1	CHEMICAL FROST PROTECTION OF ROAD SURFACES - A LABORATORY
2	INVESTIGATION

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1 ABSTRACT

- 2 Anti-icing chemicals are commonly used to protect against hoar frost formation on roadways and
- 3 bridges. Due to their negative impact on both environment and infrastructure, their use should4 be optimized. During conditions for hoar frost formation, this means that good knowledge about
- 5 when it is needed to apply chemicals and the corresponding protection time is needed.

A laboratory setup has been used to study the freezing process for a salted road surface 6 during conditions for hoar frost formation and a description of the process is given. It has been 7 observed that freezing starts in the top layer of the applied solution, indicating the occurrence of a 8 concentration gradient due to accumulation of water molecules in the top layer. A British pendulum 9 was used to simulate the mechanical load of traffic. The pendulum successfully destroyed the ice 10 up to a certain ice fraction. This ice fraction was seen to depend on the amount of salt solution 11 applied to the test sample. Finally, it has been illustrated how the maximum ice fraction can be 12 used to calculate the amount of water allowed to be added to the road surface and estimates of the 13 protection time are given. 14

- 15
- 16 Keywords: Winter maintenance, Hoar frost, Salt

1 INTRODUCTION

2 During winter time, roads and bridge decks can become slippery due to hoar frost and create 3 dangerous conditions for motorists (1). In Sweden in the winters of 2004-2005 and 2005-2006, 4 18.1% and 14.5% of accidents respectively, occurred during hoar frost formation (2). Hoar frost 5 growth occurs when water vapor in the air goes directly from gaseous state to solid state on a 6 cold surface. For a surface without any anti-icing chemicals this can occur when the surface has a 7 temperature below both the dew point temperature and the freezing temperature of water, $T_s < T_d$ 8 and $T_s < 0$ °C.

9 Bridges have been found to cool more rapidly than adjacent roads (3), and are thus more 10 vulnerable for hoar frost formation than adjacent roads. This has lead to fatal accidents (4). The 11 Norwegian Public Roads Administration (NPRA) is planning for an upgrade of the E39 highway 12 route at the westcoast of Norway. This includes replacing ferries by bridges for several fjord cross-13 ings along this route. Knowledge about how to avoid slippery roads due to hoar frost formation on 14 bridges is therefore valuable for the E39 project.

Chemicals like NaCl, MgCl₂ and CaCl₂ are commonly used to protect against hoar frost. 15 They are often applied as solutions (brines) since liquids tend to adhere better to the road surface 16 17 than granulates. Unfortunately, chemicals have a negative impact on the environment (5, 6) and can cause corrosion of the infrastructure (7) and their usage needs to be optimized. This means 18 19 that, ideally, just enough chemical should be added to protect against slippery conditions while the conditions for hoar frost deposition are present. Winter maintenance practitioners are there-20 fore interested in the protection time (longevity) of a given application. Predicting the protection 21 time is challenging as it depends on many processes such as dilution due to added moisture on 22 23 the road surface, run-off and spray-off that can remove chemicals (8), and pavement temperature variations. The duration of hoar frost events also varies and little is known on how much hoar 24 frost can form before the pavement becomes slippery. Currently Road Weather Information Sys-25 tems (RWIS) typically can predict the duration of conditions for hoar frost to occur and there are 26 27 micrometeorological models that incorporate the presence of anti-icing chemicals (9, 10). But, to the best of our knowledge, there are no models in the public domain that predict the protection 28 time of a given chemical application for a given hoar frost event. To support such development a 29 sound physical understanding of how and how long chemicals protect against hoar frost formation 30 is required. 31

The effect of anti-icing chemicals is often explained by the freezing point depression (11). The freezing point at a certain concentration for a given chemical can be found in the respective phase diagram. For the process of hoar frost formation water is added to the road surface by humidity transport from the air, continuously diluting the concentration of any chemical present on the road surface. This raises the freezing temperature. At a certain point the freezing temperature exceeds the surface temperature, and freezing is expected to start.

In this laboratory investigation we address two fundamental questions related to hoar frost formation when the applied anti-icing chemical has been diluted to its freezing concentration: 1) how does hoar frost or ice accumulate when the freezing point of the solution has reached the surface temperature and 2) when does the accumulation of hoar frost/ice start to cause slippery conditions?

1 THEORY

2 The time it takes from when the anti-icing chemical is applied to when the road gets slippery can

3 be seen as the protection time for the anti-icing measure. We propose that this process can be

4 divided into two parts: 1) the dilution process when water is added to the applied solution due to

humidity transport from the air, and 2) the freezing process. The dilution process lasts from when
the anti-icing chemical is applied until the freezing concentration is reached, then the freezing

7 process starts and lasts until the road gets slippery.

8 The rate of humidity transport between the air and the road surface is given as (12):

$$\dot{m} = K_p (p_{\nu,a} - p_{\nu,s}) \tag{1}$$

where K_p is the mass transfer coefficient based on the vapor pressure difference, $p_{v,a}$ is the water 9 vapor pressure in the air and $p_{v,s}$ is the water vapor pressure at the road surface. For a clean surface 10 without any chemicals, the water vapor pressure at the surface is given as the saturation water vapor 11 pressure at the surface temperature, $p_{v,s} = p_v^{sat}(T_s)$, where T_s is the surface temperature. When an 12 anti-icing chemical is applied to the surface, the water vapor pressure at the surface is given as 13 water vapor pressure above the present solution, $p_{v,s} = p_v^{sol}$. In order to determine the water vapor 14 pressure above the solution it is useful to introduce the water activity, a_w . The water activity is 15 often described as the amount of free water not bound to any dissolved chemicals. The water 16 17 activity of a solution is defined as (13):

$$p_v^{sol} = a_w^{sol} p_v^{water} \tag{2}$$

18 where p_v^{water} is the water vapor pressure over pure water at the solution temperature. The water 19 activity ranges from 0 for a solution with no free water to 1 for pure water. As described by Wåhlin 20 et al. (14) the water activity can be found by using The Extended UNIQUAC model (15) which is 21 valid from the freezing points of the solutions to 100 °C. Similarly to Eq. (2) the water activity of 22 ice, p_c^{ice} , is given as (13):

$$p_{\nu}^{ice} = a_{\omega}^{ice} p_{\nu}^{water} \tag{3}$$

23 where p_v^{water} is the water vapor pressure over pure water at the ice temperature.

24 For wet pavement anti-icing it has been reported that a much lower salt concentration than found from the freezing curve is enough to keep the friction at acceptable levels (16, 17). This is 25 explained by anti-icing chemicals reducing the mechanical strength of the ice forming, allowing 26 the traffic to destroy the ice. This allows the tires to get in direct contact with the pavement, 27 and sufficient friction is obtained. Klein-Paste and Wåhlin (17) found that a brine fraction of 28 $F_{b,min} = 0.4$ was sufficient to ensure mechanical load to destroy the ice. This means that an ice 29 fraction of $F_{ice,max} = 0.6$ is allowed without reducing the friction. For the system of an anti-icing 30 chemical and water, ice and solution can coexist for temperatures above and concentrations below 31 the eutectic point. The ice fraction describes the amount of ice present in the system, i.e. the mass 32 of ice divided by the total mass of ice and solution. The ice fraction can be found from the phase 33 diagram of NaCl using the lever rule: 34

$$F_{ice}(T) = 1 - \frac{c}{c_f(T)} \tag{4}$$

- 1 where c is the calculated concentration of the solute on the stone surface, i.e. the mass of added
- 2 chemical divided by the total mass of chemical and water. $c_f(T)$ is the freezing concentration at
- 3 the surface temperature. Hence $F_{ice} = 0$ means that everything is liquid and $F_{ice} = 1$ means that
- 4 everything is frozen. The process of hoar frost formation differs from the experiment performed by
- 5 Klein-Paste and Wåhlin (17) by the continous addition of water to the system, due to the humidity
- 6 transport between air and road surface. Determining a maximum ice fraction for hoar frost forma7 tion will make it possible to determine the maximum amount of humidity allowed to be transported
- 8 to the road surface without getting slippery driving conditions.

9 METHOD

10 Hoar frost growth on a salted surface

11 The experiment was performed by the use of a setup designed to simulate typical conditions for 12 hoar frost formation on road surfaces. The setup consists of an open loop wind tunnel, where 13 humid air flows over a cold stone surface of 8x8 cm. Water vapor is added to the air by a water 14 bath, the air flow is driven by a tangential fan and the stone is cooled by Peltier elements. The 15 air velocity can be controlled within the range from 0.6 m/s to 1.2 m/s, relative humidity within 16 the range from 60% to 100% and the surface temperature can be set from air temperature to 8 °C 17 below air temperature. More details about the setup will be published elsewhere (*18*).

18 In the presence of any anti-icing chemical, the moisture added to the surface stays in liquid form until the freezing point is reached. In order to avoid run-off of the liquid solution, a 1 mm 19 thick silicon rim was attached along the edges of the stone. The remaining area for application 20 of salt solution was 45.5 cm^2 . The setup was placed inside a walk in cold laboratory with T_a = 21 2°C. The surface temperature was set to approximately -5 °C and the relative humidity was set to 22 approximately 85%. The relative humidity of the air, RH, the air temperature, T_a , and the stone 23 surface temperature, T_s , were measured during all tests and logged with a frequency of 2.4 Hz. The 24 25 wind was 0.6 m/s for all tests.

A (pre-diluted) NaCl solution ($T_f = -6.4$ °C) was chosen as the anti-icing agent. By ap-26 plying a solution with T_f close to T_s , the process of dilution before c_f was reached was reduced to 27 a minimum. This made it possible to isolate only the freezing process. The tests were performed 28 29 by applying about 0.3 or 0.5 ml 10% NaCl solution on the stone surface. The amount of applied solution was determined by weighting the stone before and after applying the salt solution. The salt 30 solution was spread evenly over the surface by use of a glass plate. The tests started when the stone 31 32 cooling system was turned on. The length of each test was determined based on a combination of 33 visual judgement and weighting, in order to achieve a range of different ice fractions. 18 tests were 34 performed, 12 with approximately 0.3 g of applied salt solution and 6 with approximately 0.5 g of applied salt solution. This correspond to to film thicknesses of 0.06 and 0.1 mm respectively for 35 the two series. In Norway it is recommended to use $20 - 40 \text{ g/m}^2$ of 23% NaCl solution during 36 conditions for hoar frost formation (19). This corresponds to $4.6 - 6.9 \text{ g/m}^2$ NaCl. The amounts 37 38 of NaCl used for the two film thicknesses in this study (6.6 and 11.0 g/m²) are in this range.

A camera was placed at a low angle towards the test sample and photos were taken every minute during the tests. A light source was placed in the back of the sample in order to produce reflections, thus making it possible to see the surface of the solution. The images taken during the tests were studied in order to determine two different transitions in the frost growth process: (a) the point when the first ice crystals were observed in the salt solution and (b) the point when the first small, white hoar frost crystals were observed on the frozen surface of the salt solution. The

1 mass of moisture added to the stone surface by condensation and deposition were measured by2 weighing the stone before and after the hoar frost growth tests.

At the start of the test the rate of water molecules transported from the air to the solution was found by combining Eq. (1) and Eq. (2):

$$\dot{m} = K_p \left(p_v^a - \left(a_w^{sol} p_v^{water} \right) \right) \tag{5}$$

5 where K_p is the mass transfer coefficient based on the vapor pressure difference, p_v^a is the water 6 vapor pressure in the air flow, a_w^{sol} is the water activity of the solution and p_v^{water} is the water vapor 7 pressure over pure water.

8 At the end of the test, when the entire surface was covered with ice crystals, the rate of 9 water molecules transported to the surface was given as:

$$\dot{m} = K_p \left(p_v^a - \left(a_w^{ice} p_v^{water} \right) \right) \tag{6}$$

10 where a_w^{ice} is the water activity of ice.

For a 10 wt % solution of NaCl at -5°C the water activity of the solution, a_w^{sol} , is 0.93. The water activity of ice at the same temperature, a_w^{ice} , is 0.95. Due to this small difference, the rate of water transported to the surface was assumed constant during the experiments. This allowed to calculate the amount of added water (and thereby F_{ice}) during the experiment from interpolating the measured mass before and after the experiment.

16 Mechanical strength of hoar frost

A British Pendulum Tester (20) was used to test the mechanical strength of the hoar frost present 17 on the stone surface after the frost growth periods. In order to avoid melting prior to the pendulum 18 19 test, the pendulum was placed inside a neighboring cold room. Here the air temperatur was -5 °C, 20 which is close to the stone surface temperature. The width of a standard rubber block was reduced to 40 mm to ensure the block did not touch the silicon rim and the temperature sensor. The hoar 21 22 frost from each test run was exposed to five pendulum passes before the sliding track was studied visually. The amount of hoar frost removed was found for each test. Similarly to the procedure of 23 Klein-Paste and Wåhlin (17), levels of <25%, 25-75% and >75% of hoar frost removed after five 24 pendulum passes were classified as being "intact", "partly removed" and "removed", respectively. 25 All pendulum tests were performed on samples with a distinct layer of hoar frost. Figure 1 shows 26 images of two different hoar frost samples after five pendulum passes. In (a) the hoar frost layer 27 28 was intact after five pendulum passes, while in (b) the hoar frost layer was removed after five

29 pendulum passes.

30 **RESULTS**

31 Hoar frost growth

- 32 For the 18 tests performed RH ranged between 78 % and 92%, T_s ranged between -4.8 °C and -6.1
- 33 °C and T_a ranged between 1.2 °C and 1.7 °C. Within each test, the RH was stable within $\pm 2\%$,
- 34 T_a within ± 0.2 °C and T_s within ± 0.2 °C. Figure 2 shows photos taken during different stages of
- 35 the freezing process. Initially the entire surface was covered with liquid salt solution, shown in
- 36 Figure 2(a). The freezing always started with frozen crystals floating on top of the solution, even

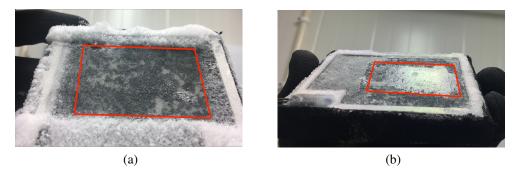
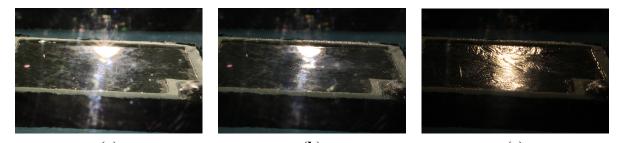


FIGURE 1: Image of hoar frost samples after five pendulum passes for (a) a test where the hoar frost was intact (0 % removed) and (b) a test where 95 % of the hoar frost was removed by the pendulum. The area where the pendulum is in contact with the stone surface is marked with red.

- 1 though the system is cooled from below. Figure 2(b) shows this second stage where ice crystals
- 2 start to appear in the salt solution. This is seen as small lines in the reflection from the light. The
- 3 ice crystals continued to form on top of the solution until the entire surface was covered with ice,
- 4 seen in Figure 2(c). By touching the frozen layer of ice with a glass plate, it was observed that
- 5 liquid brine was present below the frozen layer. The start of hoar frost formation on top of the
- 6 frozen layer was seen by less reflections and a more white surface. Figure 2(d) show an early
- 7 stage of this hoar frost formation. The hoar frost dendrites continued to grow until the experiment 8 was terminated. Figure 2(d) shows a distinct layer of hoar frost covering the entire surface. The
- 9 further development of ice below the first observed frozen layer was not possible to study visually.
- 10 However, the pendulum tests revealed that after a certain time the liquid layer disappeared and the
- 11 ice adhered to the stone surface.



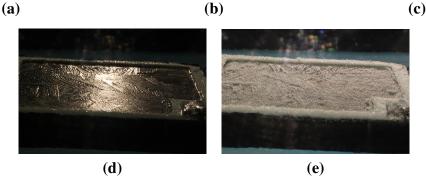


FIGURE 2: Development of hoar frost formation on surface with anti-icing chemical. (a) Only liquid salt solution (b) First observable frozen crystals floating on the top of the liquid (c) Frozen crystals cover the entire surface with liquid salt solution below (d) Early stage of hoar frost formation on top of the frozen layer (e) Surface completely covered with hoar frost

The first observable ice crystals occurred at a mean ice fraction of 0.19 with a 95% confidence intervals of [0.10 0.26]. No difference was seen between the two applied film thicknesses for the ice fraction at which the first frozen ice crystals were observed. The mean amount of humidity added to the test sample when the first ice crystal was observed was 0.15 and 0.22 g for the two film thicknesses of 0.06 and 0.1 mm. This corresponds to 33.3 and 44.4 g/m².

6 The first observable hoar frost on top of the frozen layer occurred for a mean ice fraction of 7 0.44 and 0.37 two film thicknesses of 0.06 mm and 0.1 mm. The corresponding 95% confidence 8 intervals were [0.36 0.52] and [0.29 0.44]. The mean amount of humidity added to the test sample 9 was 0.35 g for the film thickness of 0.06 mm and 0.39 g for the film thickness of 0.1 mm. This 10 corresponds to 77.8 and 87.8 g/m². The small difference between the ice fraction at which hoar 11 frost was observed for the two film thicknesses was not found to be statistically significant when 12 using the one-way Anova test.

13 Mechanical strength of hoar frost

14 Figure 3 shows the amount of removed ice plotted against the ice fraction F_{ice} for all pendulum

tests. Blue dots are representing the tests with applied film thickness of 0.06 mm and black dots
are representing the tests with film thickness of 0.1mm.

Logistic regression of the tests categorized as "intact" and "removed" was performed by the use of the Scikit-learn machine learning library for Python. This calculated the probability of removal of the hoar frost as a function of the ice fraction, F_{ice} :

$$p(F_{ice}) = \frac{1}{1 + e^{-(\beta_0 + \beta_1 F_{ice})}}$$
(7)

1 where β_0 and β_1 are the linear fitting coefficients. The threshold for successful ice removal was 2 set to more than 75 % of the ice removed. The tests categorized as "partly removed" (25-75 % of 3 hoar frost removed) were therefore treated as "intact" in the logistic regression. The probability 4 of successful removal of the hoar frost for different ice fractions as determined by the logistic 5 regression is also shown in Figure 3 for the two test series.

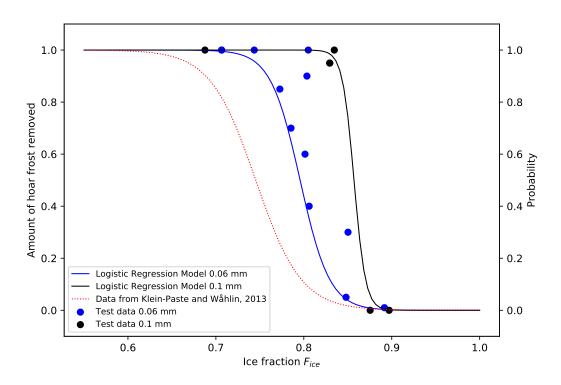


FIGURE 3: Left y-axis: Amount of hoar frost removed after five pendulum passes for the applied film thicknesses of 0.06 mm (blue dots) and 0.1 mm (black dots) for different ice fractions F_{ice} . Right y-axis: Probability of removal of hoar frost as a function of ice fraction F_{ice} for 0.06 mm applied film (blue line) and 0.1 mm applied film (black line). Dotted red line show data from Klein-Paste and Wåhlin (17).

6 It is seen that by applying a thicker film of brine, a higher ice fraction is allowed for a certain 7 probability of hoar frost removal than for a thinner film thickness. This means that a thicker film 8 allows a larger amount of water transported from the air to the surface for each gram of NaCl 9 applied than a thinner film, without becoming slippery.

10 Klein-Paste and Wåhlin (17) have studied the mechanical strength of frozen salt solutions 11 without any addition of humidity from the air. Their calculated probability of ice removal from 12 laboratory tests is shown with dotted red line in Figure 3. It is seen that a higher ice fraction is 13 allowed during hoar frost conditions than for freezing without humidity transport.

From the regression it was found that for the applied film thickness of 0.06 mm the 99.9 % probability of sufficient ice removal occurs at $F_{ice} = 0.67$. For a surface temperature of -5 °C, an ice fraction of 0.67 (p=0.999) corresponds to a salt concentration of 2.6 %. This occurs after an 1 added amount of 0.84 g of moisture from the air to the test sample.

2 For the series of 0.1 mm applied film thickness it is seen that the 99.9 % probability of

3 sufficient ice removal occurs at $F_{ice} = 0.81$. For a surface temperature of -5 °C, an ice fraction of

4 0.81 (p=0.999) corresponds to a salt concentration of 1.5 %. This occurs after an added amount of

5 2.80 g of moisture from the air to the test sample.

6 **DISCUSSION**

7 The freezing process

The first ice crystals were observed when the ice fraction was well above 0 ($\bar{F}_{ice} = 0.19$). This could 8 be due to supercooling of the solution since there was no seeding initiating the freezing process. It 9 could also be that it was not possible to detect the first ice crystals as soon as they appear. Since 10 11 heat is extracted below it is expected that the stone surface is colder than the top surface of the 12 brine film. Nevertheless, the freezing always started from the top, with liquid solution beeing 13 present below the ice. This indicates that there is a concentration gradient in the brine film. This is likely because the diffusion coefficient for water vapor in air, $(-10^{-5}m^2/s)(21)$, is five orders 14 of magnitude larger than the diffusion coefficient for water in salt solutions, ($\sim 10^{-10} \text{m}^2/\text{s}$) (22). 15 The result is an accumulation of water molecules in the top layer which leads to a higher freezing 16 temperature in the top layer than in the bottom layer of the solution. The solution of anti-icing 17 chemicals thereby continues to protect against slippery conditions even when ice starts to form on 18 19 top of the solution.

There was no significant difference in the amount of humidity added to the surface to the 0.06 mm and 0.11 mm film until the first hoar frost crystals were observed. This is also an indication that there is a concentration gradient in the solution. If the added water molecules were homogeneously distributed in the solution, it would require (almost) double the amount of humidity added to the 0.11 mm film compared to the 0.06 mm film before the entire surface was covered with ice, and hoar frost was observed.

After a large enough humidity transport, it was observed by the pendulum that frozen ice was stuck to the stone surface. This indicates that the diffusion of water molecules towards the colder road surface continues also after the surface is entirely covered with ice. Due to this diffusion, the liquid layer below the ice layer continues to dilute until the freezing temperature is reached also for the solution closest to the stone surface. The remaining solution is probably captured inside small pockets in the ice layer, similarly to the observations done by Klein-Paste and Wåhlin (17).

33 Mechanical strength of hoar frost

The mechanical action of the pendulum was able to remove the ice up to a certain ice fraction. After 34 this point the diffusion of water molecules down to the salt solution had reduced the concentration 35 36 sufficiently for ice to form also in the bottom of the salt solution. The ice therefore adhered to the stone surface. Successful removal of hoar frost and ice due to mechanical exposure is explained 37 to be important for cars to obtain sufficient friction (17). The maximum ice fraction at which the 38 ice was removed successfully can therefore be used to calculate the amount of water allowed to 39 40 be added to a salted road surface before it becomes slippery during hoar frost formation. This information is valuable in order to optimize the usage of chemicals during hoar frost formation. 41 It was found that by applying a thicker film of brine, a higher ice fraction is allowed for 42 43 a given probability of hoar frost removal than for a thinner film thickness. This could possibly

be explained by the diffusion of water in the salt solution. At a given ice fraction the liquid layer
 below the ice layer is thicker for higher film thicknesses. This makes the diffusion process for
 water molecules down to the stone surface slower for higher film thicknesses, resulting in higher
 allowed ice fractions until ice adhered to the surface. Using other chemicals like MgCl₂ and CaCl₂
 with lover diffusivity in water (22) could possibly extend the protection time during hoar frost
 formation.
 The higher allowed ice fraction reported here compared to the tests by Klein-Paste and

8 Wåhlin (17) might be explained by the occurrence of a frozen layer with liquid solution below. 9 Parts of the humidity transported to the system after the occurrence of this layer will be kept as 10 hoar frost on top of the ice. This hoar frost will add water to the system and raise the ice fraction 11 without actually diluting the solution below the ice layer. Using the criterion $F_{ice} = 0.6$ proposed 12 by Klein-Paste and Wåhlin (17) is therefore a conservative criterion during hoar frost formation.

The presented laboratory setup and test method does not take into account how exposure of traffic will influence the freezing of the salt solution. The traffic will probably enhance the mixing of the added water and the salt solution, reducing the concentration gradient. The situation will then be more similar to the freezing of a homogeneous solution studied by Klein-Paste and Wåhlin (17), and their proposed $F_{ice} = 0.6$ should therefore be valid also during hoar frost formation. However, this traffic induced mixing is probably not that effective in the area between the wheel tracks. Keeping good friction is also important for this area.

20 Implications for calculation of hoar frost protection time

One of the critical questions when predicting the protection time for an applied anti-icing chemical 21 during hoar frost formation is how much humidity is allowed to be transported from the air to 22 the road surface. A very conservative criterion is to keep the concentration of anti-icing chemical 23 above the freezing concentration, c_f . This corresponds to an ice fraction $F_{ice} = 0$. However, 24 25 the presented pendulum tests have shown that an ice fraction up to 0.81 can be removed by the 26 mechanical load of the pendulum with 99.9% probability. So allowing only humidity to accumulate 27 until the solution starts to freeze is likely to be over-conservative. The protection time in real 28 situations also depends on the rate of the humidity transport, Eq. (1). All weather variables like air 29 temperature, air humidity, wind speed and surface temperature influences this mass transport rate. In addition a mass transfer coefficient representative for the specific road site has to be determined. 30

To illustrate the effect of the chosen criterion before the road gets slippery we calculated 31 32 the protection time for four different cases, shown in table 4. Two different amounts of 23% 33 NaCl solution were chosen in order to correspond to the amounts of NaCl used in the presented laboratory experiment. Case 1 and 3 use $F_{ice} = 0$ as criterion. Case 2 and 4 use the ice fraction at 34 which the ice was removed by the pendulum with 99.9 % probability as criterion. A field study 35 36 has been performed by Karlsson (23) in Sweden during three winter seasons. Reported amounts of hoar frost deposited during one night are in the range from 55 to 495 g/m^2 , with an average 37 38 of approximately 150 g/m^2 . Assuming one night to be 12 h, this corresponds to an average of $12.5 \text{ g/m}^2\text{h}$. The calculations are based on this rate of humidity transport and a surface temperature 39 of -5° C. For simplicity, it is assumed that the rate of humidity transport in constant throughout 40 the entire process for the protection time calculation. 41

It is seen that by allowing an ice fraction of 0.67 4 times more water can be added to the road surface compared to an ice fraction of 0 for the lowest application rate. For the higher application rate an ice fraction of 0.81 allows more than 7 times more water to be added compared

Case	Applied 23 % NaCl solution (g/m ²)	Applied NaCl (g/m ²)	Criterion	Water allowed to be added (g/m^2)	Protection time (h)
1	28.5	6.6	$F_{ice} = 0$	54	4.3
2	28.5	6.6	$F_{ice} = 0.67$	222	17.8
3	48	11.0	$F_{ice} = 0$	92	7.4
4	48	11.0	$F_{ice} = 0.81$	688	55.0

TABLE 1: Calculation of amount of added water allowed and protection time for four differ-
ent cases. Calculations are based on an assumed amount of humidity transport of $12.5 \text{ g/m}^2\text{h}$.

1 to an ice fraction of 0. In case 2 each applied gram of NaCl allows 33.6 g of water to be transported

2 to the surface. In case 4 each applied gram of NaCl allows 62.5 g of water to be transported to the

3 surface. This difference is a consequence of the larger allowed ice fraction for the highest applied

4 amount of NaCl.

5 CONCLUSION

6 The presented laboratory investigation has shown that a salt solution diluted by humidity transport

7 from the air started to freeze from the top. This is explained by the slower diffusion of water

8 molecules in the solution than in the air, resulting to a concentration gradient with the lowest salt

9 concentration in the top layer.

10 It was shown that the time a certain amount of anti-icing agent protects a surface from

11 becoming slippery due to hoar frost formation is under estimated when using the freezing curve.

12 The allowed ice fraction was found to be dependent on the thickness of the applied brine film. For 13 a 0.06 mm thick film of 10 % NaCl the pendulum will remove the ice with 99.9 % probability for

an ice fraction of 0.67. For a 0.1 mm thick film of 10 % NaCl the pendulum will remove the ice

15 with 99.9 % probability for an ice fraction of 0.81.

Further work should include studies with other chemicals like MgCl₂ and CaCl₂ in order to determine how different diffusivities affects the freezing process and the protection time. Field test should be performed in order to further examine the process of hoar frost formation with the presence of practical issues such as salt losses and traffic.

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1 **REFERENCES**

- [1] Norrman, J., M. Eriksson, and S. Lindqvist, Relationships between road slipperiness, traffic
 accident risk and winter road maintenance activity. *Climate Research*, Vol. 15, 2000, pp.
 185–193.
- [2] Andersson, A. and L. Chapman, The use of a temporal analogue to predict future traffic
 accidents and winter road conditions in Sweden. *Meteorological Applications*, Vol. 18, No. 2,
 2011, pp. 125–136.
- [3] Knollhoff, D. S., E. S. Takle, W. A. Gallus Jr, and D. Burkheimer, Use of Pavement Temperature Measurements for Winter Maintenance Decisions. In *Transportation Conference Proceedings*, 1998, pp. 33–36.
- [4] SHT, Rapport om møteulykke mellom vogndtog og to personbiler på E16 i Flåm 16. november
 2007. Statens Havarikommisjon for Transport (SHT), 2010.
- [5] Ramakrishna, D. M. and T. Viraraghavan, Environmental Impact of Chemical Deicers A
 Review. *Water, Air, and Soil Pollution*, Vol. 166, No. 1, 2005, pp. 49–63.
- [6] Fay, L. and X. Shi, Environmental Impacts of Chemicals for Snow and Ice Control: State of
 the Knowledge. *Water, Air, & Soil Pollution*, Vol. 223, No. 5, 2012, pp. 2751–2770.
- 17 [7] Xu, G. and X. Shi, Impact of Chemical Deicers on Roadways Infrastructure: Risks and Best
- Management Practices. In *Sustainable winter road operations* (X. Shi and L. Fu, eds.), John
 Wiley & Sons, 2018.
- [8] Lysbakken, K. R. and H. Norem, Processes that Control Development of Quantity of Salt
 on Road Surfaces after Salt Application. *Transportation Research Record*, Vol. 2258, No. 1,
 2011, pp. 139–146.
- [9] Denby, B. R., I. Sundvor, C. Johansson, L. Pirjola, M. Ketzel, M. Norman, K. Kupiainen, M. Gustafsson, G. Blomqvist, M. Kauhaniemi, and G. Omstedt, A coupled road dust and surface moisture model to predict non-exhaust road traffic induced particle emissions (NORTRIP). Part 2: Surface moisture and salt impact modelling. *Atmospheric Environment*, Vol. 81, 2013, pp. 485–503.
- [10] Fujimoto, A., R. Tokunaga, M. Kiriishi, Y. Kawabata, N. Takahashi, T. Ishida, and
 T. Fukuhara, A road surface freezing model using heat, water and salt balance and its validation by field experiments. *Cold Regions Science and Technology*, Vol. 106–107, 2014, pp. 1–10.
- 32 [11] Atkins, P. and J. D. Paula, *Physical Chemistry*. Oxford University Press, 9th ed., 2006.
- [12] Webb, R. L., Standard nomenclature for mass transfer processes. *International Communica- tions in Heat and Mass Transfer*, Vol. 17, No. 5, 1990, pp. 529–535.
- [13] Koop, T., The Water Activity of Aqueous Solutions in Equilibrium with Ice. *Bull. Chem. Soc. Jpn.*, Vol. 75, 2002, pp. 2587–2588.
- [14] Wåhlin, J., J. S. Fjærestad, K. Thomsen, and A. Klein-Paste, Thermodynamics of deicing
 chemicals. In *Transportation research board*, 96th annual meeting, At Washington DC, 2017.
- Information 39 [15] Thomsen, K., Modeling electrolyte solutions with the extended universal quasichemical (UNIQUAC) model. *Pure and Applied Chemistry*, Vol. 77, 2005, pp. 531–542.
- 41 [16] Haavasoja, T., J. Nylander, and P. Nylander, Relation of Road Surface Friction and Salt Con-42 centration. In *Proceedings of the 16th SIRWEC conference 23–25th may 2012.*, 2012.
- 43 [17] Klein-Paste, A. and J. Wåhlin, Wet pavement anti-icing A physical mechanism. Cold Re-
- 44 gions Science and Technology, 2013.

- 1 [18] Fjærestad, J. S., J. Wåhlin, and A. Klein-Paste, An experimental setup simulating hoar frost
- formation on roadways. *Journal of Cold Regions Engineering*, Accepted for publication
 2019.
- 4 [19] Norwegian Public Road Administration, D2-ID9300a-7 Usage of salt (in norwegian), 2017.
- 5 [20] Giles, C. G., B. E. Sabey, and K. H. F. Cardew, *Development and Performance of the Portable* 6 *Skid-Resistance Tester*. Road Research Laboratory, London, 1964.
- [21] Bolz, R. E. and G. L. Tuve (eds.) *CRC Handbook of Tables for Applied Engineering Science*.
 CRC Press, 2nd ed., 1973.
- 9 [22] Wåhlin, J. and A. Klein-Paste, The effect of mass diffusion on the rate of chemical ice melting
- using aqueous solutions. *Cold Regions Science and Technology*, Vol. 139, No. Supplement C,
 2017, pp. 11–21.
- 12 [23] Karlsson, M., Prediction of hoar-frost by use of a road weather information system. Meteo-
- 13 *rological Applications*, Vol. 8, No. 01, 2001, pp. 95–105.