$)
SMA+hydrohalite (o)	65.6	Sample SMA+hydrohalite (n) added extra road salt. Measurement of FI 30 minutes after addition of salt.

For the experiments SMA+hydrohalite (g-h-i), the pavement sample was covered by an unbroken layer of hydrohalite. The surface can be characterized as a thin, grey, hard layer (Fig. 4). The friction index is 67-68 which is significantly higher than the friction index of a similar pavement covered with islands of hydrohalite (45-50). From the measurements (g-h-i) we see again that the orientation of the pavement sample relative to the skid-resistance tester is of no importance.

Figure 3: Sample denoted SMA+hydrohalite (c)

It was examined whether or not the total amount of salt on the road sample had any influence on the friction index. In the experiments (j-k-l-m) various amounts of road salt were placed on the pavement sample and 100 ml of a 20 mass % salt solution was added. After 14 hours at –10°C the friction index was determined. From the results in table 1 it can be seen that none of the surfaces can be characterized as potentially slippery, and there is only little variation in the friction index with the amount of salt.

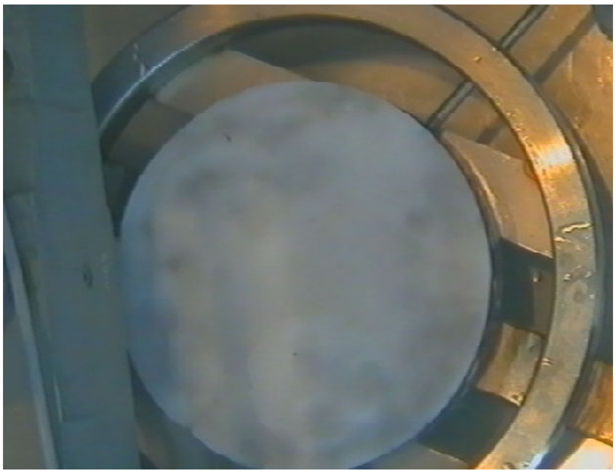

Figure 4: Continuous surface layer of hydrohalite on pavement sample, SMA+Hydrohalite (g)

The total salt concentrations in these four experiments correspond to 27, 36, 47 and 60 mass % salt. At these compositions we would expect to find saturated solutions in equilibrium with hydrohalite at -10°C (Fig. 1). Contrary to the expected, these surfaces were dry and the excess water was found in liquid inclusions. Although hydrohalite has a specific gravity of 1.61 and the saturated salt solution has a specific gravity of around 1.2 hydrohalite has a tendency to form a hard shell on the surface rather than precipitating like most other salts would.

For the experiment SMA+hydrohalite (n) a solution containing 61.9 mass% sodium chloride, corresponding to the composition of hydrohalite ($NaCl·2H_2O$), was placed on the pavement sample which was then kept overnight at –10°C. The friction index was measured to 65.4. After the measurement, additional road salt was sprinkled over the surface. 30 minutes later the friction index was determined to be 65.6 (o).

In the eight experiments (g-n) the surface on which the friction index measurement was performed consisted of an unbroken layer of hydrohalite. The average value of the friction index for these eight experiments is 65.8. A surface consisting of an unbroken layer of hydrohalite therefore can not be classified as slippery.

Panagouli and Kokkalis (1998) mentioned several factors which influence the level of friction between tire and road, and therefore has a potential effect on slippery accidents: “type, tread pattern and depth, pressure and condition of vehicle tires, the vehicle suspension and breaking system, speed, type, load and load distribution, temperature, existence of water and water film thickness, existence of soil, detritus or othe substances on the pavement surface, driver experience, higway geometrics, pavement age and traffic intensity, surface condition and structural deficiencies, mix design and type of surface and aggregate petrography, angularity, hardness, density, gradation and size”.

Conclusions

A comparative study on the level of friction has been performed. By this investigation another parameter, hydrohalite formation, adds to the abovementioned list of parameters determining the tire-pavement friction. An attempt to quantify the effect of hydrohalite formation on the tire-pavement friction has been made.

The level of friction was measured on the following surfaces: dry and wet ice, dry and wet pavement sample (SMA, Stone Mastic Asphalt), pavement samples with different amounts of ice formed directly on the pavement, pavement samples with different amounts of hydrohalite affixed, pavement samples with different amounts of hydrohalite grown randomly directly on the pavement, pavement sample covered with hydrohalite. The friction measurements were performed in a cooling chamber at constant temperature.

The friction indices of pavement samples with different amounts of ice varied, depending on the amount of water applied, from the value corresponding to pavement to the value corresponding to ice. The friction indices of pavement samples partly covered by hydrohalite formed from different amounts of salt solutions and salt had a lower friction index than that of the pavement surface and that of pure hydrohalite. These discontinuous surfaces consisting of small islands of hydrohalite could be classified as potentially slippery. Hydrohalite formation therefore may contribute to slippery accidents.

Hydrohalite formation requires low temperature and high concentrations of salt, and hydrohalite has a superficial resemblance to ice. The phenomenon of icy roads being resistant to salt at low temperature and low relative humidity can therefore be explained by the formation of hydrohalite. The salt concentration required for hydrohalite formation can be achieved by evaporation of water at the low relative humidity accompanying the phenomenon.

Acknowledgments

The authors appreciate the financial support of this research by Akzo Nobel – Dansk Salt A/S, Copenhagen County (Technical Department), and the Danish Road Directorate.

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