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Effectiveness of Combinations of De-icing Salts With NaCl or $CaCl_2$ Brines for Friction Control On Roads

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EFFECTIVENESS OF COMBINATIONS OF DE-ICING SALTS WITH NACL OR $CACL_2$ BRINES FOR FRICTION CONTROL ON ROADS

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ABSTRACT

$CaCl_2$ is frequently used as a de-icing agent especially in situations when it is important to quickly melt ice in very cold conditions. In milder conditions rock salt is the preferred de-icing agent due to its lower cost. To be cost efficient the winter road maintenance operations must adapt according to the conditions on the road and the forecast. FS30 is a frequently used technology to distribute pre-wetted rock salt. In this paper we compare different solutions that can be used in FS30 and explore disadvantages and advantages with the different options. It is concluded that $CaCl_2$ solution is a viable option to the conventional NaCl solution. The $CaCl_2$ solution dissolves more rock salt immediately after mixing than NaCl solution do. This creates more active ice-melting solution on the road and will also facilitate the de-icer to stick to the road surface rather than being transported to the side of the road. $CaCl_2$ solution and mixes of $CaCl_2$ and NaCl does not create a more slippery road surface than pure NaCl solution does.

Résumé

Le chlorure de calcium, $CaCl_2$, est fréquemment utilisé comme agent fondant, en particulier dans les situations de très basses températures quand une action rapide de fonte est requise. À des températures plus douces le sel gemme est généralement employé comme déverglaçant à cause de son coût inférieur. Afin d'être efficaces, les opérations d'entretiens des routes doivent être adaptées aux conditions sur la chaussée et aux prévisions météorologiques.

La technique FS30 dite du sel humidifié est une technologie fréquemment utilisée pour épandre le sel gemme. Dans cet article nous comparons différentes solutions qui peuvent être utilisées pour préparer un mélange de type FS30. Nous comparons les différentes alternatives présentées. Nous démontrons qu'une solution de $CaCl_2$ est une option viable et alternative à une solution de NaCl conventionnelle. La solution de $CaCl_2$ dissout plus de sel immédiatement après mélange comparé à une solution de NaCl. La combinaison sel-$CaCl_2$ développe sur la chaussée une solution déverglaçante plus efficace. Le mélange contenant $CaCl_2$ facilite également l'adhésion du sel humidifié à la surface de la route, au lieu qu'il soit projeté sur les bas-côtés.

Nous constatons qu'une solution de $CaCl_2$ seule ou un mélange de $CaCl_2$ et NaCl ne dégradent pas plus le degré d'adhérence sur la chaussée que ne l'aurait fait une solution de NaCl seule.

1. INTRODUCTION

Rock salt (sodium chloride) is the most frequently used agent to melt snow and ice on roads and for anti-freezing operations although there are a variety of other de-icers available with properties and costs that makes them interesting options in a variety of cases. For example, $CaCl_2$ is used for de-icing purposes. A winter road maintenance strategy needs to adopt the most cost-effective de-icing and anti-icing measures depending on the weather and traffic conditions. Although rock salt may be the cheapest de-icing agent at moderately cold temperatures it may not be the most cost-effective one considering all kinetically controlled processes occurring at the road level.

$CaCl_2$ and $MgCl_2$ have some features compared to NaCl that makes them particularly interesting in winter road maintenance. The lowest freezing points (eutectic points) for calcium chloride and magnesium chloride solutions are approximately -50°C and -33°C respectively, while NaCl solutions has a eutectic point at -21°C. Hence $CaCl_2$ alone or mixed with NaCl is used for de-icing on very cold days. The ternary phase diagrams of $NaCl-CaCl_2-H_2O$ at sub-zero temperatures [1] shows for example that a mixture of equal parts of NaCl and $CaCl_2$ at a total concentration of 20 % will remain in the liquid phase at -28°C. Moreover, the dilution of $CaCl_2$ solutions is an exothermic process. The differential heat of dilution for $CaCl_2$ solutions at mass fraction of 0,4 and 0,3 are approximately 117 and 34 J/g(water), respectively [11, 12]. The heat released at dilution could assist in dissolving NaCl as this is an endothermic process requiring 65.8 J/g [2].

Different weather conditions require different spreading methods for optimal de-icing. Solid rock salt melts ice slowly and when granular NaCl is applied, it will quickly be transferred to the side of the road by traffic [4-6]. Moist granular material and solutions however adhere better to the road surface compared to dry material and will stay on the road for a longer time. It has been shown that preventive de-icing is more efficiently performed with either a 20 % NaCl solution alone, FS100(NaCl) or with brine wetted salt, for example 70 % of granular rock salt spread together with 30 % of a 20 % NaCl solution, FS30(NaCl) [4]. A drawback of using FS100(NaCl) compared to FS30(NaCl) is that larger volumes of material must be transported, limiting the operating range of de-icing vehicles. As moist road surfaces can hold de-icers better than dry surfaces there should be a difference in the permanence of the anti-icing effect using $CaCl_2$ or NaCl as the former stays wet until 30% air humidity and the latter dries below 85 % air humidity.

In this study, the performance of four different salt solutions that can be used as pre-wetting agents in the FS30 technology have been compared. Slip resistance, dissolution kinetics of rock salt with the solution and permeance of the de-icer on road surface replicas during simulated weather changes has been investigated. All salt solutions were 20 % by weight in total and are presented in table 1. Solution A and B are representative of the liquids used in wetted salt spreading while solution C and D have the same mass ratio between NaCl and $CaCl_2$ as FS30($CaCl_2$) (solution C) and FS50($CaCl_2$) (solution D).

Table 1 – Salt solutions used for the laboratory evaluation tests

Solution:	**A**	**B**	**C**	**D**
NaCl	20 %	0	18,4 %	16,7 %
$CaCl_2$	0	20 %	1,6 %	3,3 %

2. FRICTION

To evaluate if there are reasons to expect a difference in friction properties of road surfaces with the different de-icing solutions road replica surfaces soaked with the de-icers were tested with the pendulum friction tester as specified in EN 14231 [7] and CEN/TS 16811-3 [8]. The test was performed both at 5°C and at -5°C with ten individual measurements in two directions on each of six specimens mimicking asphalt concrete with 10 mm maximum chipping size and with a texture depth of at least 0,6 mm. The mean of the slip resistance values (SRV_1) for each de-icer and temperature are presented in table 2. In addition, the ratio between slip resistance values for the de-icers and the slip resistance value for water, SRV_e, on the same surfaces at 5°C are shown in table 2. The slip resistance for water at 5°C was 70,3.

Table 2 – Slip resistance values, SRV_1, and ratios, SRV_1/SRV_e at 5°C and at -5°C

Solution	**A**	**B**	**C**	**D**	
SRV_1 @ 5°C	64,5	62,5	64,4	64,5	
SRV_1/SRV_e @ 5°C	0,92	0,89	0,91	0,92	
SRV_1 @ -5°C	63,1	62,8	63,3	65,7	
SRV_1/SRV_e @ -5°C	0,90	0,89	0,90	0,93	

The slip resistance on the replica surfaces with all four salt solutions are of similar magnitude which is a strong indication that mixtures of NaCl and $CaCl_2$ will not decrease tire/road friction compared to NaCl solutions. Slip resistance test of NaCl/$CaCl_2$ mixtures has also been performed by Gaudé et al. [9] who recorded average SRV_1/SRV_e ratios between 0,85 and 0,96 in the same temperature range from -5°C to 5°C.

3. DISSOLUTION KINETICS

It is the salt solution applied or created on the road surface that will melt ice or snow, or prevent ice formation when the temperature drops. As shown by the measurements carried out by Hausmann [4] salt solutions have a considerably longer lying time than granular salt on trafficked roads when applied in preventive anti-icing operations. When the FS30 technique is used in anti-icing or de-icing operations it is of importance that as much solid salt is dissolved as quickly as possible.

To quantify and compare the rate of dissolution of solid NaCl in the different salt solutions A-D the following test, adopted from [9] were used: Five holes with a diameter of 1 mm was drilled on one side of a graduated and transparent plastic tube with an inner diameter of 15 mm and an outer diameter of 20 mm. The holes were drilled 20 mm, 40 mm, etc. from the bottom of the tube and a 1 x 1 mm mesh was placed 10 mm from the bottom of the tube. Granular NaCl was dried at 105 °C and 45 g with a sieve size between 2 mm and 3,35 mm was used for each test. The salt was transferred to the tube which in turn was placed in a 600 ml beaker with an inner diameter of 85 mm filled with 350 g of the test solution. The bottom of the tube rested on the bottom of the beaker. A magnetic 34 x 5 mm stirrer at 250 rpm kept the solution in motion. The height of the granular NaCl column was recorded for 60 minutes. The test was performed twice for water and each solution A-D at 22 °C. The test was also repeated with water at 5 °C. The results of the dissolution test are shown in figures 1 and 2.

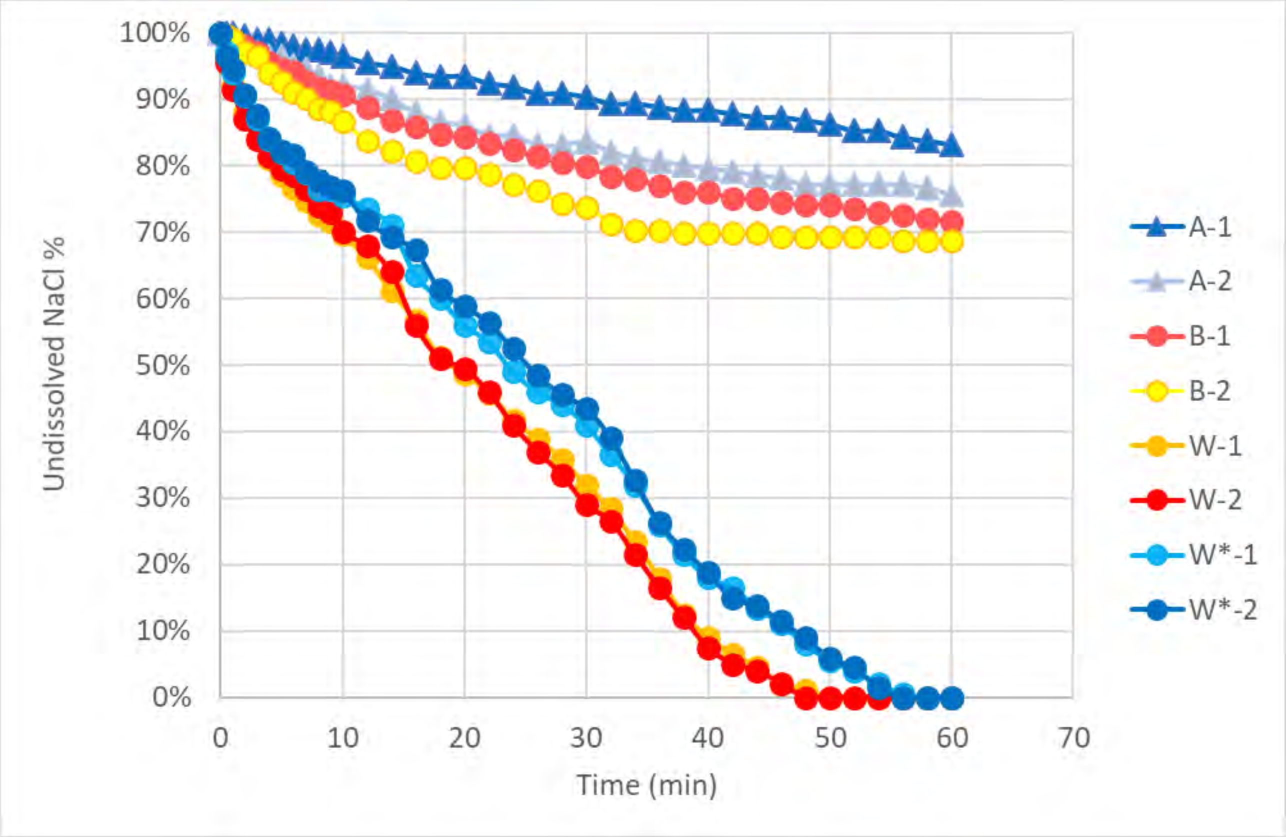

Figure 1 – Dissolution of NaCl in solution A, B and water (W) at 22 °C. Dissolution of NaCl in water at 5 °C (W*).

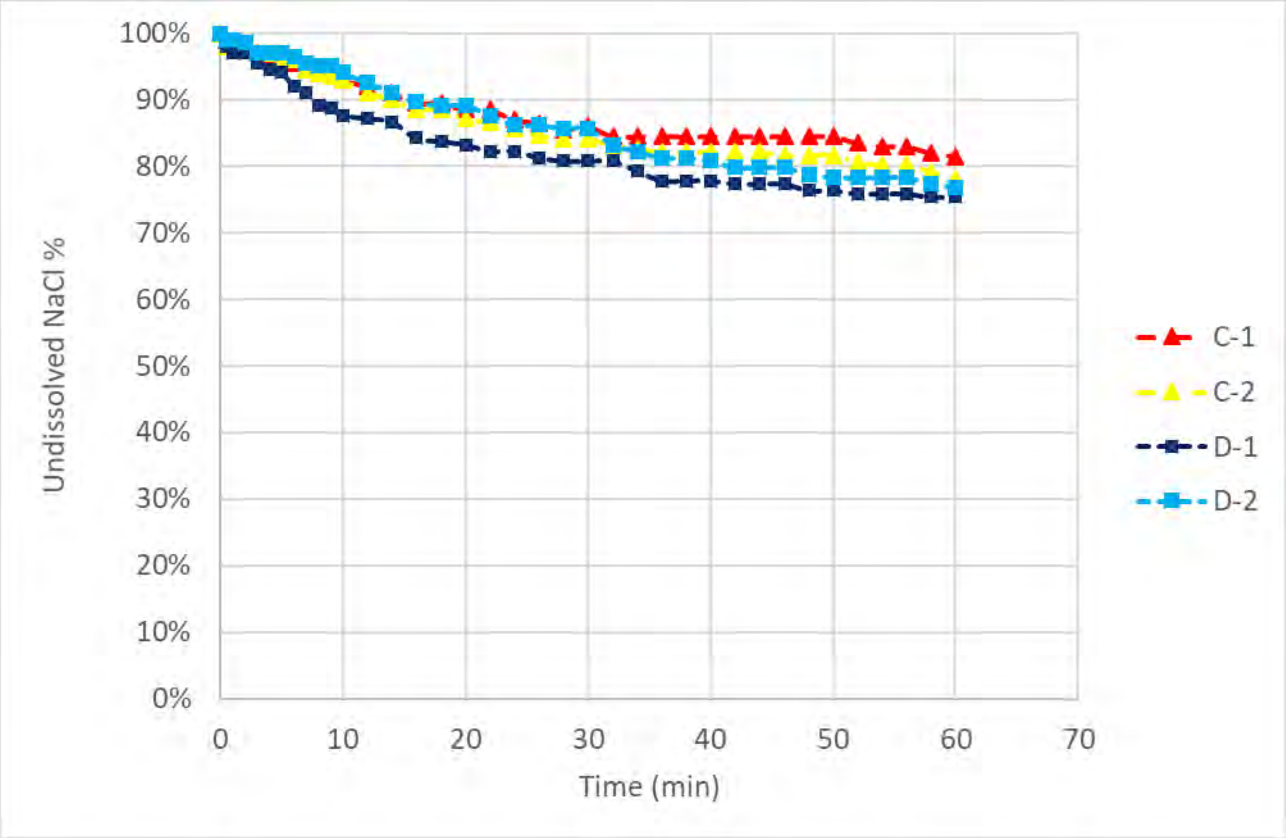

Figure 2 – Dissolution of NaCl in solution C and D at 22 °C.

The two sets of tests with dissolution of NaCl in water at two temperatures shown in figure 1 demonstrate that there is a slight temperature dependence of the dissolution rate of

NaCl. Figure 1 also show that the dissolution rate of NaCl is faster in a 20 % solution of $CaCl_2$ than in a 20 % solution of NaCl. The dissolution rate of NaCl in the two solutions C and D consisting of mixtures $CaCl_2$ and NaCl, falls in between the rates recorded in the pure solutions of 20 % NaCl and $CaCl_2$, respectively.

The rate of dissolution is of importance for the permanence of the de-icer on the road surface using the FS30 technology. It has been shown that solutions of de-icers stay much longer on a trafficked road than granular material and that most of the spread de-icer could be lost during the first hour [9]. Hausmann argues that use of FS100 is more efficient than FS30 for anti-icing purposes [4]. However, the operation range for de-icing vehicles using FS30 is longer. Since de-icing distributing vehicles could carry and distribute more salt using the FS30 compared to the FS100 technique it is crucial that as much as possible of the solid salt is dissolved as rapidly as possible after distribution. The data in figure 1 indicates that using FS30($CaCl_2$) will give a significant increase of the amount of dissolved NaCl in the crucial initial phase after spreading compare to using FS30(NaCl).

4. PERSISTENCE OF DE-ICING SOLUTION

As described earlier dry de-icers are easily transferred to the road-side by the traffic while solutions and wetted de-icers adhere better to the road surface. Keeping the de-icers on the road will create a long lasting anti-icing effect. During winter, cold fronts often carry dry air and the road surface dries up.

To examine the difference of how different de-icers dries up and consequently either sticks to the road surface or is blown away by the traffic the following test were performed on six pieces, 125 mm x 100 mm, of road replica surfaces with identical properties to those used to characterize slip resistance above. After equilibrating the plates and the de-icing solution to 4 °C and weighing the plates, a large quantity of de-icer solution was applied on each plate and distributed with a brush. The plates were tilted approximately 45° and excess de-icer solution was removed with a dry cloth. After weighing the plates were placed horizontally in a climatic chamber at 10 °C and 80 % relative humidity. After 30, 60, 90 and 120 minutes, the plates were quickly transferred from the climatic chamber to a scale for weighing. The climatic chamber was programmed to lower the relative humidity in three steps. After 30, 60 and 90 minutes the set-point for the relative humidity was decreased to 60 %, 40 % and 20 % relative humidity, respectively. The actual relative humidity in the climatic chamber fell gradually from 80 % at 30 minutes to 20 % at the end of the test. The average remaining mass of the de-icer was calculated from recorded data. The initial mass of de-icer solution at the beginning of the test on each plate were between 1,2 and 2 g. The data is presented in table 3 and in figure 3.

Table 3 – Residual mass of de-icer on horizontal road replica surface. Temperature and relative humidity see text.

De-icer solution	**A**	**B**	**C**	**D**
Time (min)				
0	100	100	100	100
30	87,6	92,1	88,7	89
60	68,7	73,5	69,6	70,6
90	51,5	59,4	52,4	53,9
120	35,8	55,6	40,3	38,2

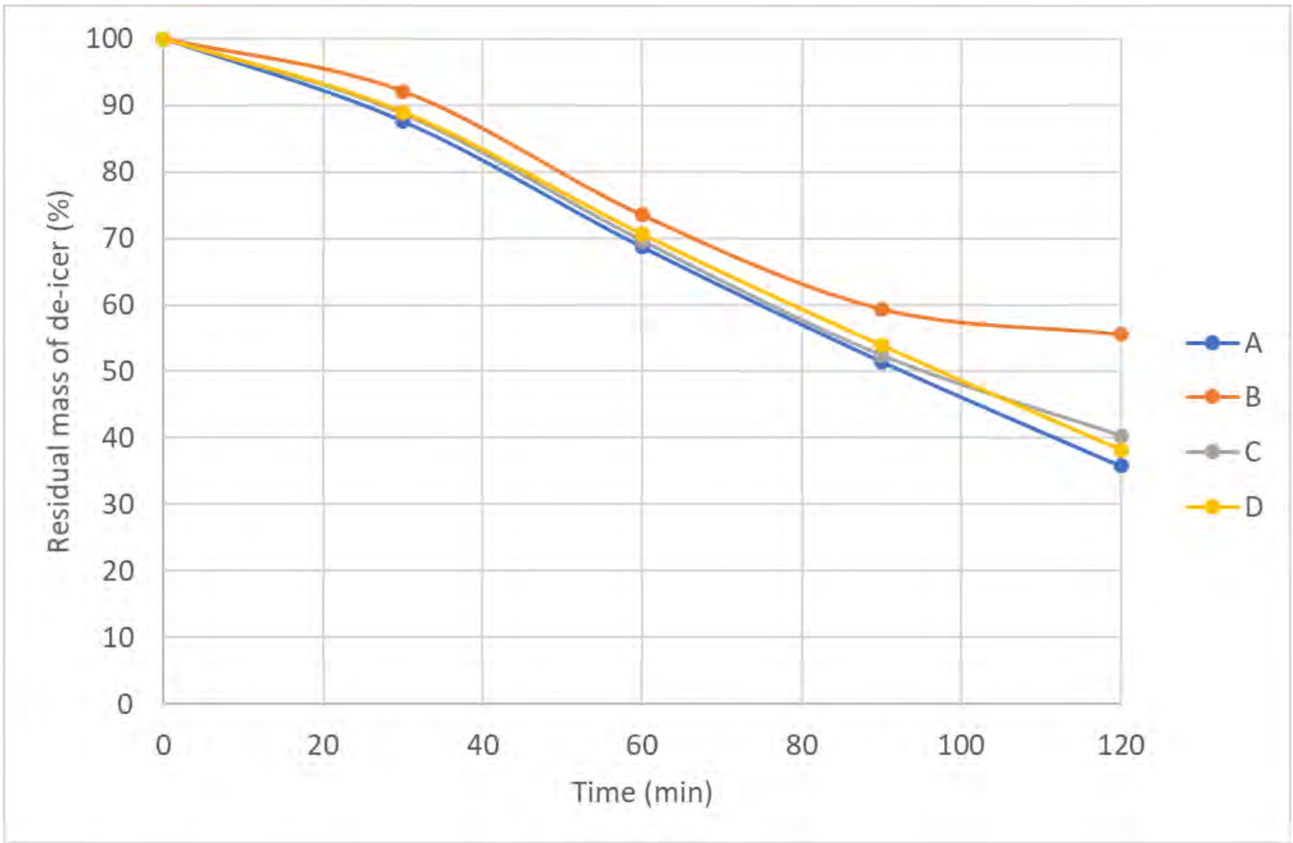

Figure 3 – Residual mass of de-icer solutions on road replica surface during a simulation of an approaching cold front. Temperature was kept at 10 °C and the relative humidity fell from 80 % to 20% between t=30 min. and t=120 min.

During the simulation of an approaching cold front with dry air the mass loss of the de-icer solutions with NaCl (A) and mixtures of NaCl with a small fraction of $CaCl_2$ (solution C and D) were quite similar. The mass loss is due to the evaporation of water from the solution. The solution with $CaCl_2$ differed from the other de-icer solutions with a significant lower mass loss at the end of the simulation. The slower evaporation rate from the $CaCl_2$ solution is beneficial from an anti-icing perspective as it will help make the de-icer stick to the road surface.

5. CONCLUSIONS

Based on the results, the following conclusions can be drawn for practical applications:

- Using FS30 with $CaCl_2$ solution or mixes of $CaCl_2$ and NaCl solutions will not create more slippery surfaces than the same technology with NaCl solutions.
- FS30 with $CaCl_2$ solution dissolve more NaCl in the initial phase after applying the de-icer. This is beneficial for two reasons since solutions stick to the road surface to a higher degree than granular material thus reducing the amount of de-icer transported to the side of the road and it increases the amount of active de-icing solution on the road.
- In winter conditions when weather changes from warm damp conditions to dry and cold conditions the hygroscopic properties of $CaCl_2$ could increase the time when the road is moist with de-icing solutions and thus in some cases increase the time to the next de-icing operation.

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