Investigating Pre-Wetting with a New Ice Melter Performance Test

Salt, Safety, and the Environment

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Abstract: Pre-wetting of deicing salt has been shown to be an effective way to decrease chemical application rates, increase ice melting speed, and improve performance at colder temperatures. The optimization of chemical deicing strategies - e.g. application rates, choice of pre-wetting brine and performance enhancing additives, ratio of pre-wetting brine to rock salt, etc. - requires an understanding of how these factors affect ice melting performance at different temperatures and this, in turn, requires reliable testing methods. The most commonly used salt deicer performance tests at the moment are based on the SHRP Standard H205.1 and suffer from a relatively high degree of variation due to the difficulty of quantitatively recovering all of the ice melt and of maintaining consistent contact between deicer particles and ice. A new ice melter performance test method has been developed in which ice cubes and deicer are mixed in a jacketed, insulated reactor maintained at a precise temperature by a recirculating temperature bath. Instead of attempting to physically recover and measure all of the ice melt directly, the quantity of ice melt can be determined indirectly by a new “tracer dilution” approach. By analysis of two “tracers” (such as Mg^{+2} or Ca^{+2} ion from a pre-wetting salt brine containing $MgCl_2$ or $CaCl_2$) and Cl^- ion before and after a given period of time, the quantity of ice melt can be calculated from a mass balance. This approach permits the simultaneous measurement of ice melting rates and deicer dissolution rates under different conditions. The method provides ice melting capacities for salt that are in good agreement (within 1.7%) with theoretical values predicted from the binary sodium chloride/water phase diagram and with much more precision than the SHRP approach . This method was used to measure the ice melting rate of pre-wetted salt treated with different pre-wetting brine formulas at -19.3 ^{0}C. The effect of different pre-wetting brine compositions on acceleration of salt’s ice melting rate have been measured by this new approach.

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Introduction

As urbanization increases, there is increasing demand for quickly returning roads to a safe condition following winter storms, but there is also increasing need to manage the cost and environmental impact of deicing. A variety of best practices have been developed in recent years which permit substantial reductions in the amount of road deicing chemicals entering the environment[1]. The use of liquid deicers, in particular, for anti-icing and pre-wetting is one of the most effective strategies for maximizing the efficiency of ice melting chemicals and minimizing application rates. The practice of pre-wetting and anti-icing has increased dramatically in recent years as its value becomes more widely recognized.[2] General guidelines for anti-icing and pre-wetting have been developed based upon field experience[3]. Attempts to more precisely optimize pre-wetting conditions have been made through controlled field tests in recent years.[4-5] While field performance is always the ultimate effectiveness gauge of any winter maintenance practice, the high intrinsic variability and difficulty of control in field tests is not ideal for developing a precise understanding of how different variables affect deicer performance. Precise measurements of deicer performance are best made under lab test conditions, where variables can be tightly controlled. However, even lab measurements of deicer performance have proved challenging. A variety of approaches for measuring deicer performance have been proposed over the years. Nilssen recently reviewed published test methods for measuring the ice melting capacity of salt (NaCl) and found that there was substantial variability between methods and often a significant deviation between experimental measurements and the expected theoretical value.[6] Thus, as deicing practices become more sophisticated, moving beyond the simple application of rock salt to salt pre-wetted with various liquid compositions at various ratios, there would be value to a test method that could accurately and precisely measure the ice melting performance to better understand how different pre-wetted salt compositions perform and to better identify optimum deicer chemical treatments for different conditions.

We have recently developed[7] a novel approach to measuring the ice melting performance of deicers which is significantly more accurate and precise than the standard SHRP H205.1 method[8]. Most of the previous test methods for measuring deicer ice melting performance are variations on the SHRP approach, which simply involves contacting ice with a quantity of deicer at a controlled temperature and then measuring the volume of ice melt produced after a period of time. A chief source of variation in measurements by this approach is the difficulty of quantitatively recovering all of the ice melt, and the relative uncertainty increases when trying to measure the smaller ice melt values that occur in the colder temperature ranges where enhanced deicer formulas are of most interest. Thus, it would be preferable to measure ice melting indirectly, if possible, and avoid the difficulty of collecting and measuring small quantities of ice melt. This may be done by a new “tracer dilution” method. By this approach, rather than directly separating and measuring all of the ice melt, it is only necessary to remove a small aliquot of ice melt for chemical analysis. The quantity of ice melt is determined from the change in concentration of suitable “tracers” in the deicer. The tracer can be a component of the deicer itself, such as Ca^{+2} in $CaCl_2$, or it may be a separate chemical added specifically for the purpose, such as a dye. This approach is very useful for measuring the ice melting performance of prewetted salt. When ice and solid salt are added to a prewetting brine of known composition, the prewetting brine will be diluted by the ice that melts and by the solid salt that dissolves. Analysis of the change in concentration of two tracers permits calculation of both

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of these terms. This method was shown to measure the ice melting capacity of salt to within 1.7% of the theoretical value from the NaCl/water phase diagram.[7]

Previously, this approach was applied to measuring the ice melting rate of salt prewetted with brines which had first been equilibrated with ice so that there would be no ice melting contribution from the prewetting brine itself.[7] This provided insight on the ability of different prewetting brines to increase the ice melting rate of solid salt at very cold temperatures but was somewhat "unrealistic" since diluted brines of that sort are not used for prewetting in the field. We report herein for the first time the application of this method to measuring the ice melting rate of salt prewetted with typical "full strength" prewetting brines at very cold temperatures.

Experimental Procedures

A detailed explanation of the experimental procedure has been published elsewhere.[7] In brief, ice melting tests were carried out in a 1 liter jacketed reaction vessel connected to a recirculating temperature bath which held the internal temperature to -19.3 +/- 0.05 ^{0}C. Pre-wetting brines and solid salt and small ice cubes were stored in a separate freezer at -19 ^{0}C until used. Prewetting brines were prepared from reagent grade NaCl, $CaCl_2$, $MgCl_2$, potassium acetate, potassium formate, and deionized water. The pre-wetting brines were made by blending 70 parts by weight of a 23.3% NaCl brine (which had been saturated with $CaSO_4$ to provide Ca^{+2} as a tracer) with 30 parts of 30% $CaCl_2$, 30% $MgCl_2$, 50% potassium formate, or 50% potassium acetate. The prewetting brines were stored in a freezer at -19 ^{0}C for several weeks before use, over which time some NaCl precipitated in the form of large crystals. All of the brines were analyzed to determine initial tracer ion concentrations just prior to use. All of the brines were analyzed for Cl^- and Ca^{+2} except for the $MgCl_2$ brine blend, which was analyzed for Mg^{+2} as the tracer rather than Ca^{+2}. In a typical experiment, 100.00 grams of prewetting brine was added to the reaction vessel. Then 60.00 grams of solid salt (solar salt screened to 1.68 - 2.00 mm in size) and 200.0 grams of ice cubes made from deionized water were rapidly added and a stop watch started. The system was quickly sealed and stirred with an overheard mixer at 130 rpm. After 10.0 minutes, the mixer was stopped and a ~ 10 mL aliquot of ice melt was removed from the vessel with a pipet. The aliquot was subsequently analyzed for tracers and the mass of ice melted and the mass of solid NaCl dissolved were calculated from the tracer analysis as described previously.[7] At least triplicate measurements were made for each prewetting brine and salt combination, but only a single measurement was made on the prewetting brine alone. Separate experiments were done to measure the ice melting contribution from the prewetting brine alone after mixing with ice for 10.0 minutes and after mixing for at least 5 hours to determine the brine's equilibrium ice melting capacity.

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Results and Discussion

Table 1 shows the total mass of ice melted by the prewetted salt mixtures Standard deviations of the average mass of ice melted and mass of salt dissolved are listed parenthetically. Table 2 shows the mass of ice melted by the prewetting brine alone after 10 minutes and at equilibrium. Subtracting the value of ice melted by the prewetting brine alone after 10 minutes from the total mass of ice melted by the prewetted salt mixture gives a formalized mass of ice melted by the solid salt component only.

Prewetting Brine	Average Mass of Ice Melted (grams)	Average Mass of Solid NaCl Dissolved (grams)
NaCl brine + solid salt	12.03 (0.75)	3.08 (0.18)
70/30 NaCl/$CaCl_2$ brine blend + solid NaCl	25.98 (0.79)	5.98 (0.15)
70/30 NaCl/$MgCl_2$ brine blend + solid NaCl	28.34 (0.17)	6.71 (0.10)
70/30 NaCl/K Acetate blend + solid NaCl	31.37 (0.55)	12.46 (0.20)
70/30 NaCl/K Formate blend + solid NaCl	37.90 (1.26)	16.90 (0.38)

Table 1. Ice melting action of prewetted salt at -19.3 C after 10 minutes.

Prewetting Brine	Mass of Ice Melted by Prewetting Brine Only after 10 Minutes (grams)	Equilibrium Mass of Ice Melted by Prewetting Brine Only (grams)	Mass of Ice Melted by Solid NaCl Only after 10 Minutes (grams)
NaCl brine	6.99	7.29	5.04
70/30 NaCl/$CaCl_2$ brine blend	12.43	16.50	13.55
70/30 NaCl/$MgCl_2$ brine blend	14.39	18.90	13.95
70/30 NaCl/K Acetate brine blend	11.04	14.79	20.33
70/30 NaCl/K Formate brine blend	8.60	11.69	29.3

Table 2. Ice melting action of brine and solid salt components of prewetted salt mixture at -19.3 ^{0}C.

Ice melt measurements were deliberately made at the very cold temperature of -19.3 ^{0}C to see how much increase in ice melting can be realized at a temperature where ordinary rock salt is considered ineffective (rock salt is often considered ineffective below a temperature of about -9 ^{0}C (15 ^{0}F)). Tests were done under conditions of high mixing to minimize test variation and to determine upper limiting values of ice melting rates under what might simulate a high traffic action situation. Ice melting rates would be expected to be lower under static conditions where

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diffusion rates of the dissolving salt may be limiting.[9] Even at temperatures as low as its eutectic (-21 ^{0}C) salt has substantial ice melting capacity, but its effectiveness is limited by a decrease in ice melting rate at colder temperatures.[9] Prewetting increases salt's ice melting rate, thereby effectively lowering its effective temperature range. Furthermore, different brines will accelerate the ice melting rate of salt to different extents – not all prewetting brines are "created equal.[7,9] Thus, there may be opportunities for optimizing and "tuning" a prewetted salt composition for maximum cost effectiveness and minimal environmental impact (i.e. by quantifying how much deicing chemical can be utilized and not applying more than that) under particular conditions of precipitation, temperature, traffic, etc. The ice melting action of prewetted salt is a complex process involving several interacting steps including 1) the ice melting action of the prewetting brine itself, 2) the ice melting action of the solid salt component, and 3) the rate of dissolution of the solid salt component which in turn will be affected by the previous two factors. The performance test described here provides a way to both measure the total ice melting rate of a prewetted salt mixture and also understand how the individual components are contributing.

Perhaps the first conclusion to be drawn from the experimental examples above is that initially ice melting is dominated by the prewetting brine itself, i.e. liquid deicers melt ice *much* faster than solid salt. Comparison of the ice melt values due to the prewetting brine alone after 10 minutes to the brines' total equilibrium ice melting capacities in Table 2 shows that all of the NaCl brine blends reached ~ 75% of their total available ice melting capacity in 10 minutes and the pure NaCl brine reached 96% of its total ice melting capacity. Using a value of 3.59 grams of total ice melting capacity per gram NaCl at this temperature[9], the 60 grams of solid salt in these tests had 215.4 grams of total available ice melting capacity, and the data in Table 2 shows that only between 2.3% and 13.6% of the total ice melting capacity of the solid salt was achieved after 10 minutes. This is not necessarily surprising, since the ice melting due to solid salt will be limited by its dissolution rate and that, in turn, will be limited by the rate at which ice can melt and dilute the brine to facilitate further salt dissolution. But this points to the value of prewetting for ice melting enhancement. The liquid component provides relatively fast ice melting action even at very cold temperatures, but it has limited total ice melting capacity due to its high water content. Solid salt has a much higher ice melting capacity because it is pure deicing chemical, but its action is slow due to inefficient contact between the ice and the chemical until it dissolves. Thus, the prewetting brine provides a medium which can melt ice quickly and the solid salt provides a "reservoir" of additional chemical to continually replenish the ice melting capacity of the prewetting brine.

The data in Tables 1 and 2 illustrate that different prewetting brines will do this more or less efficiently. Salt prewetted with all of the "enhanced" NaCl brine blends in this test melted ice faster at -19.3 ^{0}C than salt prewetted with a straight 23.3% NaCl brine, illustrating the value provided by the brine additives in extending the low temperature effectiveness of salt. Ice melting rates increased by a factor of between 2.2 and 3.2 compared to salt prewetted with plain NaCl brine. The tests above indicate that salt prewetted with blends of NaCl brine with potassium acetate or potassium formate provided the highest ice melting rates at this temperature. Interestingly, the mass of ice melted by the prewetting brine alone was lower for the brine blends with acetate and formate than it was for the blends with $CaCl_2$ and $MgCl_2$. A simple model might suggest that prewetting brines which produced more ice melt would better facilitate the dissolution of solid salt and a yield a faster ice melting rate, but that was not observed in these tests, and this mechanistic curiosity merits further investigation. However, while the acetate and formate blends showed higher ice melting rates than the $CaCl_2$ and $MgCl_2$ blends, the acetates and formates are considerably more expensive than $CaCl_2$ and $MgCl_2$. With an understanding of chemical costs, this type of approach could be used to calculate relative cost effectiveness of different pre-wetting scenarios under given conditions of time, mixing/traffic action, temperature, etc.

The results described above are preliminary and intended to illustrate a novel approach to more precisely measuring the ice melting performance of prewetted salt compositions and better understanding how deicer performance may be optimized under different environmental conditions (temperature, traffic action, etc.). The test conditions used in the initial test development were chosen to be experimentally convenient - permitting efficient mixing of the ice and deicer to minimize test variation. In particular, the ratio of prewetting brine to solid salt was substantially higher in these tests than is typically used in the field. Future work will involve extending these measurements to a wider range of conditions to better understand the effect of the ratio of prewetting brine to solid salt and how to optimize prewetting scenarios and application rates under "real world" conditions.

Conclusions

A novel test method has been developed for measuring the melting rate of ice by chemical deicers which avoids the imprecision associated with the direct collection and measurement of ice melt in the more commonly used approaches. Ice melt rate can be measured accurately and precisely by measuring the change in concentration of chemical "tracers" in a small aliquot of the ice melt. This method was applied to measuring the ice melting rates of 60 parts of solid salt prewetted with 100 parts plain NaCl brine and 70/30 blends of NaCl brine with brines of $CaCl_2$, $MgCl_2$, potassium acetate, and potassium formate equilibrated to a temperature of -19.3 ^{0}C. The blends with $CaCl_2$, $MgCl_2$, potassium acetate, and potassium formate melted ice 2.2, 2.4, 2.6, and 3.2 times faster than with plain NaCl brine in the first 10 minutes with high mixing. The prewetting brines were also shown to affect the ice melting rate of the solid salt component of the mixture differently. The ice melting rates due to the solid salt component only of the mixture prewetted with brine blends containing $CaCl_2$, $MgCl_2$, potassium acetate, and potassium formate were 2.7, 2.8, 4.0, and 5.8 times faster than with plain NaCl brine. The study illustrates that the chemical composition of the prewetting brine has a significant influence on the ice melting rate of prewetted salt. The testing approach has potential to be a useful tool for characterizing and optimizing the performance of various prewetted deicer compositions under different conditions. The testing approach will benefit from further work to better simulate realistic field application conditions.

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