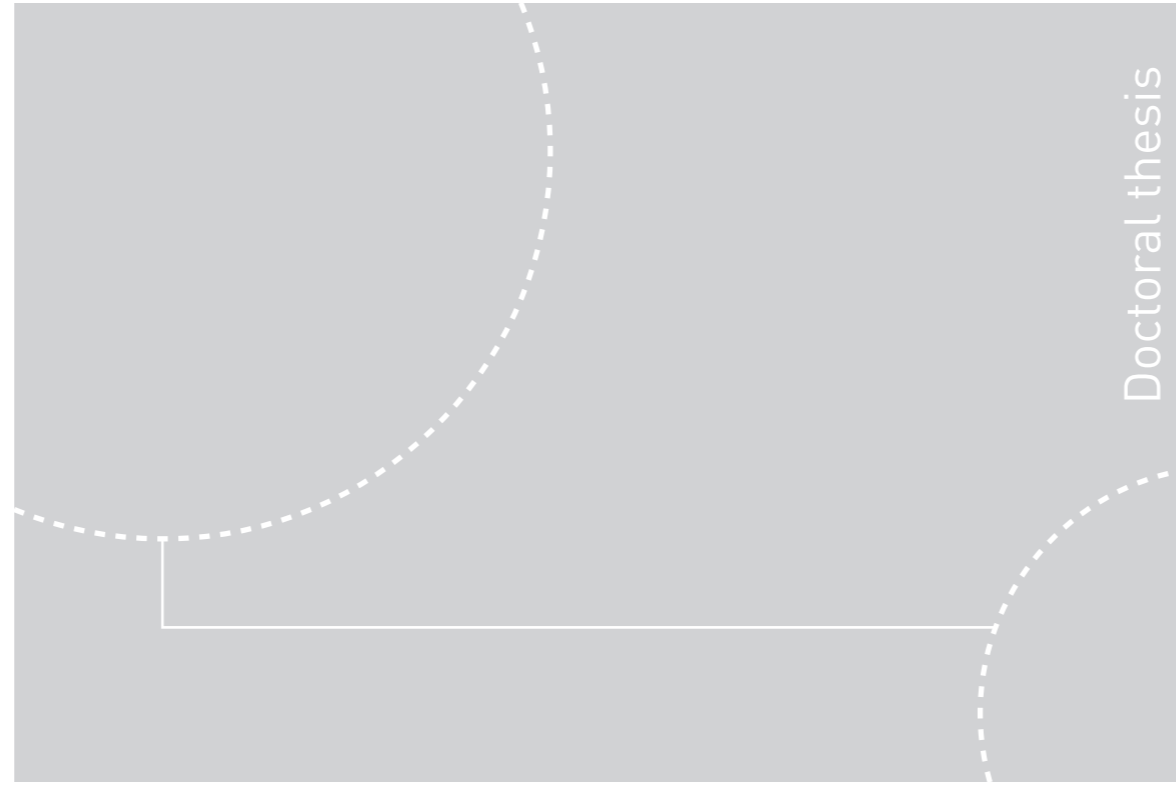


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Kine Nilssen

ICE MELTING CAPACITY OF DEICING CHEMICALS IN COLD TEMPERATURES

NTNU
Norwegian University of Science and Technology
Thesis for the Degree of
Philosophiae Doctor
Faculty of Engineering
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Abstract

Cold climates cause a great number of challenges when it comes to maintaining road conditions. For instance, snowstorms, frost and ice can all create slippery and even impassible roads. Therefore, in order to ensure vehicular mobility and general road safety, winter road maintenance requires the use of plowing and applying sand or various chemicals.

Regarding the latter method, chemicals are applied to weaken bonds in snow and ice, melt snow and ice or prevent ice from forming on the road. A deicing chemical must thus comprise several important elements, one very important element being its ability to melt snow and ice, which is also called its *ice melting capacity*.

Therefore in order to be able to compare and choose the proper deicing product, it is essential that one is knowledgeable about its ice melting capacity. There have been concerns for many years that the standardized method for measuring ice melting capacity, SHRP H-205.1 for solid and H-205.2 for liquid chemicals, is not reproducible or reliable enough for research purposes. The work performed and outlined in this particular dissertation involves a) a literature review of existing ice melting capacity tests with calculations to determine their accuracy, b) an explanation as to how ice melting capacity can be calculated if the applied chemical has a known phase diagram, c) the development of a new test method for measuring ice melting capacity and determination of equilibrium concentration of deicers, and d) measurements of the ice melting capacity of common deicers in cold temperatures.

It was confirmed that the “SHRP tests” are not accurate enough for research purpose. A new method based on calorimetry, “the calorimeter” was created, and a custom-made calorimeter was built for the research purposes. The idea behind the calorimeter was to measure the amount of energy needed to prevent temperature drop when deicing chemicals are added to ice; this reading can then be used to calculate the amount of melted ice. The calorimeter showed a great improvement in accuracy compared to earlier test methods. It was able to produce accurate results for solutions in cold temperatures; between -0.001g to 0.016g, which is an absolute error from 97% to 115% and an average error of 4%. The calorimeter was used to study the ice melting capacity of NaCl, MgCl₂, CaCl₂, CMA, KFo and sugar, both as individual chemicals and as additives to NaCl at -18°C. The test revealed the huge difference in melting capacity between solid and liquid chemicals (solutions). The ice melting capacity of the solutions was only 3% – 10% of the solid ice melting capacity. Moreover, out of all the tested chemicals, brine (23% NaCl solution) had the lowest melting capacity except for sugar, which froze at -18°C. However, in a solid state NaCl was the chemical having the highest ice melting capacity, performing 31% better than the

chemical coming in second place, calcium chloride ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$). Further, as an example, the results were used to calculate application rates for a thin ice layer (0.1mm) at -18°C . The application rate using solid NaCl was within normal ranges, about $30\text{g}/\text{m}^2$. However, it was unrealistically high when using solutions. Using MgCl_2 , CaCl_2 , CMA, KFo or sugar as additives to NaCl in a solid state decreased the ice melting capacity of NaCl. Using chloride solutions (MgCl_2 and CaCl_2) as additives to brine resulted in a melting capacity between the melting capacity of the components, the improvement was dependent on the amount of MgCl_2 or CaCl_2 . However, different results were produced by using KFo and CMA; KFo had a destructive influence on the ice melting capacity when mixed with brine, while CMA produced higher ice melting capacity than what the two components had individually. Nonetheless, the ice melting capacity was still very low.

The general conclusions of salting roads in cold temperatures, are that it is possible to achieve sufficient ice melting capacity using solid NaCl at -18°C . Used as solid, NaCl actually have relative high ice melting capacity compared to other commonly used deicers. The general conception of NaCl being “ineffective” when it is cold, must come from other qualities, e.q., low ice melting rate. Therefor, more knowledge is needed to be able to optimize the use of salt when it is cold. With temperatures below eutectic point of NaCl (-21.1°C), is the ice melting capacity of NaCl zero and should not be used. The best strategy is to dry up the road in advance to this temperature, but if the chemicals are needed the results in this dissertation implies that solid CaCl_2 or KFo would be the best replacement for NaCl. If solutions are the only option (e.q., impossible to get the solid salt to lay on the road), calculations in this dissertation show that using the right concentration of solutions is crucial. With maximum solubility of MgCl_2 and CaCl_2 solutions, the application rate for achieving sufficient ice melting capacity in cold temperatures on a thin ice layer is approximately $150\text{ g}/\text{m}^2$ at -18°C , in comparison using a 20% MgCl_2 and a 25% CaCl_2 solution gives extreme application rates of 550 and $400\text{g}/\text{m}^2$.

Preface and acknowledgments

This dissertation has been submitted to the Norwegian University of Science and Technology (NTNU) for partial fulfillment of the requirements for the degree of *philosophiae doctor* (PhD).

The work was carried out between September 2013 and June 2017 at the Department of Civil and Transport Engineering at NTNU Trondheim (Norway) and at the University of Washington in Seattle (USA) during a ten-month stay from September 2014 to June 2015. The research project presented in this dissertation was funded by the Norwegian Public Roads Administration (NPRA), for which I express my gratitude. I would like to thank in particular NPRA staff members Kai Rune Lysbakken, Torgeir Leland and Øystein Larsen for both their interest in the project and their advisement.

First and foremost, I would like to thank my supervisors, Alex Klein-Paste and PhD Johan Wåhlin, who believed in me, supported me, and contributed with significant hours of working in the lab, correcting my papers and giving me guidance: I could not have done this without you.

I would also like to thank Bent Lervik, Jan Erik Molde and Frank Stæhli for providing my lab equipment. Special thanks to my colleagues Lisbeth, Sara, Doreen, Elena, Leigh and Yanbo for making me want to come to work every day and enjoy my time at the university so much!

My son Johan was born during my time as a PhD candidate and has witnessed hours of writing during his first months of life; thank you for making my own life great. Tore, thank you for your sense of humor and your ability to cheer me up. Åse and Steinar, thank you for believing in me. Finally, I would like to thank my dad for always being there for me.

Trondheim, June 28th 2017

Kine Nilssen

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List of abbreviations and definitions

Bare road surface	Road surface clear of snow and ice
Brine	23 w% NaCl solution
CaCl ₂	Calcium Chloride
CMA	Calcium Magnesium Acetate
Cold temperatures	Not defined as one temperature, but lower than approximately -15 °C (5°F)
Deicing chemicals	Chemicals used in winter maintenance to melt snow/ice, prevent ice from forming on the road or prevent compacted snow (freezing point depressants)
Deicers	Materials/products/chemicals used in winter maintenance to melt snow/ice, prevent ice from forming on the road or prevent compacted snow (freezing point depressants)
Eutectic point	Temperature and the chemical concentration (w%) of a liquid mixture (solution) corresponding to the lowest freezing point of the mixture
IMC	Ice Melting Capacity
KFo	Potassium Formate (KCOOH)
MgCl ₂	Magnesium Chloride
NaCl	Sodium Chloride
NPRA	Norwegian Public Roads Administration
NTNU	Norwegian University of Science and Technology

Road salt	Chlorides used to clear the roads of snow and ice
Sugar	Sucrose ($C_{12}H_{22}O_{11}$)
W%	Weight percentage, percentage of total mass (g)

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1 Introduction

1.1 Motivation

Winter can cause problems for drivers in countries with cold climates. Snow and ice can lead to slippery and impassable roads, which causes dangerous driving conditions (Maze et. al., 2006) and financial consequences related to traffic delays (Hanbali, 1994) and fuel usage. Therefore, in order to ensure vehicular mobility, road maintenance is necessary. However, what is considered to be an acceptable level of service can vary from road to road and country to country, which is why various operational procedures must be implemented. While mechanical snow removal and spreading sand or gravel may be sufficient on low traffic volume roads, chemicals need to be applied on high traffic volume roads (Ketcham et. al., 1996). There are several reasons for this: Chemicals prohibit ice from forming on the road, they melt snow and ice, and they counteract the compaction of snow. The goal is often to achieve a bare surface with high friction to ensure mobility and safety.

High traffic volume is defined by the Norwegian Public Roads Administration as a road with more than 1,500 vehicles driving over it per day. Salt is applied on the road when the temperature drops below 0°C; however, when it gets very cold (colder than -10°C to -15°) operators experience that salt loses its effect (Ketcham et al., 1996). If it gets cold enough, salt does not have any effect at all regardless of the applied amount. The eutectic point of a chemical is the lowest freezing temperature possible to obtain with the corresponding concentration; surpassing this eutectic point results in zero ability to melt snow and ice and zero ability to prevent water from freezing. NaCl is the most commonly used deicing chemical and has a eutectic point at -21.1°C and 23.3w%; however, it is seldom used with pavement temperatures below -12°C due to its diminished effect (TRB, 1991) (NPRA, 2014). Additives or other chemicals are sometimes used in an attempt to obtain improved cold temperature performance (Shi et. al., 2013).

Heavy snowstorms are rare when it is very cold (Akin et. al, 2013), but precipitation might fall as light snow and occasionally freezing rain. High humidity, e.g., around open water, together with cold pavement temperature, might cause slippery roads. A thin ice layer or a thin compacted snow layer can be more difficult to spot visually, and the degree to which the surface is slippery might be difficult for drivers to see, resulting in their not adjusting their speed sufficiently (Rämä 1999) and causing accidents. It is very difficult to remove a thin ice layer in cold temperatures because 1) the salt has little or no effect and 2) changing strategy from chemicals to sanding is difficult on a road already maintained with chemicals. Sanding is an inappropriate

strategy for high traffic volume roads (Nixon, 2001) even with a layer of snow on the road. The sand simply blows off after a few cars pass by, and this process goes even faster when there is no snow or ice layer thick enough to attach the sand to the road. A Norwegian study showed that sanding only lasted for the passing of 50 cars (NPRA, 1999) on a road with a 2 cm thick ice and snow layer; on a thin ice layer, the duration would probably be even less. If operators are faced with the situation where they have a slippery road and the temperature falls under what has been known as the salt's "effective temperature", they are left with few options. While this problem is one of the reasons why the use of other chemicals or additives is being considered, more knowledge about how they perform in low temperatures is needed. In order to learn about the different chemicals' or products' performance, they need to be tested.

For clarification; The term *deicing* is used as a term for products and chemicals spread out on the road for removing and prohibiting snow and ice formation on the road (including anti-icing, deicing and anti-compaction), and the terms *deicers* and *chemicals* are used for substances to achieve this function. The term *cold temperatures* refers to temperatures colder than approximately -15°C.

1.2 Research objectives and method

There are several important qualities that must be present in order for a chemical to function as a deicing chemical, including price, accessibility, HSE (Health, Safety and Environment) and performance (Heystraeten and Diericx, 2002). Qualities regarding performance are, for example, the amount of melted snow and ice achieved (ice melting capacity) (Akin and Shi, 2010), and at what rate (ice melting rate) (Koefod et. al., 2015), penetration, disbondment and undercutting abilities (Chappelow et. al., 1992) as well as anti-compaction abilities (Wählin et. al., 2014). This dissertation focuses on testing the chemicals *ice melting capacity*, which is defined as how much ice or snow the chemical can melt or how much water it can prohibit from freezing, in grams of ice per gram of deicer. The ice melting capacity tells us something about how effective the deicing chemical is at different temperatures, and how much product that need to be applied on the road to achieve this effect (application rate).

Chemicals or mixes of chemicals and additives all perform differently regarding ice melting capacity. Deicing products are often mixes of various chemicals and/or additives that produce complex compositions in molecular structures, a result which makes it difficult or "impossible" to anticipate or calculate its performance. Hence, the ability to measure ice melting capacity is highly valuable. Unfortunately, it is a very difficult measurement to make due to the fact that it is highly dependent on temperature. As a result, laboratory testing is a better option than field testing, as in the latter it is difficult to control temperatures from the pavement, air and solar radiation. Measuring ice melting capacity has been done in the field of winter maintenance for years. The standardized test methods in the US are the SHRP H205.1 for solid chemicals and H205.2 for liquid chemicals (Chappelow et. al., 1992). "The Handbook of Test Methods for Evaluating Chemical Deicers" recommends using the SHRP H-205.1 and SHRP H-205.2 tests to assess new deicing chemicals with respect to measuring ice melting capacity in addition to describing and comparing the ice melting capacity of deicers over a limited and predefined time interval. Actually, the handbook specifies that SHRP does not quantitatively measure the theoretical or

extended time period of the deicers' ice melting capacity because melting capacity is defined as the amount of melted ice per gram of deicer, regardless of time. This means that the SHRP tests do not measure full melting capacity and that the result is affected by the deicers' melting rate (Koefod et. al., 2015) and application time (Koefod et. al., 2012). The SHRP test was meant to be a practical performance test; unfortunately, it was called an "ice melting capacity" test, and several authors seem to have forgotten that it does not actually measure ice melting capacity itself. The past year's research has questioned the accuracy of SHRP H-205.1 and 205.2 (Koefod et. al., 2015) (Muthumani et.al., 2014b), (Klein-Paste and Potapova, 2014) (Fay and Shi, 2011). If this is true, the ice melting capacity of the most common deicers might still be unknown.

There is clearly a need to state the accuracy of the SHRP test and to develop an accurate test method so that the ice melting capacity of different chemicals, products and additives can be determined. The Norwegian Public Roads Administration has initiated this PhD study and financed this dissertation because they needed more knowledge as to how deicing chemicals perform in very cold temperatures, which chemicals they should use when it is cold, and how much they needed to use to get proper effect. A method for calculating ice melting capacity from a phase diagram was established in this dissertation. The method was used as reference to state the accuracy of today's existing methods. A new method for measuring ice melting capacity, the calorimeter, was developed during this study. Two versions of the calorimeter were built, the second version contained improved elements to obtain even higher accuracy levels; however, the principle behind both was the same. While only the design of the second calorimeter has been included in this dissertation, a detailed description of the first calorimeter and results may be found in paper II, appendix B.

The objective of this study was to investigate the ice melting capacity of deicers in cold temperatures and was divided into the following sub-objectives:

- Review of existing published ice melting capacity methods and results
- Establish a method for calculating melting capacity from a phase diagram
- Develop a new test method for measuring ice melting capacity
- Determine ice melting capacity for common deicing chemicals in cold temperatures

The sub-objectives are addressed in the three papers published during this study. Figure 1 describes the main content of each paper.

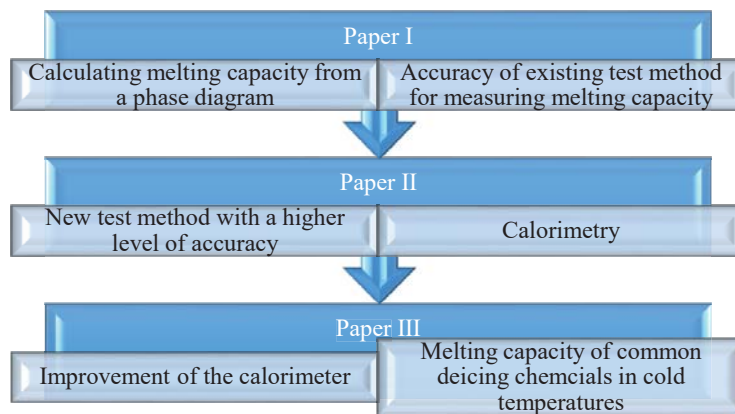


Figure 1. Three papers were published during the PhD study. The main content of the paper is described inside each box.

1.3 Dissertation structure

This dissertation is divided into seven main sections, the three published papers having been attached in Appendix A-C. After the introduction in chapter 1, chapter 2 provides a summary of how chemicals are used in winter maintenance. Chapter 3 describes the status quo of ice melting capacity tests. Chapter 4 describes the method for calculating ice melting capacity from a phase diagram in addition to the development of the new test method, the calorimeter. Chapter 5 describes the accuracy of existing test methods and the accuracy of the calorimeter. It also presents the results of tests performed with the calorimeter for $MgCl_2$, $CaCl_2$, KFo , CMA and sugar at $-18^\circ C$, and the same chemicals used as additives to $NaCl$. Chapter 6 contains a discussion of the results, how they effect winter road maintenance in cold temperatures and an example of how data on ice melting capacity can be used to calculate application rate. Conclusions of the dissertation are presented in chapter 7.

1.4 Publications

The articles written during this project are outlined below:

Paper I

Nilssen, Kine; Klein-Paste, Alex; Wåhlin, Johan. (2016)

Accuracy of Ice Melting Capacity Tests.

Transportation Research Record: Journal of the Transportation Research Board. 2551. pp 1-9. doi: <http://doi.org/10.3141/2551-01>.

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The paper summarizes published data on the measured ice melting capacity of sodium chloride ($NaCl$) and describes how melting capacity can be calculated from a phase diagram. The published data was compared to the calculated melting capacity of $NaCl$

to investigate the accuracy of current test methods. The findings confirm previous suspicions that the standardized test methods for measuring ice melting capacity (SHRP H205.1 and H205.2) have low levels of accuracy and reproducibility and are therefore not able to measure full melting capacity. The newer test methods in the literature produced measurements closer to full melting capacity than SHRP did. They also showed higher levels of accuracy; however, the insufficient data published from these methods prevented the opportunity to draw any firm conclusions.

My contribution to the work was collecting data in previously published literature, undertaking both analyses and calculations and writing the final paper. Alex Klein-Paste generated the idea regarding how to calculate ice melting capacity from a phase diagram. Johan Wählin demonstrated how to include the unrealized ice melting capacity, provided scientific discussions and assisted in structuring the paper.

Paper II

Nilssen, Kine; Klein-Paste, Alex; Wählin, Johan; Michele Ann Delapaz. (2017)
Use of calorimetry to measure ice melting capacity
Transportation Research Record: Journal of the Transportation Research Board. 2613.
pp 1-7. doi: <http://doi.org/10.3141/2613-01>.
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This paper describes how calorimetry (the measurement of heat) can be used to measure the ice melting capacity of deicing chemicals. A calorimeter was built for this paper's research purposes which required a minimum of mechanical handling and had a high level of temperature control precision and excluding most causes for measurement errors in previously developed test methods. The NaCl solution was tested and compared with the calculated melting capacity. The calorimeter produced more accurate results than previous test methods. Tests were also performed using MgCl₂, and the results demonstrated that MgCl₂ had a higher level of ice melting capacity than NaCl. In retrospective, the explanation of the results for MgCl₂ should have been stated more clearly. While they are true for solid MgCl₂, MgCl₂ often exists as MgCl₂·6H₂O in a solid state, resulting in the ice melting capacity being lower than presented for pure MgCl₂.

My contribution to the work was completing the testing in the calorimeter and improving the design during its development, which required several iterations of testing and design adaptations. I performed the NaCl tests and analyses as well as wrote the paper. Alex Klein-Paste had the original idea of using calorimetry; additionally, he was the design head and wrote a part of the paper's design chapter. Johan Wählin provided scientific discussions, theoretical assistance and contributed to the writing process. He was also 'the brain behind' how to calculate the latent heat at set point. Michelle wrote her Master's thesis on the calorimeter, performing the MgCl₂ tests and analyzing MgCl₂ results.

Paper III

Nilssen, Kine; Klein-Paste, Alex; Wåhlin, Johan (Submitted June 2017)

The effect of additives on the low temperature ice melting capacity of NaCl.

Submitted to: Transportation Research Record: Journal of the Transportation Research Board, June 2017.

This paper used calorimetry to study the effect of additives on the low temperature ice melting capacity of NaCl. Other common deicers, including MgCl₂, CaCl₂, KFo, CMA and sugar, were both added to NaCl at -18°C and tested individually. The calorimeter was an improved version of the calorimeter presented in paper II, which produced an even higher level of accuracy.

My contribution to the work was ideas for new design, initial testing to determine the accuracy and performing the data collection. Alex Klein-Paste completed the practical changes of the design. Johan contributed a great deal in forming the equations to convert the results from solutions to solids. Both Alex and Johan played a great part in the scientific discussions, and both assisted during the writing process.

2 Chemicals in winter maintenance

2.1 Use of chemicals

Sodium Chloride (NaCl), better known as salt, is the most commonly used deicer; indeed, salt has been used for snow melting operations on highways since the 1960s (Paschka et al., 1999). Evidence of salt usage actually dates back to the late 1800s, where it was used to counteract icy sidewalks in Paris and London (Scientific American, 1887) (The Lancet, 1894). An estimated 14 million tons of deicing salts are applied every winter in North America (Hopkins et al., 2013). Salt has crucial properties, making it possible to achieve a bare road surface with high friction even below 0°C, and is thereby used for three purposes (Wählin et al., 2014):

- **Anti-icing:** To prevent ice from forming on the road. Salt (and other deicers) can lower the freezing point of water, meaning that it prevents moisture or water from freezing, even if it is below 0°C. The lowest freezing point of a mixture of components is called the eutectic point, and is dependent on the type of chemical being used. The chemical is spread out on the road before there is a weather incident that can cause slippery roads, e.g., before freezing rain, snow and high levels of humidity combined with decreasing temperatures. This is called a preventive or pro-active measure. The public sometimes question the anti-icing strategy (O'Keefe and Shi, 2006), because it is difficult to understand why salt is being applied when they do not see the snow or if the temperature is above 0°C. But the decision maker has a weather forecast and are performing measures before the weather incident strikes. This has shown to improve the winter driving safety, to reduce environmental impacts, human and health impacts and corrosion effects, and improve the level-of-service at the same cost as doing the measure after the incident (deicing) (TRACK, 2002). However, at cold temperatures, the anti-icing strategy may cause a problem instead of curing a problem, especially if the temperatures are decreasing (Technology Transfer Center, 1996). It can cause the snow to stick to the road surface, while traffic and high wind speed could have been sufficient to prevent accumulation and compaction of snow if the road was left dry and without salt. Also if the weather forecast is not correct or the salt simply blows off, it might result in overuse (Akin et al., 2013) (Muthamani et al., 2014a). The anti-icing strategy requires a reliable weather forecast, road weather information and trained personnel (Technology Transfer Center, 1996).
- **Deicing:** To melt snow and ice already on the pavement. The deicer is applied after a layer of snow or ice has formed on the road with the aim of melting and removing it. However, not all the ice is necessary to

melt, the deicers will assist the mechanical removal through ice penetration and ice undercutting, as well as ice melting. Although the deicer can melt ice down to the its eutectic point, the ice melting capacity is diminished when temperatures decrease and approaching the eutectic point. A deicing situation is not a desirable situation. First of all it requires more salt to melt ice than to prevent water from freezing (O'Keefe and Shi, 2006) (Klein-Paste and Wåhlin, 2013), second of all it takes more time. If we end up in a deicing situation, we have failed our strategy to prevent a dangerous driving condition. It takes time to get rid of that situation, time with ice and snow on the road, when accidents can happen.

- Anti-compaction: To make snow removal easier. Salt weakens the bonds between snow granules, making the snow less able to form a compact layer on the road and easier to plow. The salt is often applied during a snowstorm to prohibit compaction when traffic is driving on top of the snowy surface.

Deicers makes it possible to achieve a bare road surface even when it is below 0°C. A bare road surface has higher friction, with typical friction numbers from 0.7 (wet) to 1.0 (dry), than a road surface covered with ice or snow, with typical friction numbers of 0.05-0.3 (Wallmann and Åström, 2001). There is a strong correlation between decreasing friction and increasing accident risk (Brodsky and Hakkert, 1988) (Shankar et. al., 1995) (Khattak et. al, 1998) (Normann et. al., 2000) (Maze et. al., 2006) and since drivers do not adapt their behavior sufficiently for the lack of friction (Rämä, 1999) (Leppänen, 1995) (Wallmann, 1998), improving friction is a necessary measure for increasing traffic safety (Usman et. al., 2010) (Gilfillan, 2014). However, it is difficult to single out the exact correlation between traffic safety and friction (Wallmann and Åström, 2001). Friction is a difficult measure and drivers adapt their driving behavior depending on many factors such as the visual appearance of the road, the weather, the sound of the tires and the movements of the vehicle. In addition, winter roads often have rapid changes in conditions (Wallmann and Åström, 2001). This makes safety benefits research not always conclusive, and some research actually points out that despite number of accident decreasing, the severity actually increases due to higher speed (Khattak et. al., 1998) (Brown and Baase1997). However, the majority of research point to increased traffic safety with increased friction.

A bare road surface is also important to ensure vehicle mobility (Strong et. al, 2010) (Shi, 2005) and decrease delays (Ye et. al., 2009). Statements are made that the economic impact of snow-related closures far exceeds the costs of timely snow removal, and that deicing pays for itself within the first 25 minutes after salt is applied on American highways (Snowfighters handbook, 2016).

Despite their benefits, deicers have negative consequences. Applied amounts of salt in nature/on roads should be minimal, as any scattered salt eventually ends up in the environment through runoff/blow-off, airborne spreading, infiltration and plowing (Blomqvist and Johansson, 1999). Increased chloride concentration in fresh water degrades habitats for aquatic organisms and can impact supplies of drinking water (Kaushal et al., 2005). Further, salt may damage vegetation next to the road, percolate downward into the underlying water and soil, soaking plant roots (Ramakrishna and Viraraghavan, 2005). Salt also has a detrimental corrosive effect on traffic infrastructure, including steel bridges, parking garages, pavements and concrete as

well as motor vehicles (Shi, 2005). Optimizing the use of road salt is therefore important, and mechanical removal of snow is crucial because without it extremely large amounts of salt would be needed to melt all of the accumulated precipitation. Later years there has been a focus on finding environmental friendly (Fay et al., 2008) and non-corrosive (Fangming et al., 2010) deicers.

There are mainly four application methods for spreading salt; 1) Dry, 2) Pre-wetted, 3) Slurry and 4) Brine. 1) Dry application means applying solid salt particles. The process requires relatively cheap, simple equipment and works well on wet pavement (not to wet) and during precipitation. It needs sufficient moisture or accumulation to prevent loss of material and to trigger the solution of the salt (Technology Transfer Center, 1996). On dry roads has the salt a tendency to end up on the roadsides due to traffic and wind, a situation called blow-off (Lysbakken and Norem, 2008), before doing its job. Dry solid salt should therefore not be used for anti-icing. However, for deicing solid salt is the most effective application method (with the exception of very thin ice layers) (Blackburn et al., 2004), and also for anti-compaction. 2) Pre-wetted application. This is a method where solid salt is pre-wetted with water or other chemicals before being applied on the road. According to Minsk (1998) has 100 liter water per ton salt (14 gal/100 lb) shown good effect. However, typically application rates in Norway are 30w% water or other solutions (NPRA, 2014). This process improves adhesion between the salt and road (Alger and Haase, 2005), reducing blow-off. The salt also disintegrates faster when it has access to moisture, and salt needs to be dissolved in order to be able to melt snow and ice or prevent water from freezing (O'Keefe and Shi, 2006). 3) Slurry application. Also called pre-wetted fine-grained salt. This is pre-wetted and crushed salt, and is believed to give even better adhesion and disintegration rates than pre-wetted. 4) Brine application. A 23w% solution of dissolved NaCl in water, allowing a high level of adhesion. Brine is especially effective for anti-icing and on thin hoarfrost due to the fact that it is already dissolved and works immediately after application. It should not be used during snow storms. Deicers other than salt can also be used in solutions and are often referred to as liquids or solutions. When adding solutions to the road, water is also added, so solutions might not be cost-effective or effective in cold temperatures (Technology Transfer Center, 1996).

There are other deicing products with lower possible freezing points than NaCl, including MgCl₂ and CaCl₂ (Ketcham et al., 1996), they are typically used at lower temperatures (Minsk, 1998). Commonly used chlorides beside NaCl are; MgCl₂ (magnesium chloride) and CaCl₂ (calcium chloride) (Fu et al., 2006). Frequently used non-chloride chemicals are for example CMA (calcium magnesium acetate) and KCOOH (Kfo/potassium formate) (Atkin et al., 213). There are also several additives mixed into deicers used, such as sugar products (Muthumani et al., 2014a). Sucrose (C₁₂H₂₂O₁₁) is included in this dissertation as a representative for sugar-based additives, however the deicers including sugar products are often a mix of different types of sugar. Table 1 provides an overview of some common deicing chemicals' technical data including NaCl, MgCl₂, CaCl₂ and Kfo (Haynes and Bruno, 2014), CMA (Ketcham et al., 1996) and Sucrose (Young and Jones, 1949). These are the deicers studied in this research.

Deicer	Chemical symbol	Eutectic temperature	Eutectic concentration	Maximum solubility 0°C	Mol weight (g/mol)
Sodium Chloride	NaCl	-21°C	23.4%	23.4%	58.44
Magnesium Chloride	MgCl ₂	-33°C	21.8%	24%	95.23
Calcium Chloride	CaCl ₂	-50°C	30.5%	32%	110.99
Potassium Formate (KFO)	KCOOH	-51°C	48%	50%	84.12
Calcium Magnesium Acetate	CMA	-27.5°C	32.5%	32.5%	Unknown composition. CaA: 158.16 MgA: 142.39
Sucrose	C ₁₂ H ₂₂ O ₁₁	-30°C	80%	84%	342.3

Table 1. Deicer data

2.2 Freezing point depression

The freezing point of water is depressed when foreign molecules or ions are dissolved, the degree of which is roughly determined by the number of solute particles (Atkins and Paula, 2012) and the solubility. The number of particles is the only contribution for ideal solutions and low concentrations. For real solutions we need a phase diagram or measurements to determine the freezing point. The equilibrium between phases is represented in a phase diagram (Atkins and Paula, 2012): Figure 2 shows the phase diagram for NaCl. The line entitled “freezing curve” shows when the solution is at equilibrium with ice, where no melting or freezing takes place. The eutectic point is defined as the temperature and chemical concentration (w%) of a solution corresponding to the lowest freezing point of the solution (Smith and Hashemi, 2009) or, in other words, the lowest achievable freezing point. NaCl has the eutectic point at approximately -21.1°C with a corresponding concentration of 23.3w% solution (Haynes and Bruno, 2014). If the temperature is milder than the freezing point, the water is liquid and the NaCl is in solution (H₂O(l) + NaCl(aq)). If the temperature is colder than the freezing point, some of the water will be transformed to ice, and the remaining salt solution becomes more concentrated (H₂O(l) + NaCl(aq) + H₂O(s)). The salt solution is trapped in pockets inside the ice and weakens it (Klein-Paste and Wählin, 2013). The freezing process will continue until the eutectic point is reached, and if the temperature drops further; all water will freeze (H₂O(s) + NaCl(s)). If the temperature is above eutectic, but the concentration of the solution exceeds the solubility limit, some of the salt remains solid (H₂O(l) + NaCl(aq) + NaCl*2H₂O(s)).

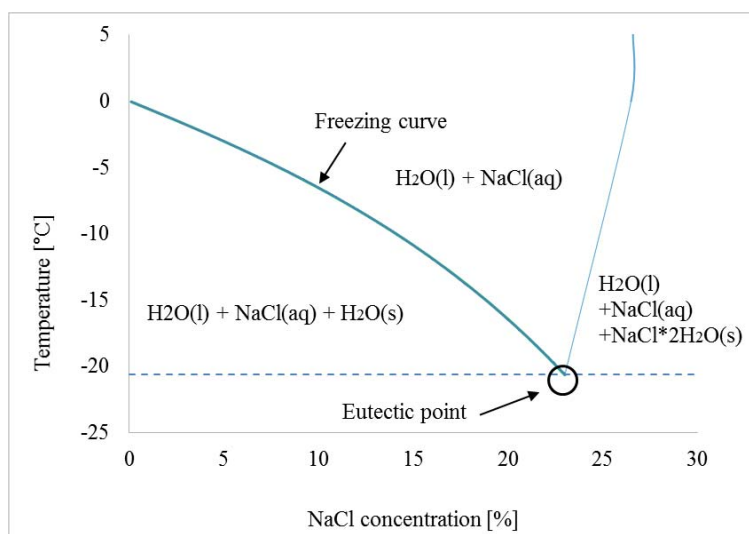


Figure 2. Phase diagram for NaCl. Data from source: (Haynes and Bruno, 2014). (l) represents liquid state, (aq) represents dissolved salt and (s) represents solid state.

2.3 How salt melts ice

The freezing curve in Figure 2 is where solid ice and liquid solution co-exist in equilibrium, and can also be seen as the ice's melting point. Molecules in ice are situated in a fixed position, while water molecules move around freely. When ice and water are in an equilibrium state, there are no changes in the composition; there is only an exchange during which some molecules move freely (liquid) while others are in a fixed position (ice). The ice molecules next to the water molecules steal energy from the water molecules, causing the ice molecules to move more freely around and melt while the robbed water molecules become colder and freeze. When salt is present, this process is different: The salt prevents the water molecule from freezing. So when the ice molecules continue to steal energy, it still melts, but since the freezing temperature has dropped, the robbed water molecule will only become colder but not freeze, causing a change in the composition. More and more ice molecules melt, but there is no equivalent number of molecules freezing. As more and more ice becomes liquid, and all the salt gets dissolved, the concentration of the salted water decreases. Eventually, a new freezing point is reached, and no more melting takes place. The ice and water have then returned to equilibrium. The amount of ice that has melted to achieve equilibrium, is the ice melting capacity.

Exactly how solutes depress the freezing point is a comprehensive question outside the scope of this thesis. However, from thermodynamic point of view, the reason why the chemicals lower the freezing point is that they lower the chemical potential of water. The ice and water finds it more desirable to be in the state with the lowest chemicals potential, as this is the most stable phase, and therefore exists as a deicer solution instead of as ice (Atkins, 2014).

3 Ice melting capacity

As mentioned in the introduction, there are several qualities important for a chemical or product to be functional as a deicing chemical; nonetheless, when it comes to low temperature performance, there are mainly two important qualities that distinguish the different chemicals: (1) melting capacity and (2) melting rate. And the focus of this dissertation was the ice melting capacity.

Ice melting capacity is the amount of ice we can melt per gram of deicer. Consider one gram of salt laid out on ice. The salt melts ice and dissolves in the meltwater to a salt solution. The solution melts ice until it is diluted by the meltwater and reaches equilibrium with the ice. The melting stops, and the melted ice until this point is defined as the ice melting capacity. Hence, the ice melting capacity is a physical constant for a given chemical and temperature.

Ice melting capacity tells us especially two important measures to use in the field of winter maintenance. 1) If the chemical has the ability to melt snow and ice at the needed temperature, e.g., in cold temperatures. 2) How much of the chemical is needed (application rate) to melt the amount of ice or snow we need to melt.

Often when using salt in very cold temperatures, we are situated in a deicing situation (Akin et. al, 2013). Often “to do nothing” when the pavement temperature is very cold might be the best strategy. The new snow is cold and light, so traffic and wind may be sufficient to prevent accumulation and compaction in tire tracks, and in this case, application of chemicals can create instead of curing a problem (Ketcham et. al, 1996). A wet surface in cold temperatures can freeze and can also cause snow to adhere and build up on the road. Deicing when needed is therefore beneficial versus anti-icing in cold temperatures (Akin et. al, 2013). As explained in chapter 2, in a deicing situation, the chemical needs to melt snow and ice already established on the pavement. The ice melting capacity tells us if and how much deicer that is needed. However, ice melting capacity is also important in an anti-icing and anti-compaction perspective. In an anti-icing strategy, the applied salt is supposed to prevent water from freezing on the road. The amount of salt needed for this is the same as the amount needed to prevent water from freezing. As shown in sub-section 6.5, the application rates for anti-icing and deicing measures are closely linked to ice melting capacity. To achieve anti-compaction effect, a minimum water content is needed (Schaerer, 1970), and the ice melting capacity can be used to calculate how much salt is needed to achieve this water content.

Ice melting capacity has been measured for many years in the field of winter road maintenance. In sub-section 3.2, is a list of published methods for measuring ice

melting capacity with a short summary on how they are performed. Freezing point measurements are beyond the scope of this dissertation; however, the published papers where these are used to calculate or correlate with ice melting capacity were included. Results from tests performed with these methods where NaCl has been used, were collected and presented as a part of the chapter 5 “Results”. They were compared to calculated values of NaCl, to investigate the accuracy of the different test methods that are used today.

3.1 Ice Melting Capacity vs Ice Melting Rate

It is important to distinguish between ice melting capacity and ice melting rate. Ice melting capacity is a physical constant, but there are no such limitations for the rate (Koefod et. al 2015). Koefod et al. (2015) completed a very interesting research project demonstrating the importance of distinguishing between melting rate and melting capacity. Figure 3 is a copy of their study performed with NaCl and MgCl₂ in -20°C. They used the SHRP H-205.1 and measured the amount of ice the deicers had melted after 1, 3, 5, 7 and 24 hours. If the test is stopped after one hour, the impression would be that NaCl has very low melting capacity at -20°C and that MgCl₂ has high. But if the test is carried out for as many hours as it takes for both chemicals to achieve their ice melting capacity, NaCl and MgCl₂ have almost the same ice melting capacity. This result shows the importance of distinguishing between melting rate and melting capacity when comparing deicing chemicals.

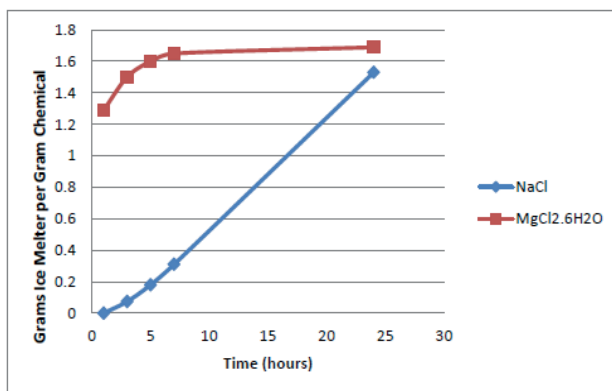


Figure 3. Ice melting capacity and ice melting rate, NaCl and MgCl₂ (Koefod et al., 2015). Reproduced with permission of the Transportation Research Board.

3.2 Ice melting capacity testing – status quo

Several different test methods for measuring ice melting capacity have been developed since the 90s, and 20 years later, testing still seems to be relevant, which demonstrates the need for making an objective comparison of the existing methods. The former test methods can be divided into two groups, one with physical separation of the melted water (SHRP, air, the shaker test, the mechanical rocking test procedure and inzell slab procedure) and one using other methods to determine the amount of melted ice (VPA,

DSC, the ice cube titration test, the tracer dilution method). Published methods for measuring ice melting capacity are:

The SHRP tests

This is the standardized test methods in the US for measuring ice melting capacity, and are named SHRP H-205.1 “Test Methods for Ice Melting of Solid Deicing Chemicals” and H-205.2 “Test Methods for Ice Melting of Liquid Deicing Chemicals” (Chappelow et al., 1992) (Akin and Shi, 2010). They should be performed according to the descriptions provided in “Handbook of Test Methods for Evaluating Chemical Deicers” (Chappelow et. al., 1992). The tests are performed by fabricating a 3.175 mm (1/8 in) thick ice layer in a Plexiglas dish with a recommended diameter of 22.86 cm (9 in) and a recommended depth of 1.91 cm (3/4 in). The recommended sample size is 4.17 g for solid deicers and 5 ml for liquid deicers. The deicer is scattered over the ice. Next, at specific time intervals (10, 20, 30, 45 and 60 minutes), the amount of melted ice is measured by collecting the melted water in a syringe, weighing the syringe, and pouring the melted water back to the ice. The handbook recommends completing three replications for each test.

As mentioned in the introduction, the SHRP tests do not quantitatively measure the theoretical or extended time of the deicers’ ice melting capacity because melting capacity is defined as the amount of melted ice per gram deicer regardless of time. There have also been concerns that the test includes procedures that produce a low level of accuracy, as it can be difficult to separate the entire melted portion from the remaining ice (Muthumani et. at., 2014b). There is also a risk of supplying additional heat when handling the measurement equipment (Klein-Paste and Potapova, 2014). Additionally, for certain chemicals such as NaCl, melting may continue after the specified test period of 60 minutes is over (Koefod et. al., 2015). Procedures making the test difficult to perform exactly the same way twice result in low reproducibility. Further, Fay and Shi (2011) found a relatively high variance (coefficient of variance) in their SHRP study.

Modifications of the SHRP test

In some papers the ice melting capacity test has been performed with a modified version of the SHRP test with the aim of achieving more accurate results. The modifications have been for example different amounts of NaCl used in each test, other time intervals for measurements, type of cold room/freezer and different units in the presentation of data (Akin and Shi, 2010) (Fay and Shi, 2011) (Fay et al, 2008).

DSC

Fay and Shi (2011) used a differential scanning calorimeter (DSC) to determine at which temperature the deicers started freezing (their freezing point). Since the DSC data had a lower standard deviation than the SHRP test, they made a correlation between the DSC data and the SHRP data at 0°C in order to be able to use the DSC data to find the deicers’ ice melting capacity. The DSC was set to run liquid samples, from -60°C to 25°C with heating rate 2°C/min. More results are presented in Shi et al. 2014.

The shaker test

In 2012 Gerbino-Bevins and co-workers developed a test method called “The shaker test” with the aim of measuring ice melting capacity with a higher level of accuracy than the SHRP H-205.1 and H-205.2 tests (Gerbino et. al., 2012). The shaker test was used to measure ice melting capacity of both solid deicers and solutions, and it also simulated the disruptive effect caused by vehicular traffic. They concluded that the test was reproducible and produced consistent results.

The test was performed in four insulated plastic martini shakers in a small freezer. The insulation maintained a steady internal temperature for approximately 2.5 minutes before the lid was opened and the sample taken outside the freezer to perform the shaking. The test was performed at -6.7°C , -12.2°C and -17.8°C (20°F , 10°F and 0°F). Each sample of deicer consisted of 7 ml with 23% NaCl solution. Ice cubes made from distilled water were put in the same freezer as the shaker to ensure equal temperature. Ten ice cubes were weighed and put in the shaker before it was shaken manually in two cycles per second for 5 minutes. The temperature was measured once per minute. After shaking, the shaker was placed back in the freezer upside down so the meltwater would drain into the cup portion of the lid while the ice remained above the strainer. The weight of the melted water (without any ice) was measured. The results were presented in a graph as average grams of melted ice per milliliter deicer. Three replications were performed.

The mechanical rocker test procedure

“The mechanical rocker test” procedure is a further developed version of the shaker test and was developed by Tuan and Albers in 2014. The aim was to develop a simple and repeatable test to determine the ice melting capacity of deicing solutions. The authors concluded that it was repeatable, relatively quick and provided consistent results with modest equipment requirements (Tuan and Albers, 2014). While the test procedure was quite similar to the shaker test, in the mechanical rocker test they used a mechanical rocker to mix the ice and the deicer instead of shaking it by hand. The test was performed in a small freezer at -17.8°C (0°F). 33 ice cubes of 1.3 ml each and 30 ml of deicing solution were mixed in a sealed thermos inside a vacuum and placed on a mechanical rocking platform. The rocker was set to a frequency of 90 RPM with a tilt angle of $\pm 10^{\circ}$, and a rocking time of 15 minutes. The shaker was taken out of the freezer during the rocking.

The Ice Cube Titration test

Koefod et. al. introduced the “ice cube titration test” in 2012 whose aim was to reduce the error source associated with incomplete recovery of meltwater from the ice surface and the time limitation in the SHRP test so that the full melting capacity could be measured. The test was conducted using a 400 ml beaker containing 23.3% NaCl solution (brine) in a walk-in cold room and a magnetic stir bar for mixing deicer with the melted ice. The temperature of the room was -15°C ($\pm 0.5^{\circ}\text{C}$). Ice cubes were suspended into the deicer. The beaker was weighed periodically, and the increased weight of the beaker due to melting (the remaining ice was removed) was recorded as the melting capacity. After a certain amount of melting, the ice and water were in equilibrium, and the melting stopped. The weight was then stable, and the recording took place. Melting small ice cubes in the brine took a great deal of time, so they prediluted the water.

The Visual Polythermal Analysis

The Visual Polythermal Analysis (VPA) consists of a cooling and/or heating device where the salt water is slowly cooled down (or heated up) while being stirred. The principle is to visually observe the forming (or disappearance) of ice crystals (Danilov et. al., 2011). A camera often captures the event. Danilov et. al., 2012 first used VPA to determine the freezing point of NaCl, and then used the freezing point to calculate the ice melting capacity (see chapter 4.1). VPA is used in other fields; however, in order to visually determine ice crystal formation in deicing chemicals, finding the freezing point can be very difficult for some deicers, including sugar. Published papers have furthermore estimated the accuracy of the VPA to $\pm 5^{\circ}\text{C}$ (BaB₂O₄-NaF system) (Bekker et. al., 2009).

Inzell ice slab procedure

Goetzfried and Badelt presented the Inzell ice slab procedure in 2002. Similar to the SHRP test, dry or deicer solutions were spread out on asphalt plates; yet in this case, the meltwater was removed using centripetal force after only 10 minutes of exposure. The ice melting capacity was calculated from the weight of the ice both before the test and after.

Tracer Dilution Method

Koefod presented in 2017 a method for measuring ice melting rate with the possibility of measuring ice melting capacity using titration. The test used a 1-liter insulated vessel in a temperature controlled bath, with a temperature set at -19.3°C . Pre-wetting mix and ice cubes were inserted and mixed in the reactor and the concentration analyzed by titration for tracers from an extracted sample.

Air 6170 test

The air test is based on the SHRP test, but is stopped after 30 minutes and uses an air gun to separate the melted water from the ice instead of syringes. It is mainly used for deicing chemicals used at airports (SAE, 2012). The test is not included in chapter 5 “results” because no tests performed with only NaCl was found in literature.

4 Method

As previously mentioned in the introduction; the sub-objectives of this thesis were:

- Review of existing published ice melting capacity methods and results
- Establishing a method for calculating ice melting capacity from a phase diagram
- Develop a new test method for measuring ice melting capacity
- Determine ice melting capacity for common deicing chemicals in cold temperatures

These sub-objectives required different methods when addressed. The first two sub-objectives are linked together. To be able to find the accuracy of today's test methods (the ones described in chapter 3.2), results from already published tests were compared to reference data for NaCl. As reference data, the thermodynamic ice melting capacity was used. It was found by calculating the ice melting capacity from a phase diagram; the manner in which this was done is explained in paper I and sub-section 4.1. The reference data was used to find how close the different methods were to measuring full ice melting capacity, and the results are presented in chapter 5.

Next, in order to calculate the thermodynamic ice melting capacity, a known and reliable phase diagram is necessary. Although several of the tested deicers in this dissertation have this, there are still numerous deicers that do not. Since making a phase diagram requires total insight into the deicers' content and is technically challenging in addition to being expensive the possibility of measuring the ice melting capacity could potentially be very valuable for the field of winter road maintenance. A new test method for measuring ice melting capacity was therefore developed during this study, and is explained in detail in papers II and III, as well as sub-section 4.2. This new method was used to test the ice melting capacity of NaCl, MgCl₂, CaCl₂, CMA, KFo and sugar, as individual deicers and as additives to NaCl at approximately -18°C. The test procedure is explained in sub-section 4.3, and the results are presented in chapter 5.

4.1 Calculating ice melting capacity from a phase diagram/freezing point

4.1.1 How to determine the equilibrium concentration

When calculating the ice melting capacity, the equilibrium concentration (C_{eq}) need to be determined. The equilibrium concentration is the concentration at which the solution will start freezing and can be found along the freezing curve in Figure 2. As explained in sub section 2.2, when at equilibrium, the ice melting capacity is zero (weaker concentrations freeze, and only stronger solutions can melt ice). When deicer is added to ice, melting starts and the meltwater dilutes the concentration of the solution. This continues until the concentration is diluted to C_{eq} . If C_{eq} and the amount of deicer/salt added to the ice is known, we then know how much meltwater can be produced before reaching C_{eq} . This amount of meltwater is the ice melting capacity. The concentration of a solution diluted to equilibrium by ice-melt, can always be expressed by equation 1.

$$C_{eq} = \frac{m_{solid}}{m_{melted\ ice} + m_{product}} \quad (1)$$

where:

m_{solid} = mass solid deicer (g)

$m_{melted\ ice}$ = mass melted ice (g) = meltwater

$m_{product}$ = mass of solid and water in the existing product (g)

The equilibrium concentration can be expressed as a function of the temperature. Equation 2 describes C_{eq} as a function of temperature for the NaCl and ice system, where empirical data regarding the freezing point for different NaCl concentrations was found in The Handbook of Chemistry and Physics (Haynes and Bruno, 2014). The data was fitted with a third order polynomial, with the incept forced through (0,0).

$$C_{eq} = -3.6233 \cdot 10^{-4} \cdot T^3 - 3.8985 \cdot 10^{-2} \cdot T^2 - 1.7587 \cdot T \quad (2)$$

Where:

C_{eq} = Equilibrium concentration = freezing point concentration (%)

T = the temperature (°C).

The R^2 of the fit is 1.

4.1.2 Using equilibrium concentration to calculate ice melting capacity

Rearranging equation 1 gives equation 3:

$$m_{melted\ ice} = \frac{m_{solid}}{C_{eq}} - m_{product} \quad (3)$$

Equation 3 shows us that the amount of solid salt in a deicing product can be found when the product's amount and concentration are known ($m_{solid} = C_{product} \cdot m_{product}$). Using this known entity, equation 4 shows that if the concentration, amount of solution and the equilibrium concentration are known, the ice melting capacity can be calculated. Equation 4 is valid for any product. Dividing equation 3 with the mass of the product produces the result in gram melted ice per gram solid deicer. It is important to be consistent in reporting if the results are per gram solid deicer and/or the solution's

concentration is per gram solution. The definition of a chemical's ice melting capacity is per gram solid deicer:

$$IMC = \frac{C_{prod} * m_{product}}{C_{eq}} - m_{product} = \frac{C_{prod} * 1}{C_{eq}} - 1 \quad (4)$$

where:

IMC = m_{melted ice} per gram deicer = Ice melting capacity of 1g solid deicer (g/g)

c_{prod} = concentration of the product (%)

4.1.3 Example on calculations

This subsection uses equation 4 to calculate the ice melting capacity of a few products. The amount of water in solid or pre-wetted NaCl is minor compared to the amount of melted ice and may be neglected. For example, equation 5 shows how to calculate IMC (ice melting capacity), where C_{eq} is replaced by equation 1.

$$IMC_{solid} = \left(\frac{1}{-3.6233 * 10^{-4} * T^3 - 3.8985 * 10^{-2} * T^2 - 1.7587 * T} \right) - 1 \quad (5)$$

The melting capacity of brine is much lower than for solid NaCl, because 1 gram of 23% NaCl solution (brine) only contains 0.23 grams of NaCl per gram brine (c_{prod}=0.23). In addition, the amount of water added to produce brine cannot be neglected and will reduce the total melting capacity. The melting capacity of brine is therefore given by equation 6:

$$IMC_{brine} = \left(\frac{0.23}{-3.6233 * 10^{-4} * T^3 - 3.8985 * 10^{-2} * T^2 - 1.7587 * T} \right) - 1 \quad (6)$$

where:

IMC_{brine} = Ice melting capacity of 1g brine (g ice/g brine)

Figure 4 shows the calculated ice melting capacity for NaCl, both as solid and brine, at temperatures ranging from -1°C (30.2°F) to -21°C (-5.8°F). The ice melting capacity of solid NaCl is far higher than for brine; this is natural because brine includes a high percentage of water.

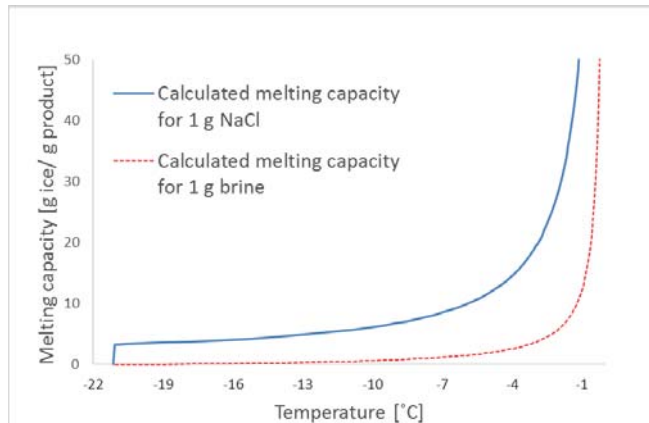


Figure 4. Ice melting capacity of 1 gram NaCl solid and 1 gram 23% NaCl solution (brine)

Solid $MgCl_2$ and $CaCl_2$ are usually delivered as hexahydrates ($MgCl_2 \cdot 6H_2O$) and dihydrates ($CaCl_2 \cdot 2H_2O$). The presence of water affects their concentration (C_{prod}). The product concentration was calculated as follows. The molecular weight of water is 18g/mol and for $MgCl_2$ 95.2 g/mol. One aggregate of $MgCl_2 \cdot 6H_2O$ therefore weighs $95.2 + 6 \cdot 18 = 203.2$ g. Out of this total, 95.2g is $MgCl_2$, corresponding to 46.8%, and the remaining 53.2% is H_2O . The molecular weight of $CaCl_2$ is 110.98g/mol. One aggregate of $CaCl_2 \cdot 2H_2O$ therefore weighs $110.98 + 2 \cdot 18 = 146.98$. Out of this total, 110.98g is $CaCl_2$, corresponding to 75.5%, and the remaining 25.5% is H_2O .

Equations 7 and 8 shows how the ice melting capacity for $MgCl_2$ hexahydrate and $CaCl_2$ dihydrate can be calculated if their C_{eq} is known.

$$IMC_{MgCl_2 \cdot 6H_2O} = \frac{0.468}{C_{eq}} - 1 \quad (7)$$

$$IMC_{CaCl_2 \cdot 2H_2O} = \frac{0.755}{C_{eq}} - 1 \quad (8)$$

4.2 The Calorimeter

The new method developed was based on calorimetry. It excluded the larger sources of inaccuracy connected to SHRP, including mechanical handling, poor temperature control and limited testing time. Two versions of the calorimeter were developed, the second one with changes in design to improve accuracy; however, the underlying principle was the same for both. Version 1 was tested for a larger temperature range, and since it showed great improvement in producing more accurate results compared to SHRP, version 2 was only tested in cold temperatures as these criteria were within the scope of this dissertation. Version 2 was used to test the ice melting capacity of NaCl, $MgCl_2$, $CaCl_2$, CMA, KFo and sugar, as individual deicers and as additives to NaCl at approximately $-18^\circ C$.

Calorimetry is the measurement of any heat changes that occur during a process (Haines, 2002). The melting of ice is an endothermic reaction, meaning that the system absorbs energy from its surroundings. The amount of energy needed to melt 1 kg of ice is called the latent heat of fusion, and for ice at $0^\circ C$ it is 334 kJ (Haynes and Bruno, 2014). So, when ice is melted, for instance by a deicer, it absorbs energy from its surroundings, causing the temperature to drop. The ice/deicer/meltwater mixture first becomes colder than the environment (pavement and air). Heat then rapidly flows from the environment towards the mixture (Klein-Paste and Potapova, 2014), and the temperature returns to its original state. In an ice/solution system, the concentration and temperature always follow each other (Atkins, 2012). Moreover, one cannot be changed without the other following. So, if the temperature is known, the solution concentration can be read from the freezing point curve in Figure 2, and vice versa. During the melting process, the meltwater mixes with the deicer and dilutes it. When enough ice is melted for the solution to be diluted to the freezing concentration (C_{eq}) corresponding to the systemic temperature, it is in equilibrium with the ice, and no more freezing or melting takes place. At this point the melting process is completed and the melting capacity reached. Hence, a certain amount of energy (heat) was needed to melt ice and bring the solution to equilibrium. The idea behind “the calorimeter” was to measure this amount of energy and then use the latent heat of fusion to calculate the amount of melted ice.

With a known latent heat of fusion, L_{ice} , the amount of melted ice may be determined, $m_{melted\ ice}$, by measuring the amount of heat Q_{added} that was added to the ice/deicer/meltwater mixture during the reaction, according to equation 9. See paperII (Appendix B) for a more detailed explanation of how the amount of melted ice was found.

$$m_{melted\ ice} = \frac{Q_{added}}{L_{ice}} \quad (9)$$

This directly produced the deicers' ice melting capacity, which can also be used to calculate C_{eq} by using equation 1 as long as the concentration of the tested deicer is known.

The latent heat of fusion is not exactly constant, but temperature dependent. As regards water, it is lower for lower temperatures. This temperature dependency was estimated in the calorimeter from the difference in heat capacity of water and ice using the method devised by Murphy and Koop, 2005.

A custom-made calorimeter was concurrently developed with this dissertation and consisted of a closed and isolated container. Temperature sensors inside the container and insulation were used to determine if a homogenous temperature was reached before test start. Ice was first added and the temperature stabilized, then the deicer was inserted through an opening in the lid and mixed with the ice inside the container. The temperature was registered before the mixing started and throughout the temperature drop (the melting process). Because of the isolation there was little heat flowing from the surroundings into the mixture. The goal was to have a homogenous temperature in the ice/solution mix. A heater was placed inside the container to provide heat to bring the temperature back to the initial temperature. The necessary amount of energy applied by the heater was measured. The solution temperature was recorded manually to correct for differences between the solution's temperature and the set point temperature.

The first constructed calorimeter was described in paper II. The second version of the calorimeter was described in paper III as well as in this chapter, and is illustrated in Figure 5;

- a) A cylindrical, insulated and hollow container separated into one bottom part and one lid. The insulation was a 15-centimetre thick extruded polystyrene layer covered with glass fiber to prevent water from penetrating the insulation.
- b) A 0.5-litre volume plastic reactor was placed inside the hollow container, which was where the mixing of ice and solution took place.
- c) One heater and two temperature sensors drawn through the insulated lid of the container and placed inside the plastic reactor. One temperature sensor monitored the heating element; it was attached inside a steel block along with the heating element and programmed to cut the power if the heater became overheated in order to prevent an outbreak of fire. The other temperature sensor measured the temperature inside the ice-solution mixture. It was the heater that provided heat to the ice/solution mix.
- d) A mixing table was fitted to the container, and constructed to roll the entire container 180° back and forth. This movement ensured the proper mixing of the ice/solution blend.
- e) A 35-mm opening in the insulation was made for inserting a deicing solution during testing; otherwise, it remained closed.

f) Wires connected the electrical elements of the heater, temperature sensors and mixing table to a power supplier and data program.

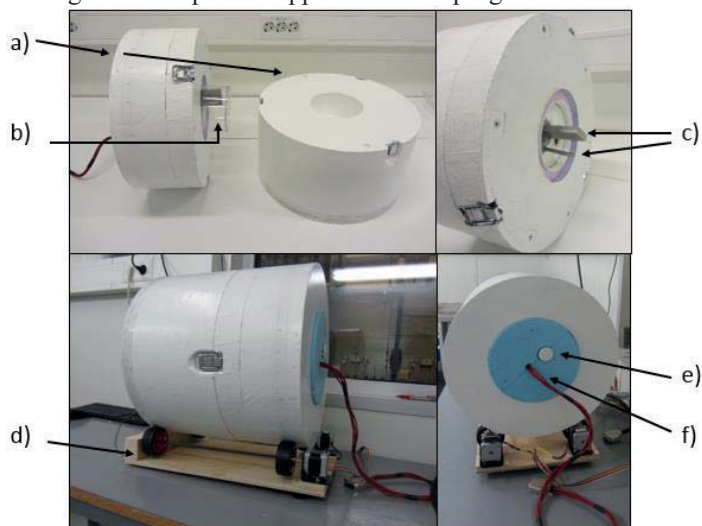


Figure 5. Construction of the calorimeter

The calorimeter was tilted to one side. All the equipment was placed in a walk-in cold room with temperature control ($\pm 1^\circ\text{C}$) to minimize heat flow through the insulation. PT100 temperature sensors measured the temperature inside the solution and at different depths in the insulation as well as the air temperature. The sensors were connected to PicoTech PT104 data loggers. A 50 W electrical heater was positioned inside the reactor and powered by a regulated 160 V DC power supply (Elektro Automatik PS8160-04). The output voltage, U (in Volt) and electrical current, I (in Ampere) measured by the power supply, was connected to a data logger (National Instruments NI-USB-6211) allowing the researchers to measure and control the amount of heat added to the system. A PC-based measurement and control application (LabView) was developed to control the calorimeter (see Figure 6). The control software kept the heater at 0.5°C above the set point until the melting process was almost finished. At the end of the procedure, this had been reduced to 0.3°C . If the heater is set much higher than the set point temperature, parts of the ice may become hotter than what the temperature sensor measures, and if it is set very low, the test will take very long time. The amount of heat needed to keep the heater at the constant temperature, meaning the added power (J/s), was integrated over the time. The container was removed between each chemical addition in order to be cleaned and prepared for a new chemical or mix.

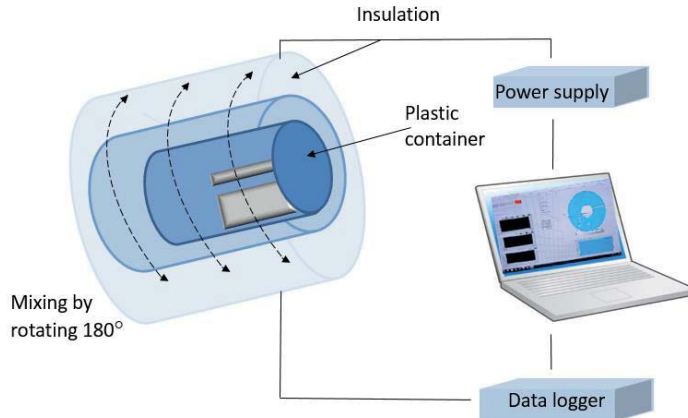


Figure 6. Illustration of the calorimeter, power supplier, data logger and pc control software (labview)

Figure 7 shows a typical graph of the temperature as a function of time. It shows that the solution's temperature rapidly dropped from the set point temperature of -17.2°C to about -17.55°C , and rose again when the heater started adding heat to the system. After 480 seconds, the temperature had returned to the initial set point temperature, and the ice melting capacity was reached and the test completed.

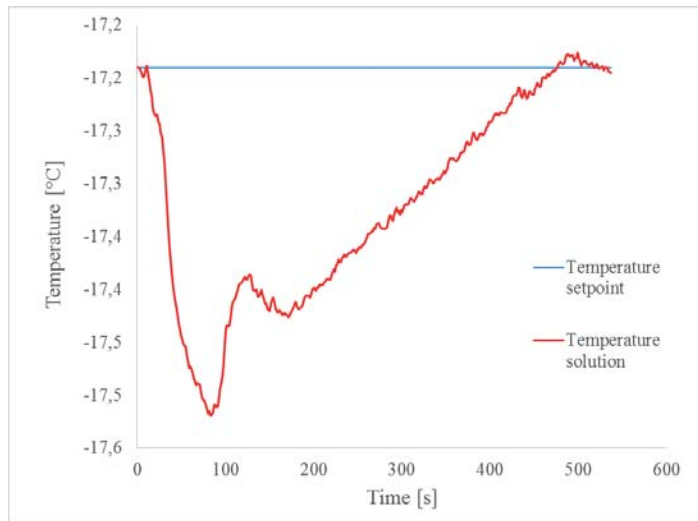


Figure 7. Temperature in solution over time

Figure 8 shows a typical graph of the added power as a function of time. It shows how the power was distributed. The area under the graph is the total added energy, which gradually declined as the solution temperature once again approached the set point. The shape of the power-time-curve comes from the fact that the system was programmed to provide heat when needed to obtain the temperature of the heater. The heat flow was at zero when the heater was hot enough, but rose as needed. The important part is the integral of the graph that produces total added energy. The heater

itself had mass, thus, there was some inertia when it was cooled down by the ice/solution mix and related by the system.

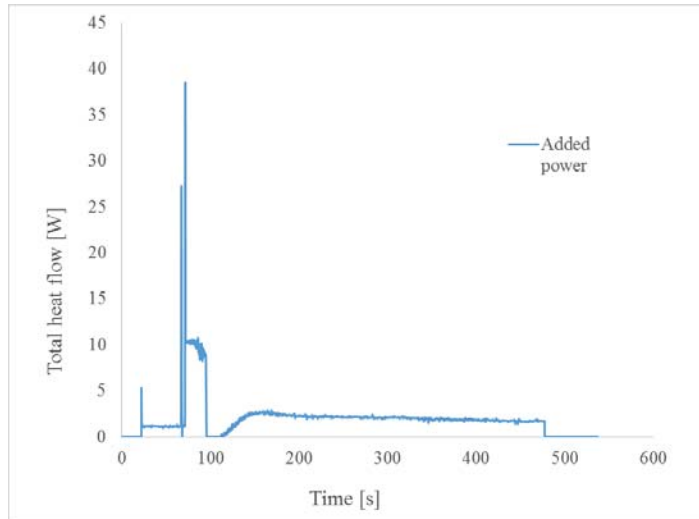


Figure 8. Typical graph of added heat over time

4.3 Test procedure

4.3.1 Accuracy of calorimeter version 1

A total of 38 ice melting capacity tests were performed using NaCl solution as a deicer. The set point temperature ranged from -2.5°C to -15.2°C . Approximately 100g (3.5 oz) of solution was used for each test with the exception of four NaCl tests, which were performed using 60g (2.1 oz) of solution.

4.3.2 Accuracy of calorimeter version 2

Accuracy was found by comparing the measured data with the calculated melting capacity. Fourteen tests were performed using 23% NaCl (brine) for the accuracy test. The temperature range varied between -17.0°C and -17.7°C . The amount of ice used was approximately 100g per test, and the amount of solution approximately 20 - 40g.

4.3.3 Ice melting capacity of common deicers in cold temperatures

A total of 63 tests were performed at approximately -18°C . Various combinations of NaCl and Magnesium Chloride (MgCl_2), Calcium Chloride (CaCl_2), Potassium Formate (Kfo), Calcium Magnesium Acetate (CMA) and sugar (sucrose/ $\text{C}_{12}\text{H}_{22}\text{O}_{11}$) were tested in the calorimeter version 2. Additionally, each of the additives/deicing chemicals were tested individually. Ice was cooled inside the calorimeter and the deicing chemicals inserted through an opening whenever a test started. The ice consisted of crushed ice cubes with an approximate size ranging from 2-6 mm.

Different solutions were prepared by the desired amount of solutes dissolved in distilled water. A concentration representing a freezing point of -27°C was chosen for MgCl_2 , CaCl_2 , Kfo and CMA. This level was under the eutectic concentration in order

to prevent precipitation of solid salt, and was the lowest before reaching CMA's eutectic temperature. According to the literature, this was 20w% for MgCl_2 (Melinder, 2007), 25w% for CaCl_2 (Melinder, 2007), 35w% for KFo (Melinder, 2007) and 35w% for CMA (Ketcham et. al., 1996). In the case of sugar, a freezing point of -19°C was chosen (70w%) (Young and Jones, 1949). This was close to the test temperature without exaggerating the concentration, as it thickened drastically at higher concentrations. The eutectic point for NaCl (-21°C) was used with the corresponding and eutectic concentration of 23w%; The tested deicers' data is shown in Table 1. The reason why the eutectic concentration was not used for all solutions, was to avoid precipitation of solid salt when mixing the solutions with NaCl solution. As described in sub-section 4.1, when C_{eq} was found with the calorimeter, it was still possible to use equation 1 to find the ice melting capacity of stronger or weaker solutions at the same temperature. Therefore, the exact concentration used in the calorimeter was not very important.

Six repetitions were performed for each chemical or mixture, except for NaCl and sugar with respectively 14 tests and one test, resulting in a total of 63 tests. Approximately 90g of ice were used in each test. The first test containing a new chemical was performed using approximately 40g of solution. The consecutive five tests with the same chemical were performed with the same ice and solutions from previous test(s) by adding approximately 20g of solution. This was done out of practical consideration in order to achieve satisfactory mixing in the beginning and without surpassing the volume capacity of the container at the test's conclusion. An overview of the tested solutions is presented in table 2.

The goal was to run all tests at -18°C . However, version 2 of the calorimeter (unlike version 1) did not have a cryostat or other installations to quickly and accurately set the temperature, which simply followed the temperature in the cold room, causing the test-temperature to vary slightly.

Deicer	Initial concentration	Temperature	Freezing point	Number of repetitions
NaCl	23%	-17.3°C (0.9°F)	-21°C	14
MgCl ₂	20%	-18.9°C (-2°F)	-27°C	6
Mix 80/20 NaCl/MgCl ₂	23% NaCl + 20% MgCl ₂ (18.4w% NaCl + 4w% MgCl ₂)	-18.8°C (-1.8°F)		6
CaCl ₂	25%	-18.6°C (-1.5°F)	-27°C	6
Mix 80/20 NaCl/CaCl ₂	23% NaCl + 25% CaCl ₂ (18.4w% NaCl + 5w% CaCl ₂)	-19.4°C (-2.9°F)		6
KFo	35%	-18°C (-0.4°F)	-27°C	6
Mix 80/20 NaCl/KFo	23% NaCl + 35% KFo (18.4w% NaCl + 7w% KFo)	-18.9°C (-2°F)		6
CMA	35%	-18.9°C (-2°F)	-27°C	6
Mix 80/20 NaCl/CMA	23% NaCl + 35% CMA (18.4w% NaCl + 7w% CMA)	-18.3°C (-0.9°F)		6
Sucrose	70%	-18°C (-0.4°F)	-19°C	1

Table 2. Performed ice melting capacity tests

5 Results

5.1 Accuracy of existing ice melting capacity test

Figure 9 shows the accuracy of existing ice melting capacity tests. The blue line is the true thermodynamic ice melting capacity, calculated using equation 1, and the markers are results from SHRP, shaker, mechanical rocker, VPA, inzell slab, ice cube titration, tracer dilution method and DSC, plotted as relative melting capacity from equation 10:

$$\text{relative melting capacity} = \frac{\text{measured melting capacity}}{\text{calculated melting capacity}} * 100\% \quad (10)$$

The relative melting capacity is in other words how much of the true ice melting capacity that was measured. The data has been converted to represent ice melting capacity per gram solid NaCl (using equation 4). The dots in Figure 9 represents tests performed with solid NaCl (it was only the SHRP test and the Inzell slab test that were performed with solids). Triangles represent tests performed with NaCl solutions and squares represents tests where pre-wetted NaCl with NaCl solution was tested. Diamonds represents results from the mechanical rocker test and the shaker test (solutions), and the small lines are the ice cube titration test and the tracer dilution method (solutions).

Figure 9 illustrated the great variation in results from the SHRP tests. Some results did not reach any or only a few percentage points of the calculated melting capacity whereas others measured more than 100%. Results above 100% are all from tests performed with solutions. These reached up to 300-400% of the calculated ice melting capacity. Five data points having values above 150% were excluded from Figure 9. The relative melting capacity of solid/pre-wetted NaCl was less than 100% for all tests. Apart from this discrepancy, no clear difference could be detected between solid/pre-wetted NaCl and solutions, as both were largely scattered. So while there may be a tendency towards lower relative melting capacity close to 0°C and the eutectic temperature (-21°C), the available data are limited at these temperatures. It appeared to be a tendency that tests performed by the same author provided more closely matching results. The VPA, ice cube titration and tracer dilution methods appeared to be closer to the true ice melting capacity than most others; however, there were only a few data points available for these methods.

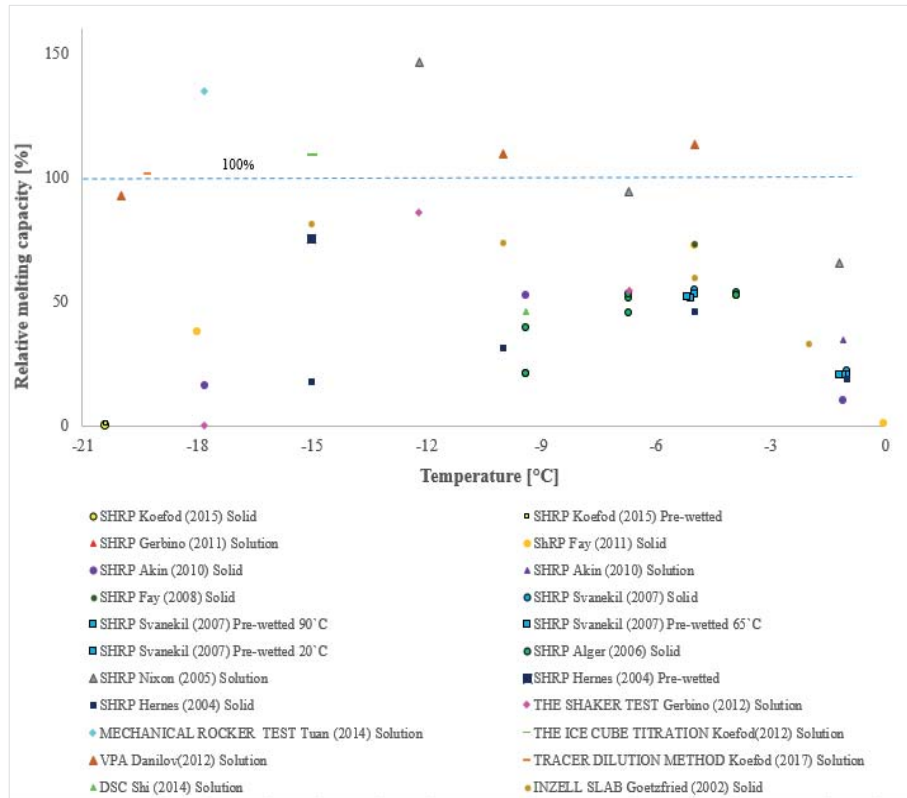


Figure 9. Relative ice melting capacity

5.2 Accuracy of the calorimeter

5.2.1 Version 1

As presented in paper II, the first calorimeter was used from -2.5°C to -15.2°C . It was a tendency that tests performed close to zero produced a higher level of accuracy than those performed in very cold temperatures. Testing in mild temperatures lead to challenges, as the ice melting capacity was very high and large amounts of ice made the mixing difficult. It was also challenging to perform tests in cold temperatures due to the fact that only a minor temperature drop occurred when it was very cold, and the first calorimeter did not provide enough time for sufficient temperature drop before heat was added. The fact that the mixing device was installed vertically inside the calorimeter, led to difficulties with achieving a homogenous temperature in the ice/solution mix, sometimes ice cubes also were stuck and the mixer stopped. The temperature sensor was installed on the wall of the calorimeter, this probably led to the temperature sensor sometimes being measuring in air, sometimes in a colder and sometimes in a warmer part of the ice/solution mix. In cold temperatures these uncertainties became large compared to the ice melting capacity.

Figure 10 shows a graphical illustration of the accuracy of measured melted ice with NaCl solution, as a percentage of the true ice melting capacity (calculated from

equation 1). Red dots represents the measured ice melting capacity in the calorimeter, and the blue line represents the calculated ice melting capacity. The calorimeter version 1 was able to measure from 95% to 158% of the actual melted water with an absolute error margin of -0.10g to 0.18g per gram solution. It is important to note that contrary to Figure 9, where the relative error was measured per gram solid NaCl, Figure 10 is per gram of solution. The relative error was larger for solutions, because the ice melting capacity for solutions is so much smaller than for solids. A constant error from the measurements, hence, had a greater influence on the relative error. When converted to represent ice melting capacity for solid NaCl (using equation 4), this equaled to an accuracy level between 96.3% to 114.4%.

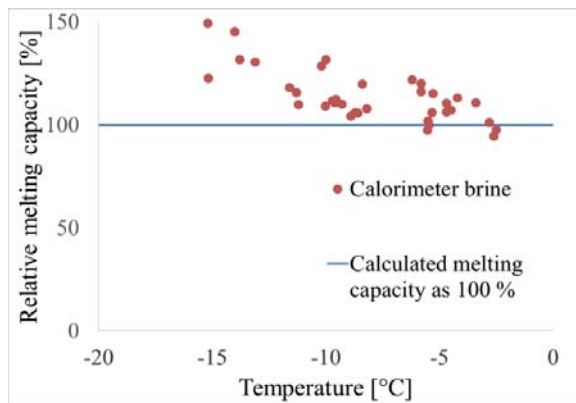


Figure 10. Relative error for solutions tested in the calorimeter version 1

5.2.2 Version 2

Next, Figure 11 shows a graphical illustration of the accuracy level of measured melted ice in grams for version 2 of the calorimeter. Red dots represents the measured melted ice in the calorimeter, and the blue line represents the calculated ice melting capacity. The calorimeter was able to measure between 97% to 115% of the actual melted water, with an average error of 104%. The absolute error ranged between -0.001g to 0.016g per gram solution. Contrary to Figure 9, where relative error was measured per gram solid NaCl, Figure 11 is per gram solution. As already mentioned, the relative error is larger for solutions due to their low ice melting capacity. When converted to solids (by using equation 4), this equaled to an accuracy level between 99.6% to 101.8%.

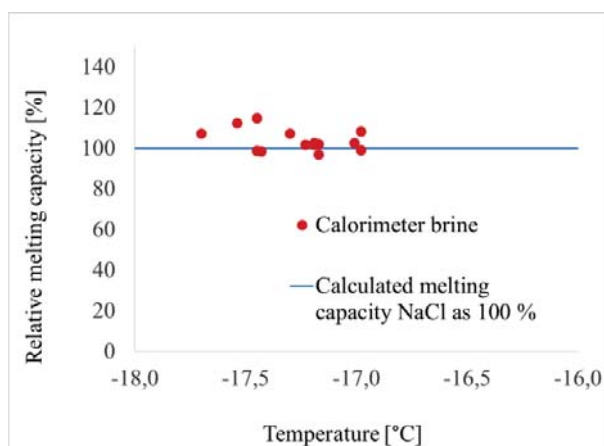


Figure 11. Relative error for solutions tested in the calorimeter version 2

The new design in version 2 produced a higher level of accuracy than the first version of the calorimeter. Both of the versions had a tendency to overestimate the amount of melted ice. Since the amount of melted ice is directly related to the amount of measured energy added to the system, the error was probably caused by overestimating the amount of heat that was added. Since the experiments were performed in a cold room at the same temperature as the set point, it is unlikely that heat leakage was the source of the overestimate. The heat from the mixer in the first version was minimal, a fact which points to the electrical heater as being the probable cause of the overestimation; however, the overestimation was very low with regard to version 2. The average overestimation was only +4%.

5.3 Ice melting capacity of common deicers in cold temperatures

5.3.1 Solutions and additives

Figure 12 shows the measured ice melting capacity in grams per gram solution for MgCl_2 (20%), CaCl_2 (25%), KFo (35%), CMA (35%) and sugar (70%) at approximately -18°C , given by the calorimeter. There were some differences in the set point temperature due to the calorimeter's design, so the average data was included in Figure 12a) and all data in Figure 12b). The blue line represents the true ice melting capacity of 23% NaCl solution (brine), calculated from equation 3. MgCl_2 (20%), CaCl_2 (25%), KFo (35%) and CMA (35%) all had higher ice melting capacity than brine. CaCl_2 (25%) had the highest ice melting capacity of the tested solutions, melting 285 % more than brine. The brine actually had lower ice melting capacity than all the other tested chemicals, except the sugar who froze and therefore had zero ice melting capacity. Using MgCl_2 (20%), CaCl_2 (25%) or CMA (35%) as additives to brine in an 80/20 brine/additive-mix increased the ice melting capacity of the brine. The chlorides seemed to increase the ice melting capacity of brine dependent on approximately the amount added to the brine, as the 80/20 NaCl/ MgCl_2 result lay between, but closer to, the individual NaCl value than the individually MgCl_2 and CaCl_2 results. Mixing CMA to NaCl gave an unexpected result. The mix actually had higher ice melting capacity

than the two components individually. In contrast, using KFo (35%) as an additive actually decreased the melting capacity, with a result lower than each of the components had individually.

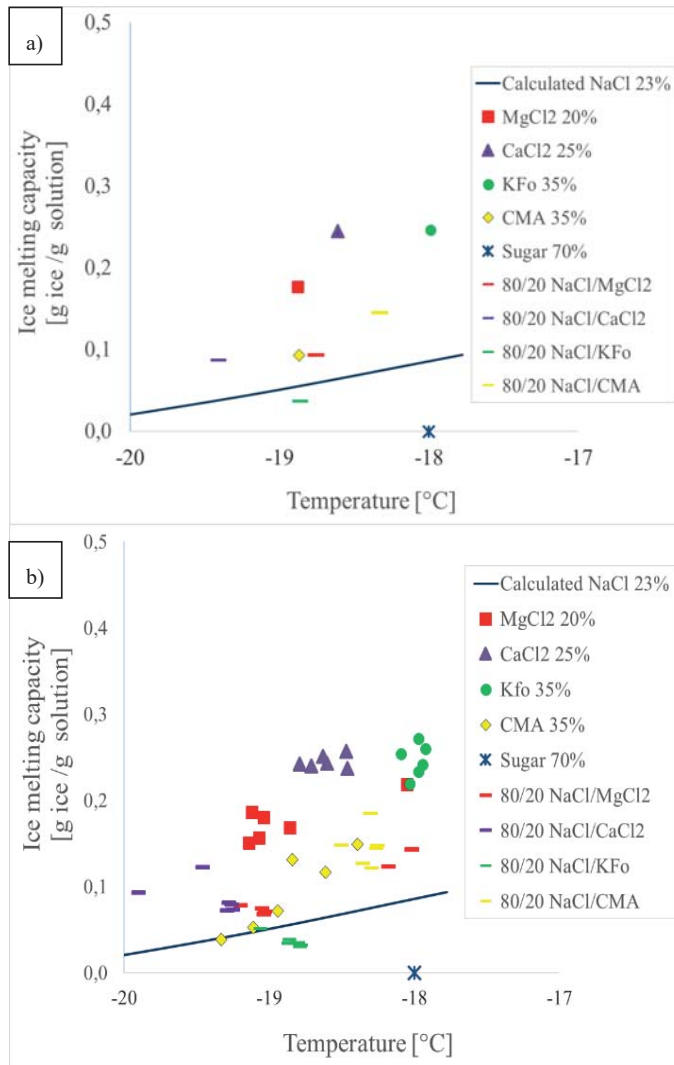


Figure 12. Ice melting capacity of deicing solutions 12a) average data 12b) all data

A significance analysis was performed using t-test with a 95% confidence interval. This test determined whether there was a difference between the tested chemicals and brine, see Table 3. Table 3 also shows the resulting C_{eq} , calculated from equation 1. The t-test showed that there was a significant higher ice melting capacity with 20% MgCl₂, 30% CaCl₂ and 35% KFo compared with brine. The individual 35% CMA result was not significant. For NaCl with additives, it was significant higher ice melting capacity adding 20% MgCl₂, 25% CaCl₂, 35% KFo or 35% CMA solution to the brine.

Deicer	Temperature °C	IMC (g/g)	More(+)/less (-) melted ice than brine		Statistically significant	C _{eq} (%)
			(g)	(%)		
MgCl ₂	-18.9	0.17	+0.12	+228	Yes	17.0
80/20 NaCl/MgCl ₂	-18.8	0.09	+0.03	+56	Yes	20.5
CaCl ₂	-18.6	0.24	+0.18	+285	Yes	20.1
80/20 NaCl/CaCl ₂	-19.4	0.09	+0.05	+144	Yes	21.5
KFo	-18.0	0.25	+0.16	+187	Yes	28.1
80/20 NaCl/KFo	-18.9	0.04	-0.02	-33	Yes	24.5
CMA	-18.9	0.09	+0.04	+61	No	32.1
80/20 NaCl/CMA	-18.3	0.14	+0.07	+97	Yes	30.6
Sugar	-18.0	0	-	-	-	-

Table 3. Difference in ice melting capacity between various types of deicers and brine

5.3.2 Solid chemicals and additives

Seen from a winter road maintenance perspective, it is important to note that the ice melting capacity of solutions, as shown by the numbers along the vertical axis in Figure 12, were low. The ice melting capacity for solutions is lower compared to solid chemicals simply because of the water content. In Figure 13 has the ice melting capacity been converted to represent solid chemicals. This was done by using the equilibrium concentration (C_{eq}) from Table 3. Because of the difference in set point temperature, Figure 13a) shows average data, while Figure 13b) shows all data. The blue line is the true ice melting capacity for solid NaCl, calculated from equation 4. The dots are measured values in the calorimeter, calculated using equation 4. Note that the results for MgCl₂ are given in hexahydrate and results for CaCl₂ in dihydrate, according to equations 7 and 8. All of the tested chemicals had less ice melting capacity than NaCl in solid state. The ice melting capacity of solid NaCl was also reduced if additives were used. The additives seemed to reduce the ice melting capacity dependent on how much of it that was added, as the ice melting capacity of the mixtures of NaCl + additives laid somewhere between the results of the two components individually.

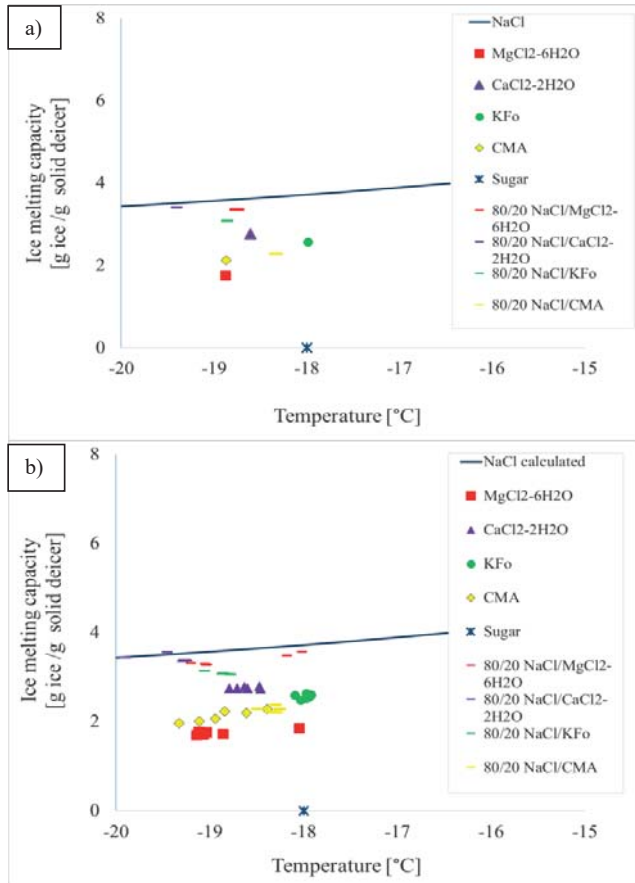


Figure 13. Ice melting capacity for solid chemicals 13a) average data 13b) all data

T-tests were performed with a 95% confidence interval, and the observed lower melting capacity was significant for all tested chemicals and additives compared to NaCl, as demonstrated in Table 4.

Deicer	Temp. (°C)	IMC (g/g)	More (+)/less(-) melted ice than NaCl (g) (%)		Statistically significant
MgCl ₂ -6H ₂ O	-18.9	1.75	-1.83	-51	Yes
80/20 NaCl/ MgCl ₂ -6H ₂ O	-18.8	3.36	-0.24	-7	Yes
CaCl ₂ -2H ₂ O	-18.6	2.76	-0.87	-24	Yes
80/20 NaCl/ CaCl ₂ -2H ₂ O	-19.4	3.42	-0.1	-3	Yes
KFo	-18.0	2.56	-1.16	-31	Yes
80/20 NaCl/ KFo	-18.9	3.08	-0.51	-14	Yes
CMA	-18.9	2.12	-1.46	-41	Yes
80/20 NaCl/ CMA	-18.3	2.27	-1.14	-38	Yes
Sugar	-18.0	0	-	-	-

Table 4. Melted ice compared to NaCl

5.3.3 Sugar in cold temperatures

The sugar produced unexpected results: according to the phase diagram (Young and Jones, 1949), the solubility for sugar is 70% at -18°C. However, this assertion did not correspond with the author's experience, even at +25°C, it was very difficult to dissolve all the sugar to make a 70w% solution, and the solution remained cloudy and the sugar was not completely dissolved even after prolonged shaking. Further, sugar crystals deposited at the bottom of the bottle in a resting state. Visually speaking, at -18°C it had a very high level of viscosity but no forming of hard ice. However, it was indeed frozen. When the solution was added to the calorimeter, the temperature increased. This increase could have been the result of released energy because of the latent heat of freezing (Atkins, 2012), meaning that heat was released when the sugar solution came into contact with ice, and freezing took place. Therefore, in order to be sure that the solution actually froze and that the ice melting capacity was zero at -18°C, the solution was studied under a microscope using cross-polarized light, see Figure 14. There were clear fragments of frozen water, as ice crystals in the solution. This means that sugar is probably not applicable in practice for very cold temperatures. It is difficult to dissolve to necessary concentration to prevent freezing.

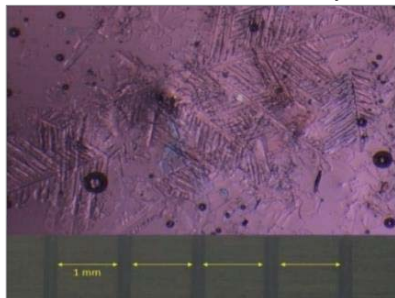


Figure 14. Ice crystals in sugar solution at -18°C

6 Discussion

6.1 Need for a new ice melting capacity test method

This study demonstrated that current standardized test methods for measuring ice melting capacity, SHRP H-205.1 for solid chemicals and 205.2 for liquid chemicals, are not accurate enough for research purposes and have low reproducibility. For instance, all results published from SHRP H-205.1 were below full melting capacity for NaCl. This fact implies that the melting process was still ongoing when the test was halted after 60 minutes, and that the chemical did not reach its full melting capacity. The data from SHRP H-205.2 showed that more of the calculated melting capacity was achieved with brine compared to solid/pre-wetted NaCl. The reason for this was most likely that the previously dissolved salt had a head start on solid salt from the outset, thereby working faster and achieving levels closer to full melting capacity in 60 minutes. The scattered data implies low reproducibility, which might be caused by 1) inconsistencies while performing the test, 2) poor temperature control from the surrounding environment and mechanical handling, 3) variations in the dispersion of grains (influencing the surface area that is in direct contact with the ice), and 4) difficulties in collecting all the melted water. The mechanical rocker test, ice cube titration test, tracer dilution method and VPA appeared to measure closer to the full melting capacity compared to the SHRP H-205.2, shaker test, inzell slab test and DSC. Further, although they have eliminated a certain number of the factors that possibly contributed to scatter, due to the limited amount of data, it is difficult to draw conclusions about their reproducibility. The ice cube titration test and VPA were the only test methods not limited by time constraints, while the others were a combination of ice melting capacity and ice melting rate. There was still mechanical handling involved, however, and poor control of the temperature difference between the ice and solution. The VPA and DSC are actually freezing point tests which use the freezing point to calculate the ice melting capacity. VPA seems to be the method closest to the true ice melting capacity, measuring from 93% - 114% of the actual melted water. However, determination of ice crystal growth through visual means might be difficult; especially for sugar-based products.

The new test method developed during this study was based on calorimetry and demonstrated great improvements in accuracy and reproducibility compared to SHRP. It was a relative simple and easy construction; at the same time, there were no commercial available calorimeters for ice melting capacity testing of deicing chemicals, and building one required a minimum of technical skills as well as programming skills. Moreover, it required having a walk-in refrigerated cooler.

Initially, the tests were performed in a room having a temperature of +20°C; heat leakage was therefore determined and taken into account; nonetheless, this action did not provide sufficient temperature control, as exposing the deicers or the ice to room temperature, even only for the seconds it took to transport them from the freezer to the calorimeter, led to an uncontrolled temperature rise and inaccurate results. The calorimeter was able to test approximately six replications for one chemical during the course of a work day. Because it needed a few hours to cool down after cleaning, switching to another chemical took quite a long time. Additionally, it took time to find a correct initial temperature since there were no integrated cooling systems, and the set point temperature had to follow the temperature in the walk-in refrigerated cooler. However, it is important to remember that ice melting capacity is physically constant, so when the ice melting capacity of a deicer is determined, there is no need to test the same chemical again. If the tested deicer in the calorimeter has a known concentration (we know the amount of solid chemical and water), the equilibrium concentration can be determined (as explained in chapter 4), and the ice melting capacity calculated for all concentrations of the specific deicer in the tested temperature. In other words, there is only a need for testing a specific product at different temperatures and not at different concentrations.

6.2 Improving the ice melting capacity of NaCl in cold temperatures by using additives

There are other deicing products with lower possible freezing points than NaCl, including MgCl₂ and CaCl₂ (Ketcham et al., 1996), but this is not synonymous with having a higher melting capacity in cold temperatures because there are several factors affecting ice melting, for example solubility (Koefod, 2008).

The calorimeter showed that solid NaCl has relatively high ice melting capacity compared to other common deicers, even at low temperatures close to its eutectic point. However, it has a low ice melting capacity when used as brine compared to other solutions. Out of the individually chemicals tested in solid state (NaCl, MgCl₂, CaCl₂, KFo, CMA and sugar), NaCl had the highest ice melting capacity. The chemicals were also tested as additives to solid NaCl, which decreased the ice melting capacity of NaCl. Both MgCl₂ and CaCl₂ contained a high amount of water in a solid state, by existing as MgCl₂·6H₂O and CaCl₂·2H₂O. This water contributes to a lower ice melting capacity in a solid state. The data also confirmed that there is not a linear correlation between freezing point and ice melting capacity (Koefod, 2008). The reason why NaCl has high ice melting capacity at -18°C is that it has a high initial concentration and low freezing concentration, a factor which is necessary according to equation 4. Experiences with NaCl suggest that it is “ineffective” in cold temperatures; nonetheless, as the data points out, this is not due to the melting capacity. This confirms the findings from Koefod, 2012. The experienced “ineffectiveness” is probably due to other mechanisms, such as a low melting rate (that NaCl works very slowly) in cold temperatures (Koefod, 2015).

In solutions the results were reversed. MgCl₂ (20%), CaCl₂ (25%), KFo (35%) had a higher ice melting capacity than NaCl (23%). The ice melting capacity of CMA solution (35%) was not significantly different from brine. Using MgCl₂ (20%), CaCl₂

(25%) and CMA (35%) as additives to brine increased the ice melting capacity by 56% - 144%. In contrast, using sugar or KFo (35%) as an additive decreased it. Previous studies (Koefod et al., 2012) have implied that the benefits of adding $MgCl_2$ to NaCl is additive of the two compounds. While this observation was not confirmed in this research project, the results imply that there is a correlation between the ice melting capacity and amount added chloride ($MgCl_2$ and $CaCl_2$) to brine. Interestingly, the experiments using KFo and CMA produced different results. More specifically, when used individually, KFo (35%) had a relatively high ice melting capacity as a solution at $-18^\circ C$. But when the KFo solution was added to brine, the results were destructive, as the ice melting capacity was reduced to a level lower than not only KFo but also NaCl. The precise reason as to why this happened is unknown; however, it might be that the quality of these two chemicals together makes them destructive with respect to ice melting capacity. Mixing CMA (35%) with brine also produced an unexpected result: The mixture increased the melting capacity to a higher level than the two components had individually. In the future, it would be very interesting to conduct more research on this mixture.

Using maximum solubility for NaCl, $MgCl_2$ and $CaCl_2$ solutions will result in a higher ice melting capacity than the results in chapter 5 show. The solubility at $-18^\circ C$ is higher than used in this particular research project; according to the extended UNIQUAC (Thomsen, 1997) model, it is 23.9% for NaCl at $-17.3^\circ C$, 27.3% for $MgCl_2$ at $-18.9^\circ C$ and 34.5% for $CaCl_2$ at $-18.6^\circ C$. Calculations according to chapter 4.1.2 and equation 4 were done using values of C_{eq} from Table 3, to find the ice melting capacity with maximum solubility:

$$IMC_{NaCl} = \frac{C_{prod} * m_{prod}}{C_{eq}} - m_{product} = \frac{0.239 * 1}{0.206} - 1 = 0.15 \text{ g/g solution}$$

$$IMC_{MgCl_2} = \frac{0.273 * 1}{0.17} - 1 = 0.61 \text{ g/g solution}$$

$$IMC_{CaCl_2} = \frac{0.345 * 1}{0.201} - 1 = 0.72 \text{ g/g solution}$$

When NaCl was used as 23.9% instead of 23% at $-17.3^\circ C$, it increased the ice melting capacity from 0.11g/g to 0.15g/g (36%). The ice melting capacity of $MgCl_2$ increased 258%, from 0.17g/g used at a 20% solution at $-18.9^\circ C$ to 0.61g used as a 27.6% solution. The ice melting capacity for $CaCl_2$ increased 200%, from 0.24g/g used at a 25% solution at $-18.6^\circ C$ to 0.72 used as a 34.5% solution. Using $MgCl_2$ and $CaCl_2$ as additives to a 23% NaCl solution probably follows the same trend as with lower solubility, increasing the brine's melting capacity. This calculation shows how using stronger solutions significantly increases the ice melting capacity. Similar calculations were not done for CMA and KFo, since the maximum solubility at $-18^\circ C$ is unknown. Despite maximum solubility increasing the ice melting capacity considerably, the ice melting capacity of solutions is still very low compared to solid chemicals.

6.3 Ice melting capacity of solid deicers vs deicing solutions

The results in this dissertation visualized the drastic decrease in ice melting capacity when solutions were used instead of solid chemicals, not only for NaCl but for all tested deicers. Quite naturally, the reason is that the solutions contain water, and water

does not contribute to melting in temperatures below 0°C. Figure 15 shows the ice melting capacity of NaCl, MgCl₂, CaCl₂, KFo, CMA and sugar in both their solid state and solutions at approximately -18°C. The blue spots represent solid chemicals, and the red dots represent solutions. In practice, as shown in sub-section 6.5, this means that extreme application rates would be needed if solutions were used to achieve the same ice melting capacity as using solids.

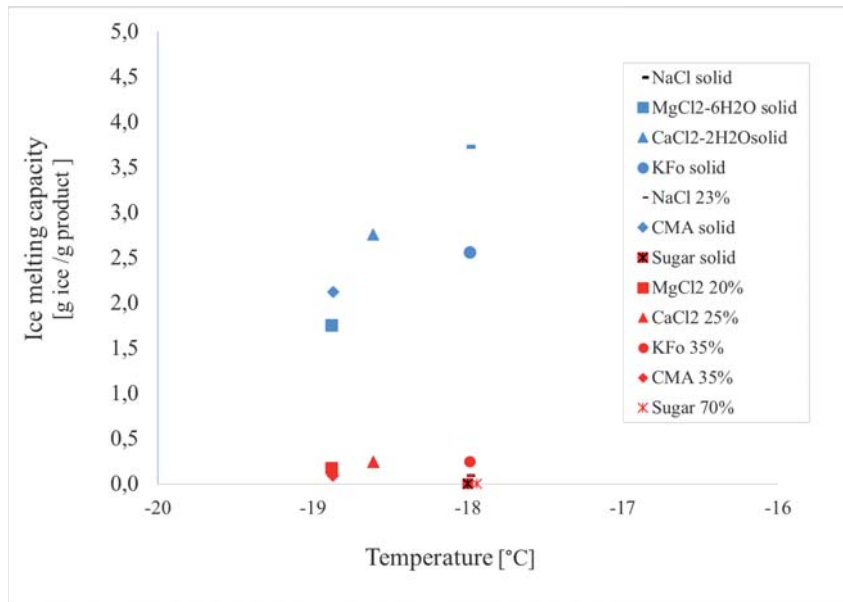


Figure 15. Ice melting capacity of solid deicers and solutions at approximately -18°C

6.4 Pre-wetting

As seen in Figure 15, solutions have far lower ice melting capacity than solids. Pre-wetting is a technique where the solid deicer is submerged into a deicer solution before added to the road. Since ice melting capacity is defined per gram, pre-wetting results in lower ice melting capacity than using only solids. However, since the amount of pre-wetting is small compared to the amount of solids, it will probably not drastically lower the ice melting capacity. Further, since there is research showing that it might impact other important measures, such as the melting rate (Koefod, 2017), it may be beneficial to pre-wet the deicer to increase longevity in cold temperatures.

6.5 Application rate determined by ice melting capacity

Ice melting capacity tells us how much ice we can melt per gram of deicer, hence it can be used to determine application rates, which is important to find if the deicer is in practice effective or if unrealistic amounts are needed. We are often situated in a deicing situation when salting at very cold temperatures (Akin et. al, 2013), where we need to melt pre-existing ice on the road. However, the ice melting capacity can also

be used to determine the chemicals' applicability for preventing the road from freezing (anti-icing). The equilibrium concentration (C_{eq}), acquired from calorimeter measurements, is the freezing point concentration; hence, it tells us both at which concentration a solution stops melting and when it starts freezing. To determine application rates for both deicing and anti-icing, consider the following example: A road section lies in a cold area, where the temperature is approximately -18°C . Due to a sudden turn in the weather, a thin hoarfrost layer of 100 g/m^2 (0.1mm) (Karlsson, 2001) forms on the road. Yet in order to prevent this ice from forming in the first place, the application rate must be in accordance with the "anti-icing" column in Table 5 if solutions are used and Table 6 if solid chemicals are used. To melt already established ice on the road, the application rate must be in accordance with the "deicing" column in Table 5 for solutions and Table 6 for solid chemicals. Research has shown that for anti-icing purposes, 60% less salt (using NaCl and KFo) is needed compared to concentrations predicted by the freezing point depression theory (Klein-Paste and Wählin, 2013), because any ice formed in a solution will be weakened and easily destroyed by traffic. While the same assumption has been made for other chemicals, its veracity is presently unknown. Also in a deicing situation, the traffic can help with destroying the ice, which in Table 5 and 6 is not taken into account. This because the help from traffic is an unknown parameter for deicing, and because the ice penetration and ice undercutting qualities of the chemical probably has less effect on very thin ice layers than thicker snow/ice layers. For comparison: Typically application rates in Norway are $15\text{-}40\text{ g/m}^2$ (NPRA, 2014).

Deicer	Temperature ($^{\circ}\text{C}$)	Ice melting capacity ($\text{g}_{\text{ice}}/\text{g}_{\text{deicer}}$)	Deicing (g/m^2)	Anti-icing (g/m^2)
NaCl 23% (calculated)	-18.5	0.070	1428.6	857.1
MgCl ₂ 20%	-18.9	0.177	565.6	339.4
MgCl ₂ 27.3% (max solubility)	-18.9	0.606	163.9	98.4
CaCl ₂ 25%	-18.6	0.245	408.2	244.9
CaCl ₂ 34.5% (max solubility)	-18.6	0.716	138.9	83.3
KFo 35%	-18	0.246	406.3	243.8
CMA 35%	-18.9	0.093	1071.8	643.1

Table 5. Application rate for deicing solutions, at approximately -18°C with 100g/m^2 ice on the road

Deicer	Temperature (°C)	Ice melting capacity ($\text{g}_{\text{ice}}/\text{g}_{\text{deicer}}$)	Deicing (g/m^2)	Anti-icing (g/m^2)
NaCl (calculated)	-18.5	3.642	27.5	16.5
MgCl ₂	-18.9	0.177	44.5	26.7
CaCl ₂	-18.6	0.245	33.5	20.1
KFo	-18	0.2461	39.1	23.4
CMA	-18.9	0.0933	47.1	28.3

Table 6. Application rate for solid deicers at approximately -18°C with $100 \text{ g}/\text{m}^2$ ice on the road

Solutions require a much higher application rate compared to solids. As demonstrated in the examples above, using solutions for deicing and anti-icing is most times practically impossible in cold temperatures. The application rate is unrealistically high, and in practice the deicers are found to be “ineffective”. There are instructions for operators stating that solid salt should never be used (Ljungberg, 2002), but the research in this dissertation cannot support this assertion. Solid NaCl had the highest ice melting capacity of the tested chemicals and is, according to Tables 5 and 6, the deicer with the lowest necessary application rate. Using brine for deicing at -18.5°C requires $1400 \text{ g}/\text{m}^2$, but for solid salt the application rate is within a standard range (Minsk, 1998), less than $30 \text{ g}/\text{m}^2$. The effect of traffic has not been included, so in practice it is most likely necessary to use less salt, as the ice layer disintegrates and small pieces of ice are removed by traffic without being melted. On the other hand, the effect of blow offs has not been included in this calculation.

6.6 Winter maintenance of high traffic volume roads in cold climates

The research in this dissertation has highlighted the fact that solid (or pre-wetted) chemicals are the only practical application method to achieve sufficient ice melting capacity in cold temperatures (approximately -18°C). A maintenance driver’s main strategy should be to avoid damp road surfaces whenever it becomes very cold; however, a road can still become slippery despite this strategy, for instance in the case of hoar frost, precipitation as light snow, freezing rain, or high levels of humidity (particularly around open water). Should these situations arise, road maintenance operators face a challenging need for deicing, requiring a chemical with both a high level of ice melting capacity and high melting rate.

The research results here demonstrated that solid NaCl actually has a relatively high level of ice melting capacity compared to other tested chemicals at -18°C . However, it has been stated by other researchers that solid NaCl works very slowly in cold temperatures. For example, Minsk (1998) writes that previous research demonstrates

that it takes about 3-5 minutes for solid salt to start working at -1°C; yet if the temperature drops to only -4°C, it takes as long as 19 minutes to accomplish the same. Further, Koefod et al. 2015 state that pre-wetting the solid salt substantially increases the melting rate and that pre-wetting with MgCl₂ increases the melting rate to an even higher degree than pre-wetting with NaCl or CaCl₂. Hence, there are reasons to believe that solid NaCl pre-wetted with MgCl₂ could work as a deicer in very cold temperatures. There remains a great deal of work to be done in researching the ice melting rate and optimizing the rate of pre-wetting. Since the dissolution of NaCl is highly dependent on the temperature, it would be very interesting to undertake more research on warm mixing (heating the MgCl₂ solution before pre-wetting it to the NaCl). NaCl has shown to have very low ice melting capacity used as solution (e.g., brine). If it is not possible to keep the salt on the road long enough for it to start working, solutions might be needed instead. MgCl₂ and CaCl₂ solutions can provide sufficient ice melting capacity used with maximum solubility but only with very high application rates (140-170 g/m²), other tested solutions and concentrations gave unrealistically high application rates.

Solid NaCl has a eutectic temperature of -21°C, and below this NaCl has zero ice melting capacity. The next example is included to find the deicer with highest ice melting capacity at -22°C, where NaCl can no longer be used. Tests were not performed in the calorimeter at -22°C, so freezing point data (Ceq) for MgCl₂, CaCl₂ and KFO was collected from earlier published data or phase diagrams. According to the literature Ceq at -22°C was 18% for MgCl₂ (Melinder, 2007), 22.5% for CaCl₂ (Haynes and Bruno, 2014) and 30.8% for KFo (Melinder, 2007). CMA is not included, as it is a less researched chemical than the others, and a comparison between the published data (Ketcham, 1991), which showed an ice melting capacity of 2.62 at -18.9°C, and the measured data in the calorimeter, who showed an ice melting capacity of 2.62 at the same temperature was made. This is a difference of 24%, far greater than the uncertainty of the calorimeter, which indicates that the previously published phase diagram for CMA is not correct. The same comparison was done between published and calorimeter data for MgCl₂, CaCl₂ and KFo, where the results were equal to one another. Sugar was also not included, as it froze already at -18°C. According to equation 4, the ice melting capacity at -22°C is;

$$IMC_{MgCl_2 \cdot 6H_2O} = \frac{0.468}{0.18} - 1 = \underline{1.6 \text{ g/g}}$$

$$IMC_{CaCl_2 \cdot 2H_2O} = \frac{0.755}{0.225} - 1 = \underline{2.36 \text{ g/g}}$$

$$IMC_{KFo} = \frac{1}{0.308} - 1 = \underline{2.25 \text{ g/g}}$$

The results are given as ice melting capacity per gram solid deicer. There seems to be very little difference in the ice melting capacity between CaCl₂-2H₂O and KFo at -22°C, giving an application rate of approximately 40g/m². MgCl₂-6H₂O had lower ice melting capacity, producing an application rate of approximately 60g/m².

6.7 Further work

It is important to remember that ice melting capacity is a physical constant dependent only on chemicals, temperatures and concentrations. Once the equilibrium concentration (C_{eq}) is determined for a chemical, there is no need to measure other concentrations, as they can be calculated. This means that when the ice melting capacity for a chemical is measured correctly, the result will be the same every time. Regarding further exploration, it would be valuable to test the most common deicing chemicals for a larger temperature range, once and for all establishing their ice melting capacity and publishing them for use in the field of winter road maintenance. The calorimeter can also be used to test commercial available deicing products. The mixture of CMA and NaCl solutions produces an elevated ice melting capacity, and it would be interesting to pursue more research on this topic; however, this mixture still had lower ice melting capacity than did the solids.

Ice melting capacity tests should be performed as laboratory tests due to the need for a high degree of temperature control. However, there are factors out in the real world that might impact practical usage, affecting other important qualities than deicers' ice melting capacity, e.g. melting rate, durability on the road (before blow off/spray off etc.), penetration disbondment and undercutting. For instance, a field study undertaken to determine how these chemicals are influenced by traffic and solar radiation might be useful, as it does not help to have sufficient application rate regarding ice melting capacity if the chemicals blow off the road before doing their job.

Further research on ice melting rate is also crucial for the understanding of cold temperature performance.

7 Conclusions

This is the dissertation from Kine Nilssen's PhD work with the title "Ice melting capacity of deicing chemicals in cold temperatures". The main conclusions of the dissertation are:

- The current standard test methods, SHRP H-205.1 and H-205.2, for measuring the ice melting capacity of deicing chemicals respectively for solid and liquid deicers, have shown to produce results that are not accurate enough for research purposes and have low reproducibility. The results were scattered between measuring 0% - 400% of the true thermodynamic ice melting capacity.
- The true thermodynamic ice melting capacity can be calculated for any chemical who has a known phase diagram/freezing curve. How this was done is described in the dissertation.
- A new method for measuring ice melting capacity was developed during this research. The new method was based on calorimetry. Calorimetry appears to be a feasible way of measuring ice melting capacity and produced far more accurate results than the SHRP tests. The calorimeter has eliminated sources of error in the SHRP test, such as mechanical separation of meltwater and ice, manual handling of the equipment during the test, issues involving different grain size or how the grains become scattered over the ice and, finally, the pre-defined testing time making the measurement dependent on the melting rate. The calorimeter was able to produce results between 97% - 115% of the true thermodynamic ice melting capacity (being 100%), with an average error of 4%.
- The calorimeter was used to measure ice melting capacity of common deicers and additives to NaCl in cold temperatures. The deicers tested were; NaCl (23%), MgCl₂ (20%), CaCl₂ (25%), KFo (35%), CMA (35%) and sugar (70%). The test temperature was approximately -18°C. The chemicals were tested individually and also as additives to NaCl in a 80/20-mix (80% NaCl with 20% additive). The calorimeter was built for testing solutions, and the results are given as ice melting capacity per gram solution, as well as converted to ice melting capacity per gram solid chemical.
- Solid sodium chloride (NaCl) had the highest ice melting capacity of all tested deicers, with a 31% higher ice melting capacity than the second best deicer,

solid calcium chloride ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$). Additives to solid NaCl resulted in lower ice melting capacity.

- The tests showed that ice melting capacity is drastically reduced when solutions are used instead of solid chemicals. The ice melting capacity of the solutions was only 3% – 10% of the solid ice melting capacity in cold temperatures. If solutions are the only option, CaCl_2 (25%) was the solution with highest ice melting capacity of the tested solutions, performing 285% better than brine (23% NaCl).
- Using highest possible concentration will increase the ice melting capacity. A calculation was done showing that using maximum concentration of CaCl_2 (34.5%) at -18.6°C increases the ice melting capacity with 200% compared to 25% CaCl_2 .
- Brine was the solution with the least ice melting capacity at -18°C of the tested chemicals. Except sugar who froze and therefore had zero ice melting capacity. The sugar solution was very difficult to dissolve to necessary concentration. For winter maintenance perspective it is likely not applicable in very cold temperatures.
- Ice melting capacity is important regarding application rate. To deice a thin ice layer at approximately -18°C requires; 27.5 g/m^2 using solid NaCl, 138.9 g/m^2 using CaCl_2 solution (34.5%) and the extreme amount of 1428 g/m^2 using brine (23% NaCl).
- From an ice melting capacity point of view, solid NaCl is the preferred deicing chemicals in very cold temperatures. Except if the temperature drops below its eutectic point of -21.1°C , where NaCl has no melting effect, but where solid MgCl_2 , CaCl_2 , KFo and CMA do.

References

Achkeeva, M.V., Romanyuk, N.V., Frolova, E.A., Kondakov, D.F., Khomyakov, D.M. and Danilov, V.P. (2015) Deicing properties of sodium, potassium, magnesium, and calcium chlorides, sodium formate and salt compositions on their basis. *Theoretical Foundations of Chemical Engineering*, 49(4), pp.481–484. doi:10.1134/S0040579515040028

Akin, M. and X. Shi. (2010) Development of Standardized Test Procedures for Evaluating Deicing Chemicals. Publication CR07-02 Project 0092-08-32. Western Transportation Institute. Montana State University.

Akin, M., Huang, J., Shi, S., Veneziano, D., Williams, D. (2013) *Snow removal at extreme temperatures*. (Clear roads program report, 3/20/12-1/31/2013). Bozeman: Montana State University, available at: http://clearroads.org/wp-content/uploads/dlm_uploads/11-04-Snow-Removal-Extreme-Temps-Final-Report.pdf

Alger, R. and Haase, J. (2005) *Analysis of the benefits of bulk pre-wetting solid NaCl with several different liquids*, (research report RC-1473), Michigan Department of Transportation, available at: http://www.michigan.gov/documents/MDOT_RC-1473_161865_7.pdf

Atkins, P. and Paula, J. (2012) *Elements of Physical Chemistry*. 6th, Oxford, United Kingdom: ed. Oxford University Press

Bekker, T. B., Kokh, A. E., Kononova, N. G., Fedorov, P. P. and Kuznetsov, S. V. (2009) Crystal Growth and Phase Equilibria in the BaB₂O₄–NaF System, *Cryst. Growth Design*, 9 (9), pp. 4060–4063. doi: 10.1021/cg9002675

Blackburn, R. R., Amsler, D. E. Sr. and Bauer, K. M. (2004) Guidelines for Snow and Ice Control Material and Methods. *Sixth International Symposium on Snow Removal and Ice Control Technology. Transportation Research Circular E-C063*. Spokane, Washington, June 7-9, pp. 31-49

Blomqvist, G. and Johansson, E-L. (1999) Airborne spreading and deposition of deicing salt - a case study, *Science of The Total Environment* 235 (1-3), pp. 161-168. doi: 10.1016/S0048-9697(99)00209-0

Brodsky, H. and Hakkert, A. (1988) Risk of a Road Accident in Rainy Weather. *Accident Analysis and Prevention*, 20, pp. 161–176.

Brown, B. and Baass, K. (1997) Seasonal Variation in Frequencies and Rates of Highway Accidents as Function of Severity, *Transportation Research Record: Journal of the Transportation Research Board*, 1581, pp. 59–65.

Chappelow, C.C., D.A. McElroy, R.R. Blackburn, D. Darwin, F.G. Noyelles, and Locke C.E. (1992) Handbook of Test Methods for Evaluating Chemical Deicers, SHRP-H-6, 332nd, Washington D.C: ed. Strategic Highway Research Program. National Research Council.

Danilov, V. P. Frolova, E. A. Kondakov, D. F. Avdyushkina, L. I. Orlava, V. T. (2011) Low-temperature anti-icing reagents in the $\text{Ca}(\text{NO}_3)_2\text{-Mg}(\text{NO}_3)_2\text{-CO}(\text{NH}_2)_2\text{-H}_2\text{O}$ system and their properties, *Theoretical Foundations of Chemical Engineering*, 45 (5), pp. 697-701. doi: 10.1134/S0040579511050058

Danilov, V. P. Frolova, E. A. Kondakov, D. F. Avdyushkina, L. I. Bykov, A.V. Orlava, V. T. (2012) Low-temperature anti-icing reagents in aqueous salt systems containing acetates and formiates, *Theoretical Foundations of Chemical Engineering*, 46 (5), pp. 528-535. doi:10.1134/S0040579512050028

Fangming, J., Guangyi, Z., Yujia, J., Yosiyuki, W., Atsushi, K. and Heiji, E. (2010) A new process for producing calcium acetate from vegetable wastes for use as an environmentally friendly deicer, *Bioresource Technology*, 101(9), pp. 7299-7306

Fay, L. and Shi, X. (2011) Laboratory Investigation of Performance and Impacts of Snow and Ice Control Chemicals for Winter Road Service. *Journal of Cold Regions Engineering*, 25 (3), pp. 89–114. doi: 10.1061/(ASCE)CR.1943-5495.0000025

Fay, L., Volkening, K., Gallaway, C. and Shi, X. (2008) Performance and impacts of current deicing and anti-icing products: User perspective versus experimental data, *87th Annual Meeting of the Transportation Research Board*. Washington D.C., pp. 1359–1382.

Fu, L., Sooklall, R., Perchanok, M.S. (2006) Effectiveness of alternative chemicals for snow removal on highways. *Transportation Research Record: Journal of the Transportation Research Board*, 1948 (1), pp 125–134. URL: <http://trb.metapress.com/index/4507755848Q845R3.pdf>

Gerbino-Bevins, B. (2011) *Performance Rating of De-icing Chemicals for Winter Operations*. Civil engineering theses dissertation, student research, University of Nebraska-Lincoln United States.

Gerbino-Bevins, B.M., Tuan C.Y., and Mattison, M. (2012) Evaluation of Ice-Melting Capacities of Deicing Chemicals. *Journal of testing and evaluation*, 40 (6), ASTM, pp. 1-9. doi: 10.1520/JTE104460

- Gilfillan, G. (2014) Road Safety Benefits of Liquid Anti-Icing Strategies and Agents. *Transportation Research Record: Journal of the Transportation Research Board*, 1700, pp 24-31. doi: 10.3141/1700-05
- Goetzfried, F. and Badelt, B. (2002) Effectiveness of different de-icing salts. *The XIth PIARC International winter Road Congress*. Sapporo, Japan. 28th-31th of January 2002. Proceedings on CD room. The Federal Highway institute
- Hanbali, R.M. (1994) The economic impact of winter road maintenance on road users. *Presented at the Ninth PIARC International Winter Road Congress*, Seefeld, Austria, pp. 429-439
- Haines, P.J. (2002) Principles of Thermal Analysis and Calorimetry. Royal Society of Chemistry, Inc., Surrey UK.
- Haynes, W.M. and Bruno, T. (2014) CRC Handbook of Chemistry and Physics, 95th, USA: ed. Taylor and Francis Group, LLC.
- Heystraeten, G. V., Diericx, R., (2002) A rapid and effective de-icing agent for open graded road surfacings. *The XIth PIARC International winter Road Congress*. Sapporo, Japan. 28th-31th January 2002. Proceedings on CD room.
- Hopkins, G.R., French, S.S. and Brodie, E.D. (2013) Potential for local adaptation in response to an anthropogenic agent of selection: effects of road deicing salts on amphibian embryonic survival and development. *Evolutionary Applications*, 6 (2), pp. 384–392. doi:10.1111/eva.12016
- Kaushal, S.S., Groffman, P.M., Likens, G.E., Belt, K.T., Stack, W.P., Kelly, V.R., Band, L.E. and Fisher, G.T. (2005) Increased salinization of fresh water in the northeastern United States. *Proceedings of the National Academy of Sciences of the United States of America*, 102 (38), pp 13517–13520. doi:10.1073/pnas.0506414102
- Karlsson, M. (2001) Predication of hoar-frost by use of road weather information system. *Meteorological applications* 8(1), pp. 95-105. doi: 10.1017/S1350482701001086
- Ketcham, S., Minsk, L., Blackburn, R. and Fleege, E. (1996) Manual of Practice an Effective Anti-Icing Program - A Guide for Highway Winter Maintenance Personnel, FHWA-RD-96-202. Virginia, United States of America: U.S Department of Transportation, Federal Highway Administration.
- Khattak, A. J., Kantor, P., and Council, F. M. (1998) Role of Adverse Weather in Key Crash Types on Limited-Access Roadways: Implications for Advanced Weather Systems. *Transportation Research Record: Journal of the Transportation Research Board*, 1621, pp. 10–19. doi: 10.3141/1621-02
- Klein-Paste, A., and Potapova, J. (2014) Thermal Aspects of Melting Ice with Deicer Chemicals. *Transportation Research Record: Journal of the Transportation Research Board*, 2440, pp 69–75. doi: 10.3141/2440-09

Klein-Paste, A. and Wåhlin, J. (2013) Wet pavement anti-icing — A physical mechanism. *Cold Regions Science Technology*, 96, pp 1–7. doi:10.1016/j.coldregions.2013.09.002

Koefod, S. (2008) Eutectic Depressants. Relationship of eutectic, freezing point, and ice melting capacity in liquid deicers. *Transportation research circular. 4th National Conference on Surface Transportation 35 Weather: Improving Transportation through Weather Information*. Indianapolis, Indiana, USA, 36, pp. 73-84

Koefod, S., J. Adkins, and M.R. Akin (2012) Alternative Approaches to Measuring Deicer Ice-Melting Capacity: Optimization of Test Accuracy and Precision. *Transportation Research E-Circular. Presented at the International Conference on Winter Maintenance and Surface Transportation Weather*, Iowa United States, pp. 432-442

Koefod, S., R. Mackenzie, and Adkins, J. (2015) Effect of pre-wetting Brines on the Ice Melting Rate of Salt at Very Cold Temperatures. *Transportation Research Record: Journal of the Transportation Research Board*, 2482. pp 67-73. doi: 10.3141/2482-09 Figure 1, p. 68, 2015. Reproduced with permission of the Transportation Research Board.

Koefod, S. (2017) Effect of Pre-wetting brines and mixing on the ice melting rate of salt at cold temperatures measured by a new tracer dilution method. *Journal of the Transportation Research Board*, 2613. pp. 71-78. doi: 10.3141/2613-09

Leppänen, A. (1995) *The final results of the road traffic in winter project. The socio-economic effects of winter maintenance and studded tires*. Finnish Road Administration, Helsinki. Available at URL: <http://alk.tiehallinto.fi/winter.htm>

Ljungberg, M., (2000). Expert systems for winter road maintenance. *Ninth Maintenance Management Conference*, Juneau, Alaska, July 16-20.

Lysbakken, K. R., and Norem, H. (2008) The amount of salt on road surfaces after salt application: A discussion of mechanisms and parameters. *Seventh International Symposium on Snow Removal and Ice Control Technology*, Indianapolis, Indiana, June 17–19

Maze, T., Agarwai, M. and Burchett, G. (2006) Whether Weather Matters to Traffic Demand, Traffic Safety, and Traffic Operations and Flow, *Transportation Research Record: Journal of the Transportation Research Board*, 1948, pp 170–176.

Melinder, Å. (2007) *Thermophysical Properties of Aqueous Solutions Used as Secondary Working Fluids*. PhD thesis. ISBN 978-91-7178-707-1. Royal Institute of Technology, KTH. Department of Energy Technology. Stockholm, Sweden.

Minsk, L.D., (1998) *Snow and ice control manual for transportation facilities*. McGraw-Hill, New York.

Muthumani, A., Akin, M., Huang, J., Veneziano, D.A. and Shi, X. (2014a) Strategies for Snow and Ice Control at Extreme Temperatures: Review of Current Practice.

Presented at the *Transportation Research Board 93rd Annual Meeting*, Washington D.C, USA.

Muthumani, A., L. Fay, M. Akin, S. Wang, J. Gong, and X. Shi. (2014b) Correlating lab and field tests for evaluation of deicing and anti-icing chemicals: A review of potential approaches. *Cold Regions Science and Technology*, No. 97, pp. 21-32.

Murphy, D. M. and Koop, T. (2005) Review of the vapour pressures of ice and supercooled water for atmospheric applications. *Quarterly Journal of the Royal Meteorological Society*, 131 (608) pp. 1539–1565. doi:10.1256/qj.04.94

Nixon, W. A. (2001) *The use of abrasives in winter maintenance*. (Final report of project TR 434, Iowa Institute of Hydraulic Research. Iowa: University of Iowa. Available at:
http://publications.iowa.gov/16481/1/IADOT_tr434_Use_Abrasives_Winter_Maintenance_2001.pdf

Norrman, J., Eriksson, M., and Lindqvist, S. (2000) Relationship between road slipperiness, traffic accidents risk and winter road maintenance activity, *Climate research*, 15, pp. 185-193

NPRA (1999) Internrapport nr. 2105. Uttesting av varmsandmetodene Hottstone og friction maker vinteren 1998/99. Oslo: Statens vegvesen, Vegteknisk.

NPRA (2014) D2-ID9300a – 3. Fellesdokument driftskontrakt. Bruk av salt. Oslo: Statens vegvesen. http://www.vegvesen.no/s/anbud/dkmal2016/xxxx-D2-ID9300a-Bruk_av_salt-20140501.pdf

O'Keefe, K. and Shi, X. (2006) Anti-icing and pre-wetting: Improved methods for winter highway maintenance in North America. Proceedings of the Transportation Research Board, Washington D.C, January 22-26. Available at URL: <http://citeseerx.ist.psu.edu/viewdoc/download?doi=10.1.1.563.7391&rep=rep1&type=pdf>

Paschka, M.G., Ghosh, R.S. and Dzombak, D.A. (1999) Potential Water-Quality Effects from Iron Cyanide Anticaking Agents in Road Salt. *Water Environment Research*, 71(6), pp. 1235–1239. doi:10.2175/106143096X122410

Perrier, N. Langevin, A. Campbell, J. (2006) A survey of models and algorithms for winter road maintenance. Part I: system design for spreading and plowing. *Computers and Operations Research*, 33 (1), pp 2009–2038. doi: 10.1016/j.cor.2004.07.006

Ramakrishna, D.M. and Viraraghavan, T. (2005) Environmental Impact of Chemical Deicers – A Review, *Water Air Soil Pollution*, 166(1-4), pp. 49–63. doi:10.1007/s11270-005-8265-9

Rämä, P. (1999) Effects of Weather-Controlled Variable Speed Limits and Warning Signs on Driver Behavior. *Transportation Research Record: Journal of the Transportation Research Board*, 1689, pp. 53-59, doi: 10.3141/1689-08.

SAE (2012) *Ice melting test method for Runways and Taxiways deicing/Anti-icing chemicals*. (SAE AIR6170 01/2012). Aerospace Information Report.

Schaerer, P.A. (1970) *Compaction or removal of wet snow by traffic*. (Highway research board special report no. 115) Washington D.C: Highway research board. Pp. 97-103.

Scientific American (1887) The employment of salt for the removal of snow. *Scientific American*, February 19th, pp. 113.

Shankar, V., Mannering, F. and Barfield, W. (1995) Effect of Roadway Geometrics and Environmental Factors on Rural Freeway Accident Frequencies. *Accident Analysis and Prevention*, 27 (3), pp. 371–389. Available at: [https://doi.org/10.1016/0001-4575\(94\)00078-Z](https://doi.org/10.1016/0001-4575(94)00078-Z)

Shi, X., (2005) The use of road salts for highway winter maintenance: an asset management perspective, *ITE District 6 Annual Meeting*. Kalispell, Montana, July, pp. 10–13.

Shi, X., Jungwirth, S., Akin, M., Wright, R., Fay, L., Veneziano, D.A., Zhang, Y., Gong, J., Ye, Z. (2014) Evaluating snow and ice control chemicals for environmentally sustainable highway maintenance operations. *Transportation Research Record: Journal of the Transportation Research Board*. 140(11), pp. 05014005.

Shi, X., Veneziano, D., Xie, N., Gong, N. (2013) Use of chloride-based ice control products for sustainable winter maintenance: A balanced perspective. *Cold Regions Science and Technology*, 86, pp. 104-112.

Smith, W.F., Hashemi, J. (2011) *Foundations of materials science and engineering*. 5th ed. USA: McGraw-Hill.

Snowfighters Handbook (2016), *A Practical Guide for Snow and Ice Control*, Published by the salt institute. Available at: <http://saltinstitute.org/wp-content/uploads/2015/02/SASS-Handbook-2016-1.pdf>

Strong, C.K., Ye, Z. and Shi, X. (2010) Safety Effects of Winter Weather: The State of Knowledge and Remaining Challenges, *Transport Reviews*, 30 (6), pp. 677-699, doi: 10.1080/01441640903414470

Technology Transfer Center (1996) *Manual of practice for Anti-icing of Local Roads*. USA: University of New Hampshire. Available at: http://www.ltap.org/login/resource/entryupload/uploads/20100217122816_resource_yZm9.pdf

The Lancet (1895) Snow salt, and slush, *The Lancet*, September 29th, p.356.

Thomsen, K. (1997) *Aqueous Electrolytes Model Parameters and Process Simulation*. PhD dissertation, Technical University of Denmark, Center for Energy Resources Engineering. Lyngby, Denmark

TRACK (2002) *Road weather information systems: Enabling Proactive maintenance practice in Washington State*, (WA-RD 529.1), Seattle: Washington State Transportation Centre and Washington State Department of Transportation. Available at: <http://www.wsdot.wa.gov/research/reports/fullreports/529.1.pdf> (accessed: May 2017)

TRB, Transportation Research Board, (1991) Highway de-icing: comparing salt and calcium magnesium acetate. TRB Special Report, 235. National Research Council, Washington D.C. <http://trb.org/publications/sr/sr235.html>

Tuan, C.Y., and Albers, T. (2014) Development of a Mechanical Rocker Test Procedure for Ice Melting Capacity Evaluation. Project number: NDOR Project M322, University of Nebraska, United States.

Usman, T., Fu, L. and Miranda-Moreno, F.L. (2010) Quantifying safety benefits of winter road maintenance: Accident frequency modeling. *Accident Analysis and Prevention*, 42, pp. 1878-1887.

Wallmann, C-G. and Åström, H. (2001) *Friction measurement methods and the correlation between road friction and traffic safety. A Literature review*. Linköping, Sweden, Publisher: Swedish National Road and Transport Research Institute (VTI)

Wallmann, C-G. (1998). Driver behavior on winter roads, a driving simulator study, *The Xth PIARC International winter Road Congress*. Lulea, Sweden. 16th-19th March 1998. Proceedings on CD room.

Wåhlin, J., Leisinger, S. and Klein-Paste, A. (2014) The effect of sodium chloride solution on the hardness of compacted snow, *Cold Regions Science and Technology*, 102, pp. 1–7. doi:10.1016/j.coldregions.2014.02.002

Wåhlin, J. and Klein-Paste, A. (2017) The effect of mass diffusion on the rate of chemical ice melting using aqueous solutions, *Cold regions science and technology*, 139, pp. 11-21.

Ye, Z., Strong, C.K and Shi, X. (2009) Benefit-cost analysis of Maintenance decision support system, *Transportation Research Record: Journal of the Transportation Research Board* 2107, pp. 95–103. doi: 10.3141/2107-10

Young, F.E., and Jones, F.T. (1949) Sucrose Hydrates. The Sucrose–Water Phase Diagram. *The journal of physical chemistry*, 53 (9), pp. 1334–1350. URL: <http://pubs.acs.org/doi/abs/10.1021/j150474a004>

APPENDIX A – Paper I

Nilssen, Kine; Klein-Paste, Alex; Wåhlin, Johan.

Accuracy of ice melting capacity test

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Nilssen, Klein-Paste, Wählin
Paper I. Accuracy of ice melting capacity tests

ACCURACY OF ICE MELTING CAPACITY TESTS

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Paper I. Accuracy of ice melting capacity tests

ABSTRACT

In cold climate regions, chemicals are often applied on roads to facilitate snow and ice removal. A commonly used performance indicator is the ice melting capacity. There is a growing need for stakeholders to measure melting capacity as more commercial products for deicing are available. There are two standardized test methods for measuring melting capacity: SHRP H-205.1 for solid deicers and SHRP H-205.2 for liquid deicers, but there have been concerns that these tests are not accurate. Therefore researchers have tried developed alternative test methods, including “the shaker test”, “the mechanical rocker test” and “the ice cube titration test”.

This paper summarizes published data on measured melting capacity for sodium chloride (NaCl). The published data was compared to the calculated melting capacity of NaCl. The findings confirm earlier suspicions that SHRP tests have low reproducibility and are not able to measure full melting capacity. The newer test methods measured closer to full melting capacity than SHRP. They also showed improvements in being more accurate, although more data from the newer test methods are needed to draw conclusions.

Keywords: Winter maintenance, melting capacity, test methods, SHRP

INTRODUCTION

In cold climate regions chemicals are often applied on roads to facilitate snow and ice removal. Different chemicals can be used for this purpose, but one essential quality for a de-icing chemical is the capacity to melt snow and ice (1). Ice-melting capacity is a measure of how many grams of ice one gram of the chemical can melt (2).

Measuring the melting capacity allows comparison between different deicing chemicals. For stakeholders there is a growing need for this, as an increasing number of deicing products, often lacking detailed descriptions, are released on the market.

The most commonly used methods for measuring ice melting capacity are SHRP H-205.1 for solid deicers and the SHRP H-205.2 for liquid deicers (2). These are standardized tests for measuring the melting capacity of deicers in the US (3), and they have been used in many studies. “The Handbook of Test Methods for Evaluating Chemical Deicers” recommends using the SHRP H-205.1 and SHRP H-205.2 tests to assess new deicing chemicals with respect to ice melting capacity and to describe and compare the ice melting capacity of deicers over a limited defined time interval (2). The handbook specifies that SHRP does not measure quantitatively the theoretical or extended time of the ice melting capacity of the deicers, because melting capacity is defined as the amount of melted ice per gram deicer regardless of time. This means that the SHRP tests do not measure melting capacity and that the result is affected by the deicers’ melting rate (4) and application time (5).

There are concerns that the SHRP tests are not accurate enough for making comparisons between deicing chemicals. It can be difficult to separate the entire melted portion from the remaining ice (6). There is also a risk of supplying additional heat when handling the measurement equipment (7), and for some chemicals, like sodium chloride (NaCl), melting may continue after the specified test period of 60 minutes (4). Halting the test after 60 minutes might be justified with the necessity for deicing chemicals used on roads to work more quickly. On the other hand, the ice and chemical involved in the test are not exposed to traffic or any mechanical stress, which would have accelerated the melting process.

Many researchers explain results of SHRP tests as the melting capacity of the deicer, but as the handbook specifies, this is not correct. Due to the concerns about the SHRP tests, researchers in the field of winter maintenance have tried to develop alternative test methods for measuring melting capacity - to improve reproducibility and accuracy. Published tests for this purpose includes “the shaker test”, “the mechanical rocker test” and “the ice cube titration test”. However, there are limited published data from these new tests compared to the SHRP tests. Also researchers in winter maintenance of airports have tried to modify the SHRP test so that it can be used for measuring melting capacity of deicing products used in airports (8).

This paper investigates the accuracy of the SHRP tests, the shaker test, the mechanical rocker test and the ice cube titration test by comparing the results of these four test methods on both solid sodium chloride (NaCl) and liquid NaCl (brine) with the calculated melting capacity of NaCl. Calculating full melting capacity is

possible for deicers with a known phase diagram. NaCl is a well-known deicer and has, in contrast to most of the commercial deicing products, a known phase diagram. For the purpose of this paper the word “deicer” is used in a broad sense, referring to any type of chemical that is used in winter maintenance. There are several important qualities for a deicing chemical to perform successfully on the road. Melting capacity is only one of them, although an important one. Researchers have pointed out weak correlation between lab tests and field performance (6), but this is beyond the scope of this paper, which focuses on the reliability of lab tests in measuring melting capacity of a deicing chemical.

CALCULATING THE MELTING CAPACITY FROM A PHASE DIAGRAM

Deicing chemicals depress the freezing point of water, meaning that the transition between liquid water and solid ice (melting and freezing) can take place at lower temperatures than 0°C (32°F). When ice is in contact with water that contains solutes, the ice will start melting. This melted ice water will blend with the solution, lowering the concentration of the solution and thereby increasing the freezing point (7). The solution will continue to melt ice until the solution is so diluted that the freezing point reaches the ambient temperature. At this point, the deicer is exhausted for its ability to melt and the full melting capacity is reached. In other words, the melting capacity is reached when all of the deicer is used to keep the melt water at the freezing point.

The solution's capacity to depress the freezing point can be obtained from the freezing curve in a phase diagram. For example, for water the different phases are gas, liquid and solid (ice). At eutectic point of NaCl, the temperature is -21.2°C (-6.16°F) and the solubility 23.2% (9), which means that NaCl can depress the freezing point of water to -21.2°C . In other words, it forces ice to melt even if it is as cold as -21.2°C .

The Handbook of Chemistry and Physics provides empirical data for freezing point at different NaCl concentration (10), shown in Figure 1. Along the curve the solution is in equilibrium, meaning that no freezing or melting takes place along the curve.

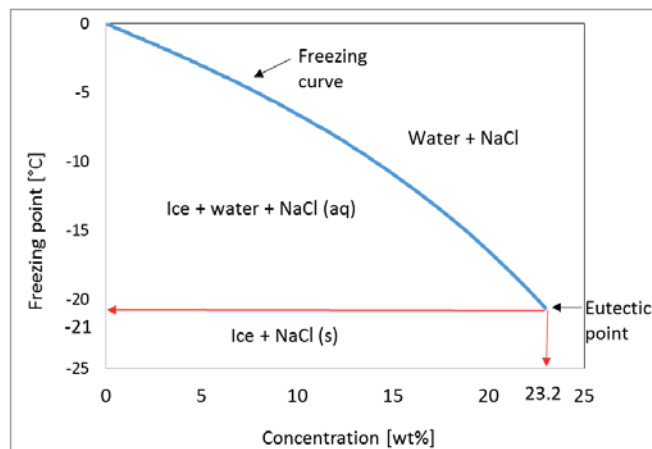


FIGURE 1 Freezing point depression curve for NaCl in water. Source: (10).

The data in Figure 1 is fitted with a third order polynomial, with the incept forced through (0,0), given in equation 1. The equation tells us the concentration for each temperature, where the brine is in equilibrium and there will be no melting or freezing.

$$C_{\text{equilibrium}} = -3.6233 \cdot 10^{-4} \cdot T^3 - 3.8985 \cdot 10^{-2} \cdot T^2 - 1.7587 \cdot T \quad (1)$$

Where:

$C_{\text{equilibrium}}$: is the concentration of the NaCl brine (wt%).

T: is the temperature (°C).

The R^2 of the fit is 1.

The concentration of a solution diluted to equilibrium can always be expressed with equation 2:

$$C_{\text{equilibrium}} = \left(\frac{m_{\text{NaCl}}}{m_{\text{NaCl}} + m_{\text{water}} + m_{\text{meltedice}}} \right) * 100\% \quad (2)$$

Where:

$C_{\text{equilibrium}}$: is the NaCl concentration (wt%).

m_{NaCl} : is the mass of NaCl (g).

$m_{\text{melted ice}}$: is the mass of the water from the melted ice (g).

m_{water} : is the mass of the water added to the deicer to pre-wet or produce brine (g).

Rearranging equation 2 gives equation 3:

$$m_{\text{meltedice}} = \frac{m_{\text{NaCl}}}{\frac{C_{\text{equilibrium}}}{100}} - m_{\text{NaCl}} - m_{\text{water}} \quad (3)$$

For simplicity, the amount of water in solid or pre-wetted NaCl may be neglected. In that case, the ice melting capacity (I_{mc}) can be calculated with equation 4, because the definition of ice melting capacity refers to melting per gram of deicer:

$$l_{\text{mcsolid}} = \frac{1}{\frac{C_{\text{equilibrium}}}{100}} - 1 \quad (4)$$

Combining equation 1 and 4 gives melting capacity as a function of the temperature. See equation 5.

$$l_{\text{mcsolid}} = \left(\frac{1}{-3.6233 \cdot 10^{-4} \cdot T^3 - 3.8985 \cdot 10^{-2} \cdot T^2 - 1.7587 \cdot T} \right) - 1 \quad (5)$$

The melting capacity of brine is much lower than for solid NaCl, because 1 gram of 23% brine only contains 0.23 gram NaCl per gram brine. In addition the amount of water added to produce brine, m_{water} , cannot be neglected and will reduce the total melting capacity. The melting capacity of brine is therefore given by equation 6:

$$l_{\text{mcbrine}} = \left(\frac{0.23}{-3.6233 \cdot 10^{-4} \cdot T^3 - 3.8985 \cdot 10^{-2} \cdot T^2 - 1.7587 \cdot T} \right) - 0.23 - (1 - 0.23) \quad (6)$$

Figure 2 shows melting capacity for NaCl, both solid and brine, at temperatures from -1°C (30.2°F) to -21°C (-5.8°F).

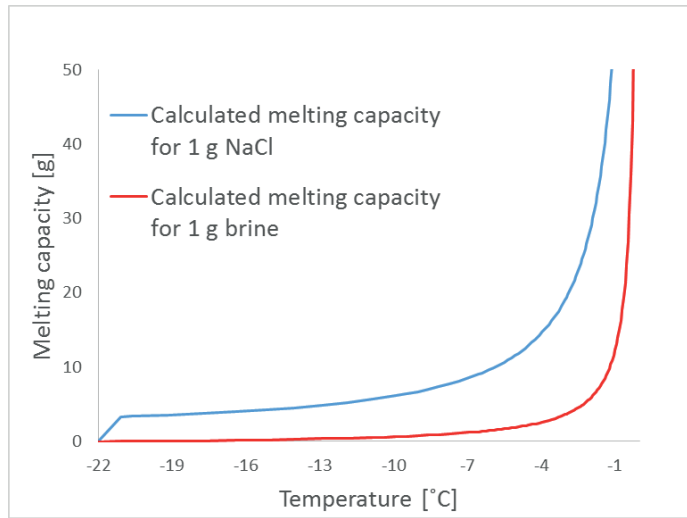


FIGURE 2 Melting capacity of 1 gram solid NaCl and 1 gram 23% NaCl brine.

EXISTING TEST METHODS

The SHRP test

SHRP H-205.1 “Test Methods for Ice Melting of Solid Deicing Chemicals” and SHRP H-205.2 “Test Methods for Ice Melting of Liquid Deicing Chemicals” should be performed according to descriptions provided in “Handbook of Test Methods for Evaluating Chemical Deicers” (2). The tests are performed by fabricating a 3.175 mm (1/8 in) thick ice layer in a Plexiglas dish with a recommended diameter of 22.86 cm (9 in) and a recommended depth of 1.91 cm (3/4 in). Recommended sample size is 4.17 g for solid deicers and 5 ml for liquid deicers. The deicer is scattered on the ice. At specific time intervals (10, 20, 30, 45 and 60 minutes) the amount of melted ice is measured by collecting the melted water in a syringe, weighing the syringe, and pouring the melted water back to the ice. Three replicates for each test is the recommendation in the handbook.

Many data sets derived from SHRP H-205.1 and H-205.2 have been published. Data sets from 9 studies on solid, liquid or pre-wetted NaCl are presented in this paper. Table 1 shows which papers are included. The test temperature, whether the NaCl was solid, liquid or pre-wetted, and how the results were reported, are described in Table 1. There were variations in how the tests were performed in the included literature. Akin and Shi (2010) introduced a modification to the standard SHRP tests. The two fundamental differences were:

- 1) They used smaller petri dishes (3.5 cm in diameter) and 1 g of solid deicer or 0.9 ml of liquid deicer.
- 2) They performed four simultaneous tests of which one was a 23% brine control sample (3).

Earlier published tests were often performed using the standard SHRP test as described in the handbook, but in some later published tests the modified test procedure was used. Very often, the authors have modified the tests beyond the procedures. There were differences in: the amount of NaCl used in each test, time intervals for measurements, type of cold room/freezer, presentation of data and units used. Data sets using other chemicals than NaCl have not been included in this research. Only measurements after 60 minutes were included. When data sets were presented in a graph, the results were read out, and some inaccuracies may arise from this.

TABLE 1 Data included in this paper

Paper	Temperature		Solid (S), Liquid (L) or Pre-wetted (Pw)	Visualization
	°C	°F		
Koefod et al., 2015	-20.4	-4.7	S + Pw	Table. Unit: g ice/g NaCl
Gerbino-Bevins, 2011	-12.2	20	L	Graph. Unit: g ice/g 23% brine
	-17.8	0	L	
Fay and Shi, 2011	0	32	S	Table. Unit: g ice/g NaCl
	-5	23	S	
	-18	-0.4	S	
Akin and Shi, 2010	-1.1	30	S + L	Table. Unit: volume (ml) melted ice.
	-9.4	15	S + L	
	-17.8	0	S + L	
Fay et al., 2008	-5	23	S	Graph. Unit: g melted ice per g NaCl
Svanekil, 2007	-1	30.2	S + Pw	Table. Unit: melted ice in ml per 4.17 g salt.
	-5	23	S + Pw	
Alger and Haase, 2006	-3.9	25	S	Table. Unit: ml melted ice/g deicer
	-6.7	20	S	
	-9.4	15	S	
Nixon et al., 2005	-1.1	30	L	Graph. Unit: mass of melted ice (g).
	-6.7	20	L	
	-12.2	10	L	
	-17.8	0	L	
Hernes, 2004	-1	30.2	Pw	Graph. Unit: volume melted ice (ml) per mass deicer (g).
	-5	23	Pw	
	-10	14	Pw	
	-15	5	Pw	
	-15	5	S	

Koefod et al. (2015) did the first measurement after 60 minutes and not every 10th minute as the standard procedure suggests. They also used non-standardized dishes and sealed them between each measurement to prevent evaporation. 6 replicates were performed and 24 grams of NaCl were used for each test (4).

Gerbino-Bevins (2011) tested melting capacity of 1 ml 23% liquid brine with a standard H-205.2 test. She used a freezer instead of a climate chamber, which according to her might be one of the reasons for the inconsistent results (11).

Fay and Shi (2011) tested 1 gram of solid NaCl with modified H-205.1 (12).

Akin and Shi (2010) introduced and performed a modified SHRP test for both solid and liquid NaCl (brine). They reported that they had problems with dilution and refreezing during the 60 minutes. This was clear from their results, since their data had lower melting capacity after 60 minutes than after the first measurement at 10 minutes (3).

Fay et al (2008) performed a modified H-205.1 test using 1 gram of solid NaCl (13).

Svanekil (2007) performed a standard H-205.1 test, but used 6 minute intervals for measuring melted ice (6, 12, 18, 24, 30, 36, 42, 48, 54 and 60 minutes). He tested 6 replicates with 4.17 gram solid NaCl and pre-wetted NaCl. The NaCl was pre-wetted with warm water at temperature of 90°C, 65°C and 20°C. Test temperature were -1°C and -5°C (14).

Alger and Haase (2006) used solid NaCl after the standard H-205.1 test. Triplicates were always performed, and in addition they performed three tests for each temperature (-3.9°C, -6.7°C, -9.4°C) (15).

Nixon et al. (2005) tested liquid NaCl with a standard H-205.2 test. They used 5 ml 23% brine for each test (16).

Hernes (2004) tested pre-wetted NaCl with 23% NaCl brine using a standard H-205.1 test. 70% was dry NaCl and 30% was a pre-wetted solution. The data were presented in a graph showing ml melted ice per gram deicer. She also performed one test with solid salt at -15°C (17).

The shaker test

“The shaker test” was developed by Gerbino-Bevins in 2012 as a performance test for deicing chemicals, with a view to ensure higher accuracy than the SHRP H-205.1 and H-205.2 tests (18). The purpose of the test was to measure melting capacity while simulating the stirring effect of traffic. Gerbino-Bevins concludes that the test is reproducible and gives consistent results. The shaker test can be used to determine melting capacity of solid and liquid deicers.

The test was performed in four insulated plastic martini shakers in a small freezer. The insulation gave a steady internal temperature for 2.5 minutes with the lid on and for some seconds with the lid off. The shaking was done outside the freezer. The test was performed at -6.7°C, -12.2°C and -17.8°C (20°F, 10°F and 0°F). Each sample of deicer consisted of 7 ml of 23% liquid NaCl in a shaker. Ice cubes made from distilled water were put in the same freezer as the shaker to ensure equal temperature. She then weighted 10 ice cubes and put them in the shaker before it was shaken in two cycles per second for 5 minutes. The temperature was measured once a minute. After shaking the shaker was put back in the freezer, upside down, so the meltwater would drain into the cup portion of the lid while the ice remained above the strainer. The weight of the melted water (without any ice) was measured. The results were presented in a graph as average grams of melted ice per milliliter deicer per three tests.

The mechanical rocker test procedure

“The mechanical rocker test” procedure is a modified version of the shaker test. It was developed by Tuan and Albers in 2014. The aim was to develop a simple and repeatable test to determine the ice melting capacity of liquid deicers. The authors concludes that it is repeatable, relatively quick and provides consistent results with modest equipment requirements (19). The test procedure is quite similar to the shaker test, but in the mechanical rocker test they used a mechanical rocker to mix the ice

and the deicer instead of shaking it by hand. The test was performed in a small freezer at -17.8°C (0°F). 33 ice cubes of 1.3 ml each and 30 ml of liquid deicing chemical were mixed in a sealed thermos in vacuum and placed on a mechanical rocking platform. The rocker was set to a frequency of 90 RPM with a tilt angle of $\pm 10^{\circ}$, and a rocking time of 15 minutes. The shaker was taken out of the freezer during the rocking. The test was performed mainly using magnesium chloride, but three tests were performed using NaCl.

The Ice Cube Titration test

In 2012 Koefod et al introduced an alternative approach to measure melting capacity of deicers, called the “ice cube titration test”. The aim was to reduce the error source associated with incomplete recovery of meltwater from the ice surface in the SHRP test (5), so that the full melting capacity could be measured. The test was conducted using a 400 ml beaker with 23.3% brine in a walk-in cold room and a magnetic stir bar for mixing deicer with the melted ice. Ice cubes were suspended into the deicer. The beaker was weighed periodically, and the increased weight of the beaker due to melting (the remaining ice was removed) was recorded as the melting capacity. This recording took place when the weight was stable, i.e when the melting had stopped and before the weight started decreasing. The test was conducted at -15°C (5°F) with four replicates.

RESULTS

Data sets from previously published SHRP H-205.1 and H-205.2 tests, the shaker test, the mechanical rocker test and the ice cube titration test were compared with the calculated melting capacity for NaCl at different temperatures. Results from the literature that was reported in volume, were converted to mass by predicting a density of 1.17 g/ml (11.7 lb/gal). The handbook suggests densities for 10% and 20% brine (2), but since the concentration after a finished test was not described in the literature, a density of 1.17 g/ml was chosen for all the data sets. The contribution of NaCl in the pre-wetting brine was not included because the amount is negligible.

Figure 3a shows the data for solid and pre-wetted NaCl. All the tests were performed using SHRP H-205.1. The dots represent solid NaCl and the squares represent pre-wetted NaCl. Figure 3b shows the data for brine. The triangles represent the tests performed with SHRP H-205.2, the diamonds represent the shaker tests and the mechanical rocker tests and the short green line represents the result from the ice cube titration test. All data points represent a mean value of at least triplicates, as already reported in the literature. The blue line in each graph represents the calculated full melting capacity.

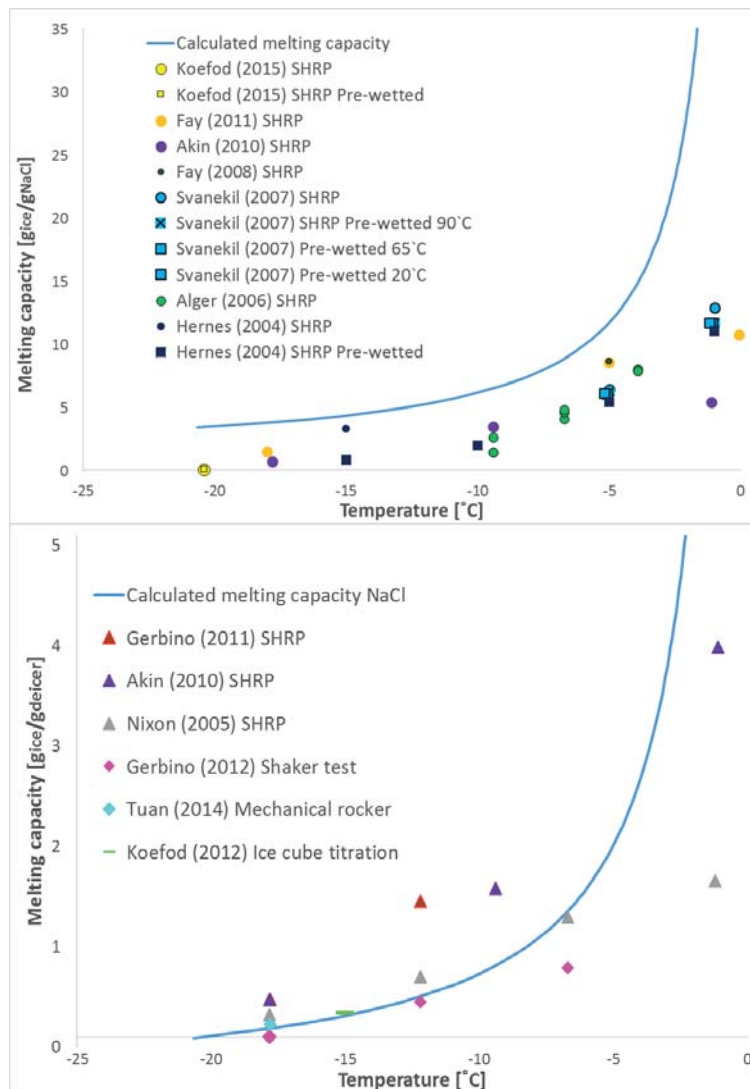


FIGURE 3 Comparison between measured and calculated melting capacity for (a) solid and pre-wetted NaCl and (b) brine. Note that the y-axis is in gram ice/gram deicer and that the melting capacity for brine is therefore lower than for solid/pre-wetted NaCl.

Figure 3a shows that the results for solid and pre-wetted NaCl are greatly scattered. In addition, all the data points are located well below the calculated melting capacity. This means that full melting capacity was not reached in any of the tests. The data for brine (Figure 3b) shows that more of the calculated melting capacity seems to be achieved, but even here, there is a large scatter in the data. The mechanical rocker test and the ice cube titration test tend to measure closer to full melting capacity than the SHRP test and the shaker test.

The relative melting capacity was calculated with equation 7 to show how much of the calculated melting capacity that was achieved. The results are shown in Figure 4.

$$\text{relative melting capacity} = \frac{\text{melting capacity}}{\text{calculated melting capacity}} * 100\% \quad (7)$$

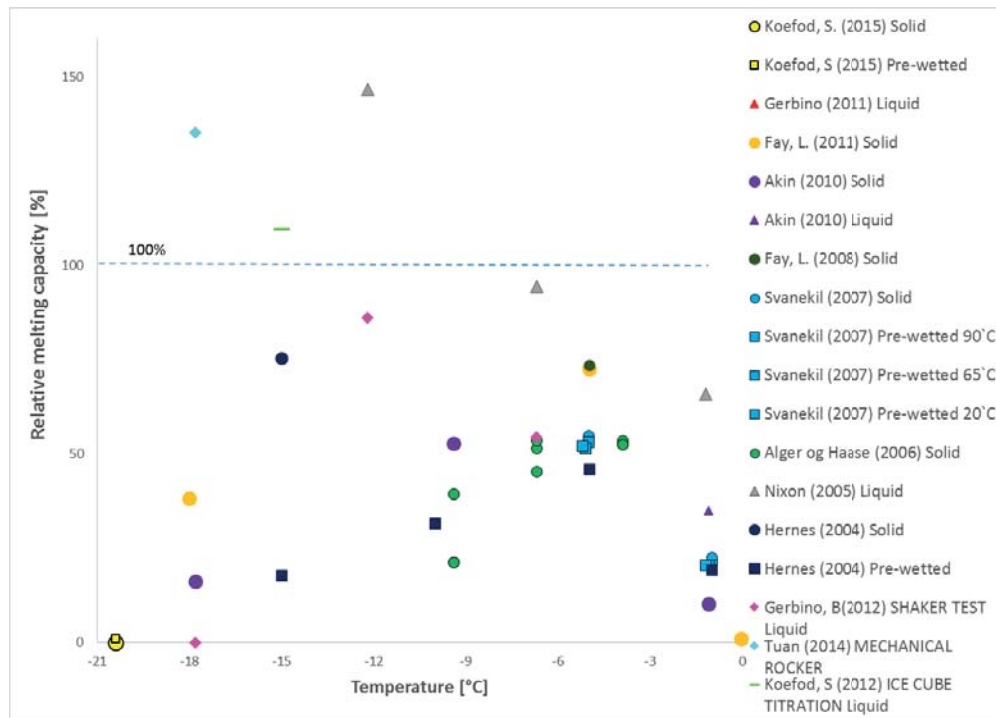


FIGURE 4 Relative melting capacity.

All data points from solid and pre-wetted NaCl are included in Figure 4, but five data points from brine, which had a value of more than 150%, are excluded. Gerbino-Bevins (2011) obtained 331% at -12.2°C and 398.9% at -17.8°C, Akin and Shi (2010) obtained 206.5% at -9.4°C and 398.5% at -17.8°C, and Nixon et al. (2005) obtained 239.6% at -17.8°C.

The large scatter that is present in the data becomes more apparent in Figure 4. Some tests do not reach more than a few percent of the calculated melting capacity whereas others (especially brine) can reach up to 300-400% of the calculated melting capacity. The relative melting capacity of solid/pre-wetted NaCl is always lower than 100%. Apart from this, no clear difference can be detected between solid/pre-wetted NaCl and brine in Figure 4. Both are largely scattered. There may be a tendency for lower relative melting capacity close to 0°C and the eutectic temperature (-21°C), but the available data are limited at these temperatures. In addition, it appears to be a tendency that some of the tests performed by the same author provide more similar results.

DISCUSSION

Melting of ice with solid NaCl (salt) consists of two phases. In the first phase, the salt will melt ice and start dissolving into melt water until all the salt is dissolved. In the second phase, the meltwater, containing all the dissolved salt will continue to melt ice until the concentration is so low that it reaches its freezing point. This is the point where the melting capacity is reached. If brine (liquid NaCl) is used to melt ice, only phase 2 will take place because all the salt is already dissolved. The amount of water that is needed to dissolve the salt is the same as the amount of ice one gram solid salt could have melted. For a 23% solution, this equals 3.3 grams water per gram NaCl. This water cannot come from ice melting, so per gram NaCl the melting capacity of brine is always 3.3 g (0.116 oz) less than the melting capacity of solid NaCl (as illustrated in Figure 5). This has to be kept in mind when comparing results from solid deicers with brine. The handbook does not specify whether the results should be measured in grams of melted ice per gram of NaCl or grams of melted ice per gram of brine. Figure 2 shows that solid salt has a higher melting capacity per gram deicer than brine. The reason for this is simply that brine has less melting capacity than dry NaCl per gram deicer, because it contains less salt per gram deicer.

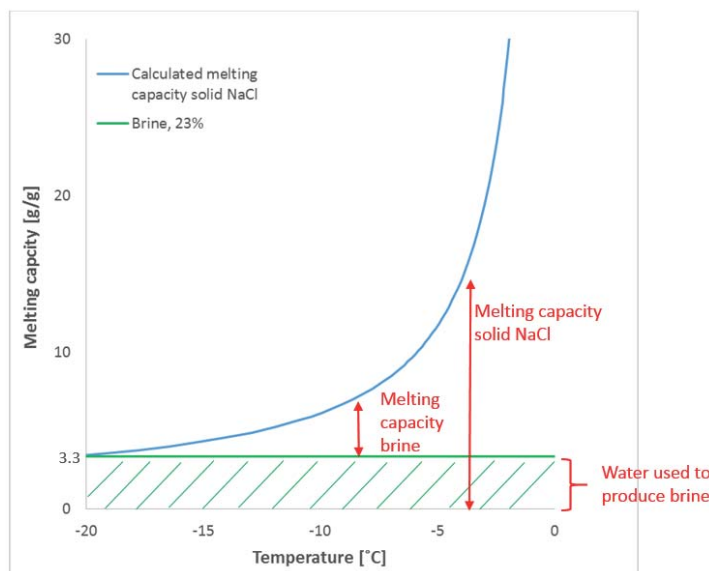


FIGURE 5 Melting capacity of solid NaCl and 23% brine, both per gram NaCl.

The two main observations from solid and pre-wetted NaCl (Figure 3a) are;

- 1) The results are greatly scattered, implying that the test methods are not reproducible.
- 2) The full melting capacity was not reached in any of the tests performed with SHRP H-205.1, implying that the test methods do not measure melting capacity, but something between melting capacity and melting rate. The melting process was still ongoing after 60 minutes at *all* investigated temperatures. This confirms Koefods'

findings that 60 minutes is not sufficient time for NaCl to achieve full melting capacity (4).

Clearly a rapidly working deicer is desirable, and since the SHRP H-205.1 was developed as a quick and easy test to compare different deicer products, one could argue that it makes sense to limit the time that the deicer is allowed to work. The downside of this approach is that the melting rate is dependent on a large number of factors that are poorly controlled in the SHRP H-205.1 test, leading to scattered data. Hence, there can be multiple reasons for the scatter. Some of these variations can be specified as described in the handbook, making the test procedure more uniform for each time. These can be:

Grain size. The size of the grains of NaCl and the amount of NaCl used can affect the results because there will be a difference in the surface area that is in direct contact with the ice.

Purity of NaCl. The purity of the NaCl varies, meaning that some tests may have used NaCl with higher water content than others.

Type of laboratory/freezer. If the test is performed in a freezer and not in a walk-in cold room, opening the lid may add heat from the surroundings.

It does appear from Figure 4 that some of the tests performed by the same author show more similar results, but since this is not consistent, it might imply that even by following the same procedure with the exact same equipment and working style, the test does not produce results that are sufficiently accurate to be used for comparing chemicals. These variations are probably due to factors related to the test method that are difficult to control, such as:

How the grains are scattered. There will be a difference in the surface area in contact between deicer and ice, depending on the way the deicer is scattered.

Separation of water from ice to collect the meltwater (6), which can be especially difficult with low volumes.

Handling of syringes. There is a considerable risk of transferring heat from the hands, affecting the melting rate (7).

A limitation of 60 minutes, may not allow the chemical sufficient time to reach its melting capacity.

The three main observations from the tests on brine (Figure 3b) are:

- 1) More of the calculated melting capacity was achieved, compared to solid and pre-wetted NaCl.
- 2) The data are largely scattered, and had even values higher than the calculated melting capacity (up to 400%).
- 3) Results from the mechanical rocker test and the ice cube titration test seem to be closer to full melting capacity than the SHRP test and the shaker test. That more of the calculated melting capacity was reached with brine can be explained by the fact that only phase 2 of the melting process takes place when brine is used. The deicer has already been dissolved and the process is ahead of the solid salt process from the

beginning. This means that the result is closer to full melting capacity after 60 minutes. However, the scatter in the data were still large. Since the melting capacity of brine is lower than that of solid NaCl, there will be low volumes of melt water that needs to be collected. This is particularly true at low temperatures. Therefore, the scatter is likely due to incomplete collection of the meltwater. However, the data also includes studies that reported melting capacities well above that (300-400%) full melting capacity. It is physically impossible to melt ice with a solution concentration that is lower than the equilibrium concentration given by equation 1. Hence, there must be other reasons for these high melting capacities. One explanation could be that the initial amount, 0.9 – 5 ml (0.3 – 1.3 gal) of brine that was used, was not subtracted from the collected meltwater. The melting capacity will then appear to be higher than what is actually is. It is not specified in the handbook that initial brine should be subtracted when reporting the melting capacity and it is not clear from the published studies whether the initial volumes were indeed deducted from the results.

The shaker test, the mechanical rocker test and the ice cube titration test yielded results that were closer to the full melting capacity. This is particularly evident in Figure 3b.

It should be noted that these test methods share certain characteristics:

- a) They require less mechanical handling (meaning less risk of transferring unwanted heat) than the SHRP tests.
- b) They use a higher volume of brine.
- c) They use a larger ice surface.
- d) The deicer is dissolved (to produce brine) before test start.
- e) Active mixing is used.

These factors may explain why the results are closer to full melting capacity, as shown in Figure 4. Not surprisingly, the ice cube titration test produced the result that was closest to the calculated melting capacity. This was the only test that allowed the mixture enough time to measure melting capacity. The available data are still too limited to assess whether these methods are accurate or reproducible when they are applied by different people in different experimental facilities, but the results so far are promising.

The need for laboratory tests to evaluate the deicing performance of chemicals will likely continue to be present since new products are continuously released on the market. In our view, the best strategy is to have and perform separate tests to measure the melting capacity and the melting rate. The ideal melting capacity test should measure the full melting capacity and therefore ensure that the melting process is indeed finished. At present, only the ice cube titration test takes this into account as it specifies that the melting capacity should be recorded when the weight of the deicer and meltwater does not increase in time. Although the shaker test and the mechanical rocker test do speed up the melting process, they are still terminated after a specified period rather than ensuring that equilibrium is reached. Another issue is the separation between meltwater and ice. Ideally, this separation is to be avoided, or at least automated, because any handling is prone to temperature disruptions. These temperature distortions can cause further melting or refreezing. At this present, none of the tests have fully solved this problem. The melting rate is

dependent on intrinsic chemical properties of the deicer, such as dissolution, its chemical potential and diffusion of the chemical on the ice interface. However, the melting rate is also dependent on external factors such as the flow of heat (the melting reaction requires heat) and the mixing by traffic. The ideal ice melting rate test is sensitive to the intrinsic chemical properties while it realistically simulates the external factors. To the best of our knowledge such tests are not developed yet. It is therefore clear that more research is needed to progress the development of laboratory deicing performance tests.

CONCLUSIONS

In this study we have compared published data on melting capacity of NaCl with calculated melting capacity.

The published melting capacity data for solid/pre-wetted NaCl (measured by SHRP H-205.1) were all well below full melting capacity for NaCl. This implies that the melting process was still ongoing when the test was halted after 60 minutes, and that the chemical did not reach its full melting capacity.

Also, the results were greatly scattered, implying poor reproducibility. The scatter was likely caused by multiple factors, including:

- 1) Inconsistencies in performing the test.
- 2) Poor control of factors in the procedure/method itself, leading to problems such as uncontrolled heat transfer during sampling/handling, difference in the dispersion of grains (influencing the surface area that is in direct contact with the ice), and difficulties in collecting all the melt water. Even though tests performed by the same author produced more similar results, the data were scattered, making it difficult to use the results from a SHRP H-205.1 to compare deicers and to determine melting capacity of the deicer.

The data on NaCl brine (measured by SHRP H-205.2, the ice cube titration test or the shaker/mechanical rocker test) showed that more of the calculated melting capacity was achieved compared to solid/pre-wetted NaCl. The reason is probably that the previously dissolved salt is ahead of solid salt from the beginning, working faster and achieving closer to full melting capacity in 60 minutes, and not that brine has a higher melting capacity than solid NaCl.

Data for NaCl brine were also largely scattered, implying poor reproducibility. Some of the measured values were even higher than calculated melting capacity, probably because the initial amount of brine was not subtracted from the results. The mechanical rocker test and the ice cube titration test measured closer to the full melting capacity compared to the SHRP H-205.2 and the shaker test. They have eliminated some of the factors that possibly contributed to scatter, but due to the limited data it is too early to draw conclusions about their reproducibility. There are still issues, for example, regarding temperature control and separation of ice and meltwater, in these newer test methods.

For future deicer performance tests we propose to develop separate tests for (full) melting capacity and melting rate. Ideally, separation of meltwater and ice is to be avoided, or at least automated, because any handling is prone to temperature disruptions.

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REFERENCES

1. Ketcham, S., L. Minsk, R. Blackburn, and E. Fleege. *Manual of Practice for an Effective Anti-Icing Program - A Guide for Highway Winter Maintenance Personnel*. Publication FHWA-RD-96-202. U.S Department of Transportation, 1996.
2. Chappelow, C.C., D.A. McElroy, R.R. Blackburn, D. Darwin, F.G. Noyelles, and E. Locke Carl. *Handbook of Test Methods for Evaluating Chemical Deicers, SHRP-H-332nd ed.* Strategic Highway Research Program. National Research Council, Washington DC, 1992.
3. Akin, M., and X. Shi. *Development of Standardized Test Procedures for Evaluating Deicing Chemicals*. Publication CR07-02 Project 0092-08-32. Western Transportation Institute. Montana State University, 2010.
4. Koefod, S., R. Mackenize, and J. Adkins. *Effect of pre-wetting Brines on the Ice Melting Rate of Salt at Very Cold Temperatures*. Report number 15-4355. In: Transportation Research board 94th Annual Meeting, Washington D.C, 2015.
5. Koefod, S., J. Adkins, and M.R. Akin. *Alternative Approaches to Measuring Deicer Ice-Melting Capacity: Optimization of Test Accuracy and Precision*. In: Transportation Research E-Circular. Presented at the International Conference on Winter Maintenance and Surface Transportation Weather, Iowa United States, 2012, pp. 432-442
6. Muthumani, A., L. Fay, M. Akin, S. Wang, J. Gong, and X. Shi. Correlating lab and field tests for evaluation of deicing and anti-icing chemicals: A review of potential approaches. In: *Cold Regions Science Technology*, No. 97, 2014, pp 21-32.
7. Klein-Paste, A., and J. Potapova, Thermal Aspects of Melting Ice with Deicer Chemicals. In: *Transportation Research Record: Journal of the Transportation Research Board*, No. 2440, Washington D.C, 2014, pp 69–75.
8. SEA. *Ice melting test method for runways and taxiways deicing/antiicing chemicals*, Aerospace information report, Report no AIR6170, 2012.
9. Oakes, C.S., R.J. Bodnar, and J.M. Simonson, 1990. The system NaCl₂-CaCl₂-H₂O. The ice liquidus at 1 atm total pressure. In: *Geochimica Cosmochimica Acta*, Volume 54, No 3, 1990, pp. 603-610.
10. Haynes, W.M., and T. Bruno. *CRC Handbook of Chemistry and Physics*. 95th edition Online. Taylor and Francis Group, LLC., California United States, 2014.
11. Gerbino-Bevins, B., *Performance Rating of De-icing Chemicals for Winter Operations*. Civil engineering theses dissertation, student research, University of Nebraska-Lincoln United States, 2011.
12. Fay, L., and X. Shi. Laboratory Investigation of Performance and Impacts of Snow and Ice Control Chemicals for Winter Road Service. In *Jornal of Cold Regions Engineering*. Vol 25, No 3, 2011, pp. 89–114.

13. Fay, L., K. Volkening, C. Gallaway, and X. Shi. *Performance and impacts of current deicing and anti-icing products: User perspective versus experimental data*, in: Proc., 87th Annual Meeting of the Transportation Research Board. Transportation Research Board Washington D.C., 2008, pp. 1359–1382.
14. Svanekil, A., *Forsøk med varmbefuktet salt for å bedre friksjonen på vinterveger*. Civil engineering theses dissertation, student research, The Norwegian Public Roads Administration and the Norwegian University of Science and Technology, Trondheim, Norway, 2007.
15. Alger, R., and J. Haase. *Analysis of the Benefits of Bulk Pre-wetting Solid NaCl with Several Different Liquids*. Report no: RC-1473. Michigan Technological University, Michigan United States, 2006.
16. Nixon, W.A., J. Qiu, L. Qiu, G. Kochumman, and J. Xiong. *Ice melting performance for ice-control chemicals*, in: Proceedings: 84th Annual Meeting of the Transportation Research Board. Washington D.C, 2005.
17. Hernes, I. *Use of magnesium chloride - solution as deicing agents*. Civil Engineering thesis, student research, The Norwegian University of Science and Tecnology, Trondheim Norway, 2004.
18. Gerbino-Bevins, B.M., C.Y. Tuan, and M. Mattison. Evaluation of Ice-Melting Capacities of Deicing Chemicals. In *Journal of testing and evaluation*, Volume 40, No 6, ASTM, 2012, pp. 1-9.
19. Tuan, C.Y., and T. Albers. *Development of a Mechanical Rocker Test Procedure for Ice Melting Capacity Evaluation*. Project number: NDOR Project M322, University of Nebraska, United States, 2014.

APPENDIX B – Paper II

Nilssen, Kine; Klein-Paste, Alex; Wåhlin, Johan; Delapaz, Michele.

Use of calorimetry to measure ice melting capacity

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MEASURING ICE MELTING CAPACITY USING CALORIMETRY

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ABSTRACT

The ability to melt snow and ice is an important feature of any deicing chemical or product. This is called “melting capacity”, and is defined as grams of melted ice per grams of deicer. A product’s melting capacity is important with regard to its applicability for use in snow and ice control. The standard procedures in the US for measuring melting capacity are SHRP H-205.1 for solid chemicals and H-205.2 for liquid chemicals. However, these test methods have proven to be inadequate with respect to their accuracy for research purposes. There is a growing need for developing improved procedures, as an increasing number of deicing products are currently being released on the market.

This paper describes how calorimetry, which is measurements of heat changes that occur during a process, may be used to measure melting capacity. A calorimeter was therefore custom made for this paper’s research purposes. It required a minimum of mechanical handling and had high temperature control precision excluding the most extreme causes for measurement errors in previously developed test methods. Liquid NaCl was tested and compared with the calculated melting capacity. The calorimeter produced accurate results. Tests were also performed using MgCl₂; the results demonstrated that MgCl₂ has a higher melting capacity than NaCl.

Keywords: winter road maintenance, melting capacity, test procedures, calorimetry

INTRODUCTION

Background

One important feature of any deicing product is the amount of snow and ice it can actually melt. This is called the product's melting capacity, which is defined as the amount of ice one gram of product can melt. The melting capacity is equal to the amount of water one gram of product can keep at the freezing point (1). It is important to know the melting capacity in order to be able to determine a product's applicability for use in snow and ice control and to calculate required application rates.

The most commonly used procedures for testing melting capacity are the SHRP H-205.1 for solid chemicals and H-205.2 for liquid chemicals (2). These procedures, and various modifications thereof, have been used in previous studies (3), (4), (5), (6), (7), (8), (9), (10), (11). However, a recent review showed that the results given by SHRP do not reflect the full melting capacity. The results are also quite scattered, and the test has low reproducibility (1). In recent years, researchers have tried to develop new procedures for measuring melting capacity, including "the shaker test" (4), "the mechanical rocker test" (12) and "the ice cube titration test" (13). Although these tests produced more accurate results than the SHRP procedures, there is still a need for improvement.

Unfortunately, ice melting capacity tests are difficult to conduct accurately. Most test procedures require mechanical/manual handling of equipment during a test. This might lead to heat being transported to the system, making it difficult to distinguish between melting caused by the chemical and melting caused by the added heat (14). Another issue is the physical separation of the melted water from the ice. It can be difficult to separate the entire portion of melted water, which can subsequently cause underestimation of the actual melting capacity (1). In addition, the separation process can transfer additional heat. If the test uses a pre-defined time interval (for example 60 minutes), the full melting capacity might never be reached (3).

A new method for measuring melting capacity is needed in the field of winter maintenance. Ideally, this new method should do the following:

- a) Measure the full melting capacity, regardless of melting rate.
- b) Not require physical separation of the melted water and ice.
- c) Have good temperature control

Calorimetry is the measurement of any heat changes which occur during a process (15). The method is used in many studies to study reactive systems (16). Since melting of ice requires a high level of heat, calorimetry appears to be a feasible measurement principle. A calorimeter provides the opportunity to follow the entire melting process without separating the ice from the melted water. The present study investigates the applicability of calorimetry for measuring the ice melting capacity of deicing products.

A calorimeter was designed and constructed for this study's research purposes. Tests were performed using NaCl and MgCl₂. The results from tests performed with NaCl were compared with the calculated melting capacity of NaCl to determine the calorimeter's accuracy.

Measuring ice melting capacity by calorimetry

The melting of ice is an endothermic reaction, meaning that heat is required (the latent heat of fusion). For ice melting at 0°C, 334 kJ is needed in order to melt 1 kg of ice (17). When ice is melted by a deicer, the temperature of the ice/deicer/meltwater mixture first decreases and becomes colder than the environment (pavement and air). This causes heat to flow from the environment towards the mixture (14). The melting capacity is reached when the temperature returns to the initial ambient temperature of the environment and the deicer solution has been diluted to its freezing concentration. With a known latent heat of fusion, L_{ice} , the amount of melted ice may be determined, $m_{melted\ ice}$ by measuring the amount of heat Q_{added} that was added to the ice/deicer/meltwater mixture during the reaction, according to equation 1:

$$m_{melted\ ice} = \frac{Q_{added}}{L_{ice}} \quad (1)$$

When ice is melted by a deicer, the latent heat of fusion is not exactly constant, but dependent on the temperature and final concentration of the deicer. However, for the purpose of this study, it is assumed to be constant ($L_{ice}=334$ kJ/kg). To measure Q_{added} a calorimeter is needed that allows mixing ice and deicer at a known set point temperature, allowing the temperature to drop and then adding a measurable amount of energy to bring the temperature back to its set point. Since we did not find a commercially available calorimeter that could perform this task, a custom-build calorimeter was developed.

DESIGN OF THE CALORIMETER

The calorimeter that was constructed for this study (see Figure 1) consisted of an insulated stainless steel reactor with a volume of 0.5 litre. The insulation was a 12.5 centimetre thick extruded polystyrene layer. A 15 cm insulated lid provided access to the reactor for cleaning purposes and filling the reactor with deicing solution. The ice was inserted into the reactor through a 35 mm hole that was otherwise closed with an insulated plug. A slowly rotating (15.5 RPM) blade mixer provided mixing while minimizing the energy added by the mixer. Mixing was necessary to reduce temperature gradients inside the reactor. The calorimeter was equipped with a cryostat and cooling coil around the reactor to cool down the reactor and deicing solution to the desired temperature prior to testing. All the equipment was placed in a large walk-in cold room with temperature control ($\pm 1^\circ\text{C}$) to minimize heat flow through the insulation.

PT100 temperature sensors measured the temperature inside the solution at different depths in the insulation as well as the air temperature. The sensors were connected to PicoTech PT104 data loggers. A 500 W electrical heater was positioned under the bottom of the reactor and powered by a regulated 160 V DC power supply (Elektro Automatik PS8160-04). The output voltage, U (in Volt) and electrical current, I (in Ampere) measured by the power supply, was connected to a data logger (National Instruments NI-USB-6211) allowing to measure and control the amount of heat added to the system. A PC-based measurement and control application (LabView) was developed to control the calorimeter.

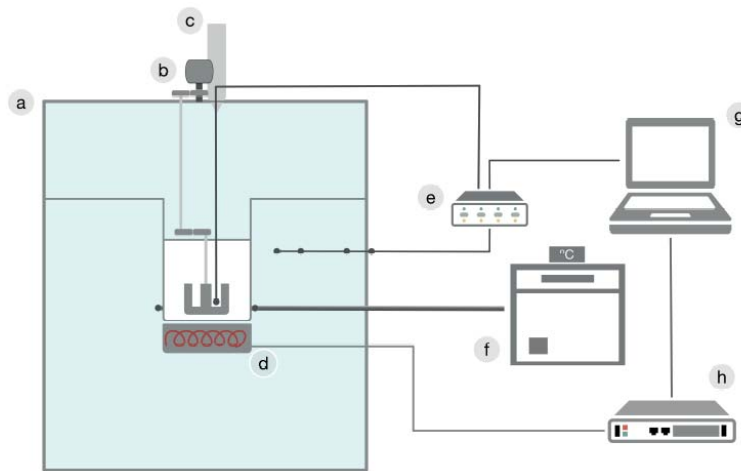


FIGURE 1 Illustration of the calorimeter consisting of: a) an insulated reactor b) a stirrer c) a re-closable opening for inserting ice d) an electrical heater e) data logger f) cryostat h) regulated power supply and g) a PC with control software.

Prior to testing, a known amount of deicer solution of a known concentration was inserted into the reactor and brought to the desired test temperature. The temperature sensors inside the insulation were used to determine if a homogenous temperature was reached. At the start of a test, the software stores the temperature of the solution as the set point T_{sp} . A 60-second delay counter starts to allow the operator to insert a measured amount of ice m_{ice} into the reactor. The ice temperature T_{ice} , and m_{ice} is entered manually to correct for differences between the T_{ice} and T_{sp} .

Next, after 60 seconds the temperature starts to drop due to the melting reaction, and the controller starts to add electric power $\dot{Q}_{electric}$ (in W) to the heater. A simple proportional control logic was found most suitable for bringing the temperature slowly back to the set point without any overshoot, as shown in equation 2.

$$\dot{Q}_{electric} = p \cdot (T_{sp} - T_{sol}) \quad (2)$$

Where p is the proportional gain, and T_{sol} the temperature of the deicing solution, an increase of $p=10$ W/°C was found suitable to prevent any overshoot and keep the test duration reasonably brief. In order to prevent unnecessarily long waiting times for the solution to reach the set point temperature, a minimum power of $\dot{Q}_{electric} = 4$ W was applied to the heater when the temperature difference between the set point and solution was less than 0.4°C.

The total amount of heat added to the system is provided by equation 3:

$$Q_{added} = Q_{electric} + Q_{heat\ leakage} + Q_{mixer} + Q_{ice} \quad (3)$$

Where $Q_{electric}$ is the total energy (in J) added by the heater, $Q_{heat\ leakage}$ is the total energy conducted through the insulation, Q_{mixer} is the energy added by the blade mixer, and Q_{ice} is the amount of energy added/subtracted when the added ice is warmer/colder than the set point temperature. $Q_{electric}$ is shown by equation 4:

$$Q_{electric} = \int_{t_0}^{t_1} (U \cdot I) dt \quad (4)$$

Where t_0 is the starting time, t_1 the time when the test is finished and dt the time step of the measurement program. U is voltage/electric tension (volt) and I is electrical current (ampere) The total heat leakage is shown by equation 5:

$$Q_{heat\ leakage} = \int_{t_0}^{t_1} (C \cdot \Delta T) dt \quad (5)$$

Where C is the overall conductivity coefficient (in W/°C) and ΔT the temperature difference between solution and the outside of the insulation. C is a constant specific for the constructed calorimeter and determined experimentally to be 0.036 W/°C. The total amount of heat added by the mixer is shown by equation 6:

$$Q_{mixer} = \int_{t_0}^{t_1} (\dot{Q}_{mixer}) dt \quad (6)$$

Where \dot{Q}_{mixer} is the effective heating power (in W) of the mixer. For the used blade mixer rotating at 15 RPM in water at room temperature, the effective heating power was experimentally measured and found to be 0.01 W (18). This was such a sufficiently low level that \dot{Q}_{mixer} was disregarded for other tests. The amount of heat added to, or subtracted from, the system when the ice is inserted is shown by equation 7:

$$Q_{ice} = m_{ice} C_{p_{ice}} (T_{ice} - T_{sp}) \quad (7)$$

Where $C_{p_{ice}}$ is the specific heat capacity of ice ($C_{p_{ice}}=2.017$ kJ/kgK).

All the calculations were done for every time step dt . Hence, the program provides a “real time” output of the amount of ice that has been melted. The time step of the control program was limited by the updating frequency of the PT104 data loggers (every 400 ms). The temperature of the solution was smoothed using a 4-second moving average filter to reduce the noise in the measurement signal.

As an example, Figures 2 and 3 show a typical graph of the temperature and added heat as a function of time. Figure 2 shows that the solution’s temperature rapidly drops from the set point temperature of -4.8°C to about -8.5°C . Figure 3 shows that after the 60-second delay, the heater starts adding heat to the system (about 35 W). The power gradually declines as the solution temperature approaches the set point again. After 2750 seconds the melting capacity at set point temperature has been reached, and the test is complete.

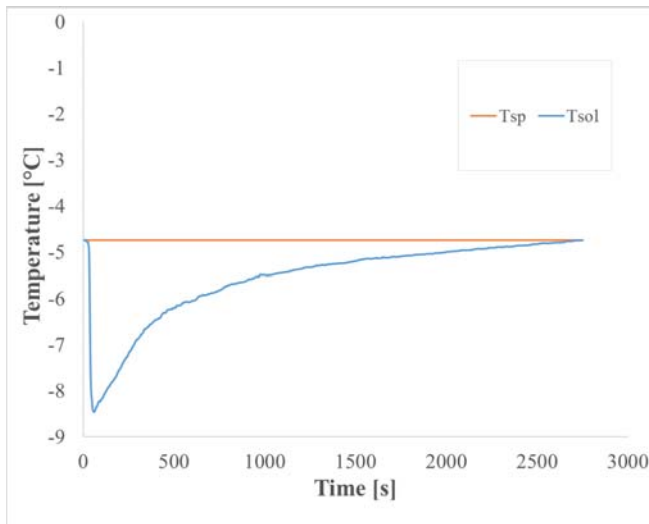


FIGURE 2 Typical graph of temperature as a function of time during a test

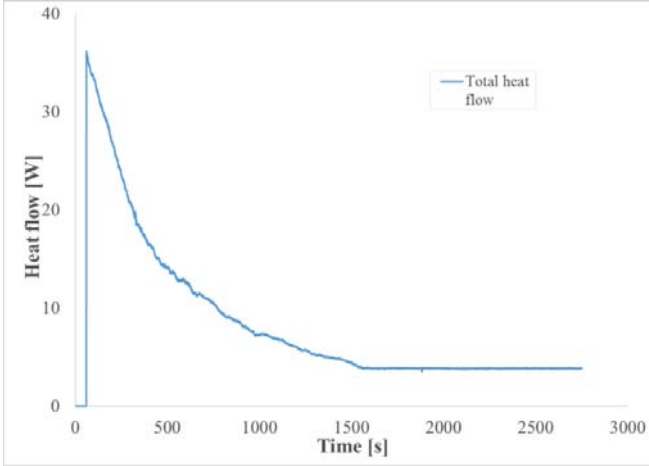


FIGURE 3 Typical total heat flow as a function of time during a test

TEST PROCEDURE

A total of 38 ice melting capacity tests were performed using liquid NaCl (brine) as deicer. The set point temperature ranged from -2.5°C to -15.2°C. In addition, four tests using 22w% MgCl₂ brine and 19 tests using mixes of NaCl and MgCl₂ were performed. An overview of the tests is given in Table 1. Approximately 100 g (3.5 oz) of solution was used for each test with the exception of four NaCl tests, which were performed using 60 g (2.1 oz) of solution. In the prepared solutions, the required amount of solutes was dissolved in distilled water. The 23w% NaCl solution was prepared with 230 g solid NaCl and then adding distilled water until 1000 g of total weight was reached. MgCl₂ was delivered as hexahydrate (MgCl₂·6H₂O) from the manufacture. To obtain correct amount of solutes to make a 22w% MgCl₂ solution; 469,3 g MgCl₂·6H₂O was weight and then distilled water was added until 1000 g total weight was achieved.

Initial concentration and deicer product	Temperature range	Number of tests
23% NaCl	From -5°C to -20.7°C (From 23°F to -5.3°F)	27
12% NaCl	From -2.5°C to -5°C (From 27.5°F to 23°F)	11
22% MgCl ₂	From -12°C to -23°C (From 10.4°F to -9.4°F)	4
Mix 50/50 (11.5w% NaCl + 11.0w% MgCl ₂)	From -11°C to -23°C (From 12.2°F to -9.4°F)	12
Mix 80/20 (18.4% NaCl + 4.4w% MgCl ₂)	From -11.5°C to -21°C (From 11.3°F to -5.8°F)	7

TABLE 1 Overview of the ice melting capacity tests

The amount of initial solution needs to reach above the bottom of the mixer to ensure mixing, and the solution temperature sensor needs to be submerged. However, the maximum volume of solution and melted water cannot exceed the volume of the container. To ensure that the melting capacity was reached, the amount of ice added to the system had to exceed the amount of ice the deicer was able to melt. The ice was crushed into pieces approximately the size of 2 – 6mm (0.079 in – 0.236 in).

CALCULATING MELTING CAPACITY

For purposes of comparison, the ice melting capacity was calculated according to Nilssen et al. (2016) (1). Empirical data for freezing point depression for NaCl are provided by *The Handbook of Chemistry and Physics* (17). Data for freezing point depression of MgCl₂ may be interpreted based on the graph illustrated by Melinder (2007) (19). Figure 4 shows the calculated melting capacity of NaCl and MgCl₂.

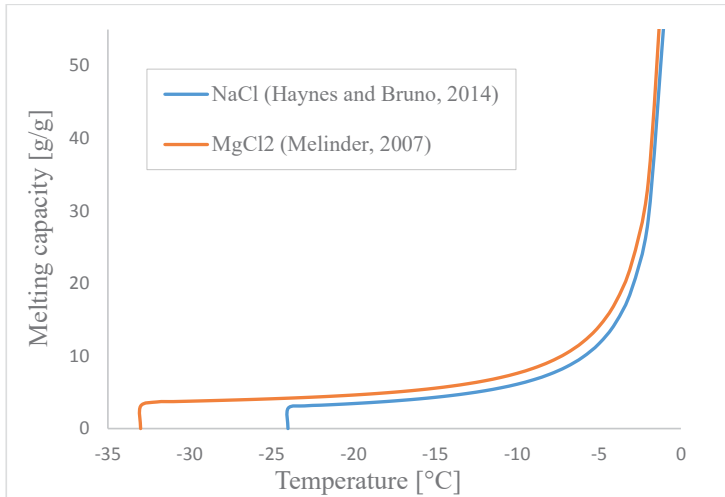


FIGURE 4 Calculated melting capacity of NaCl (blue line) and MgCl₂ (red line)

Unrealized Melting Capacity

The water that was used to dissolve the deicer to make brine could have come from melted ice if the deicer was used in a solid state. Hence, this amount of water may be regarded as “unrealized melting capacity” when brine is used. In order to be able to compare brine with dry salt/deicer, as done in this paper, the unrealized melting capacity needs to be taken into account; per gram of deicer this equals 3.3 g for a 23% solution, 4 g for a 20 % solution and 7.3 g for a 12 % solution (1). The results from the calorimeter were compared to the theoretical melting capacity of dry salt.

RESULTS

NaCl

Figure 5 shows the measured melting capacity of NaCl in the calorimeter for different temperatures. The blue line is the calculated melting capacity. All the measurements (red dots) are located close to the calculated melting capacity. This shows that the calorimeter measures the ice melting capacity close to the “real”, calculated melting capacity.

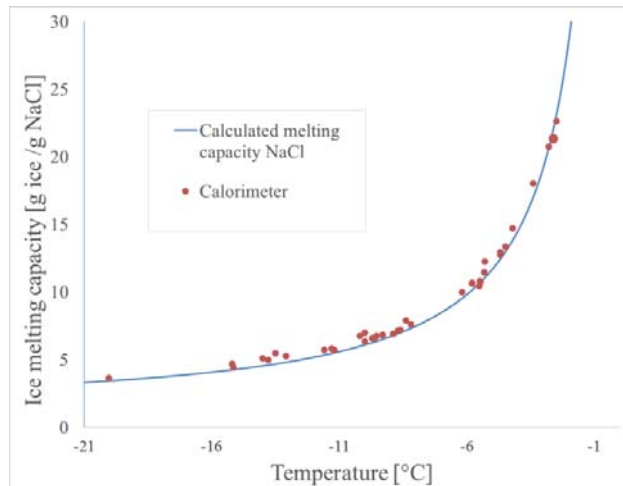


FIGURE 5 Measured vs calculated melting capacity for NaCl.

Figures 6 a) and b) show the absolute and relative errors for the data measured in the calorimeter. It appears that the spreading in the absolute error is larger at warmer temperatures. The average absolute error is 0.4 g, suggesting that the calorimeter has a tendency to overestimate the actual (calculated) melting capacity. The relative error shows a weak dependency on the temperature: as it gets colder, the relative error increases. This is most likely because the melting capacity is much lower at lower temperatures, causing the relative error to increase.

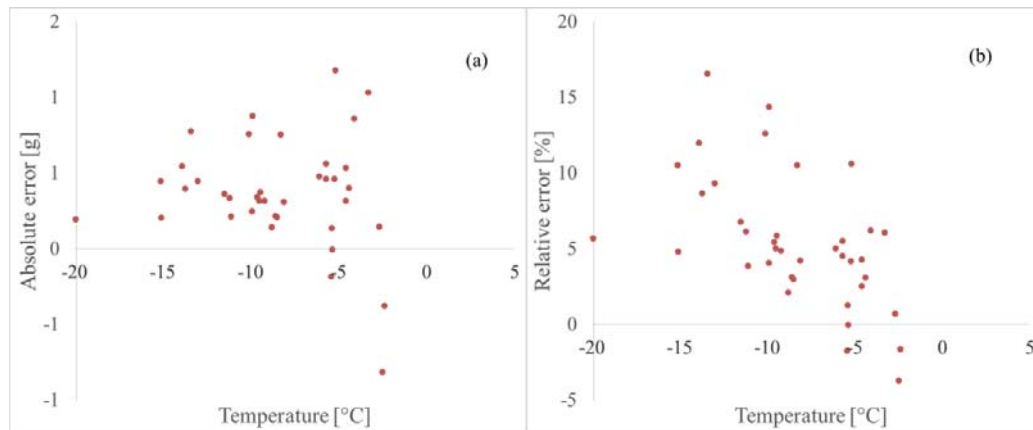


FIGURE 6a) Absolute error **b)** Relative error of NaCl measurements

MgCl₂ and Mix of NaCl + MgCl₂

Figure 7 shows the results of the tests done with MgCl₂ (orange dots), a 50/50 mix of NaCl /MgCl₂ (yellow triangles) and 80/20 mix of NaCl /MgCl₂ (green crosses). The tests were done

using brine (solutions), but the results are given in gram melted ice per gram pure solute (salt without water). The red line represents the calculated melting capacity for MgCl_2 and the blue line for NaCl . The same tendency may be seen from tests performed with NaCl , the majority of the results lying above 100% of melting capacity. The calorimeter has a tendency to overestimate the amount of melted ice. The results from the 50/50 mix are located almost in the middle of the lines for calculated melting capacity for NaCl and MgCl_2 . MgCl_2 has a higher melting capacity than NaCl . According to the results, using a 50/50 mix produces a melting capacity in the middle of the NaCl melting capacity and the MgCl_2 . The results from the 80/20 $\text{NaCl}/\text{MgCl}_2$ -mix are located closer to the calculated melting capacity curve for NaCl than for MgCl_2 . The results imply that the advantage of using MgCl_2 in a deicing mix is simply the result of the amount used.

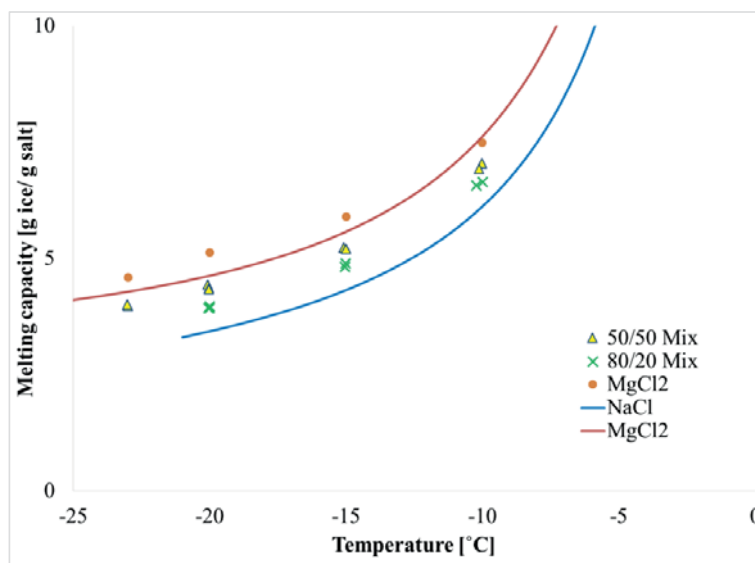


FIGURE 7 Results of the tests done with 50/50 mix NaCl and MgCl_2 , with 80/20 mix of NaCl and MgCl_2 and with only MgCl_2 .

DISCUSSION

Accuracy of the calorimeter

To summarize the results, the calorimeter provided results with the lowest measured ice melting capacity of 96.3% and the highest 116.6% from calculated melting capacity. The average absolute error was 0.5 grams, and the average relative error was 5.4%. On average, the calorimeter measured above 100% melting capacity, meaning that the calorimeter overestimated the amount of ice actually melted. Since the amount of melted ice is directly related to the amount of measured energy added to the system, the error is probably caused by overestimating the amount of heat that was added. Since the experiments were performed in a cold room at the same temperature as the set point, it is unlikely that the heat leakage was overestimated. The heat from the mixer was minimal and already neglected, so this cannot be the cause of the overestimation. This leaves the electrical heater as the probable cause of the overestimation. Although the power supply was calibrated by the manufacturer and was checked manually using a multimeter, it may be not sufficient. Since a DC power supply was used, there is no impedance loss; nonetheless, heat generation in the lead wires of the electrical heater could have led to measured energy that did not enter into the reactor, but rather dissipated as heat in the lead wires. As a recommended improvement, it is suggested to calibrate the heater as a whole system (not only the power supply).

It is useful to compare the results from the calorimeter with earlier measurements of ice melting capacity tests, summarized by Nilssen *et al.* (2016) (1). To do so, the relative melting capacity was calculated according to equation 8:

$$\text{relative melting capacity} = \frac{\text{measured melting capacity}}{\text{calculated melting capacity}} * 100\% \quad (8)$$

Figure 8 shows the relative melting capacity for the SHRP H-205.1 and 205.2, the shaker test, the mechanical rocker test, the ice cube titration test and the calorimeter. The melting capacity calculated from the phase diagram is shown as 100% (blue line) as a reference. Although the calorimeter does not exactly measure 100% relative melting capacity, it offers significant improvement compared to earlier test methods, most notably the SHRP test and shaker/mechanical rocker tests. Both of these earlier tests require a physical separation of the meltwater from the ice. The data point from the ice cube titration test (which does not require separation) is also close to 100%, but more data points are needed to conclude the accuracy

of this test.

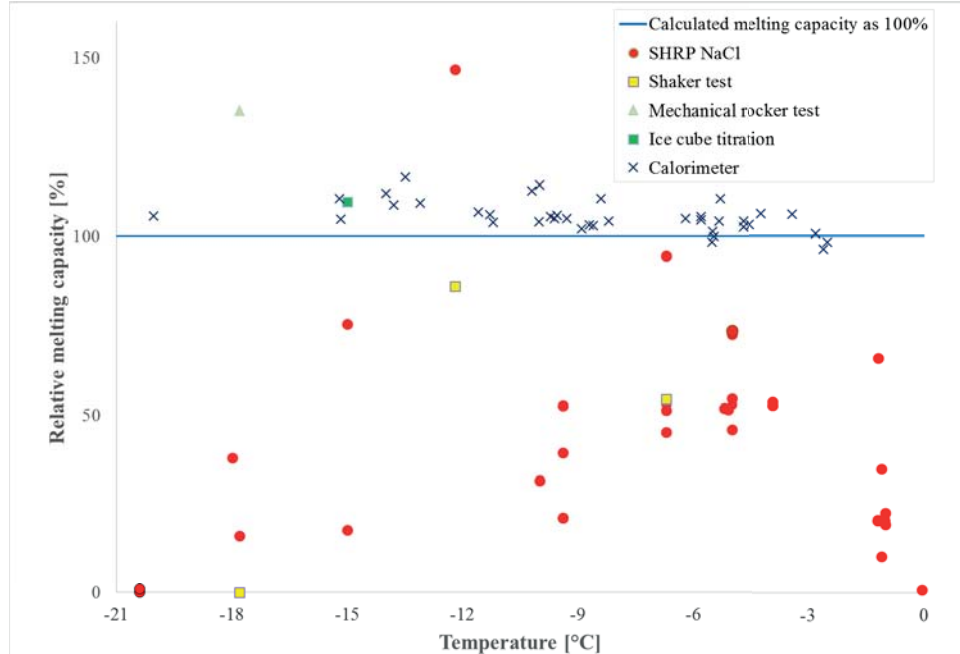


FIGURE 8 Relative melting capacity for tests performed with the Calorimeter (present study), compared with earlier ice melting capacity measurement, using the SHRP H-205.1 and H-205.2, the shaker test, the mechanical rocker test and the ice cube titration test. Data source: (1)

Possibilities and limitations of the calorimeter

The calorimeter has eliminated a certain number of the issues connected with earlier ice melting capacity tests. For example, there is no mechanical handling of the equipment during testing time and no separation of the melted water from the ice. Since only brine is used, there are no issues regarding different grain size or how the grains become scattered over the ice. There is no pre-defined limitation in testing time with the calorimeter, allowing the chemical to reach its melting capacity. However, the calorimeter has certain limitations. There is a minimum volume of solution needed to reach up to the mixer and temperature sensor. This makes it impossible to use a 23% solution for all temperatures because the required ice would exceed the volume of the reactor at a higher temperature. This was solved by reducing the solution concentration at higher test temperatures. However, when the solution concentration changes, the results cannot be compared without recalculating to a common unit (here 1g dry NaCl was used). While this calculation will not produce a biased result of any significance for strong solutions, it might do so for weaker solutions since it will be a large part of the total amount of melted ice. These issues may be solved by redesigning the reactor and mixer to allow lower initial solution volumes.

It was difficult to test at temperatures close to 0°C due to the fact that a large amount of ice is required when the temperature gets close to 0°C; consequently, the mixer occasionally had problems mixing larger amounts of ice. A redesign of the mixer that allows mixing of both large and small ice volumes, combined with the previously mentioned low initial solution

volume, may be beneficial. It was also found to be difficult to perform measurements close to the eutectic point, as at these low temperatures only a limited temperature drop takes place after the ice is inserted. Moreover, at times the control program shut down too early, incorrectly identifying that the set point temperature had yet again been reached. Since the melting reaction goes more slowly at lower temperatures, the 60-second delay may not be sufficient. This could be increased for tests at lower test temperatures. In addition, a more rigorous smoothening of the measured solution temperature might be needed in order to prevent the test's premature termination. However, this would require a more rapid temperature data collection; otherwise, the response time of the system becomes too slow.

The main finding of this study is that calorimetry can be a promising method to measure the ice melting capacity of deicing products. It is shown that a higher accuracy can be reached than earlier test methods, and the suggested improvements are implemented, we believe that test set-ups can be further developed that will exceed the accuracy achieved in this study.

Improving the melting capacity of NaCl with MgCl₂

The results in Figure 7 show that the melting capacity of MgCl₂ is higher than that of NaCl. This was found to be consistent for both the calculated and measured ice melting capacity. Hence, when NaCl is mixed with MgCl₂, the resulting product attains a higher ice melting capacity compared with pure NaCl. The effects appear to be simply additive of the two compounds, meaning that the more NaCl is replaced with MgCl₂, the closer the resulting melting capacity gets to the melting capacity of pure MgCl₂. This is consistent with findings by Koefod (2012) performed with "the ice cube titration" test (13).

CONCLUSIONS

Ice melting capacity measurements of NaCl, MgCl₂ and mixes of these two deicers were performed in a specially designed and constructed calorimeter. The calorimeter shows significant improvement in accuracy compared to earlier test methods. The average absolute error was 0.4 g, and the average relative error was 5.4 %. Using calorimetry has eliminated a certain number of the issues associated with inaccuracies concerning SHRP, the shaker test, mechanical rocker test and ice cube titration test. There is no mechanical separation of meltwater and ice needed, no manual handling of the equipment required during the test, no issues involving different grain size or how the grains become scattered over the ice. Finally, the tests are not terminated at a pre-defined testing time, making the measurement independent of the melting rate.

Unfortunately, we did not find a commercially available calorimeter and it therefore had to be custom made. There are different limitations identified with the current version of the calorimeter. These include a rather large minimum volume of deicing solution as well as difficulties conducting accurate measurements close to 0°C and close to the eutectic point. Various improvements for further development are suggested.

The results produced by the calorimeter during this test showed that the melting capacity of NaCl is drastically reduced at low temperatures. The same principle applies to MgCl₂. MgCl₂ has a higher melting capacity than NaCl. The effect of mixing MgCl₂ into the NaCl is simply the result of how much the mix contains of each of the two chemicals. If the mix is 50/50, the melting capacity of the mix will be right between the melting capacity of MgCl₂ and NaCl; if the mix contains 80% NaCl, the melting capacity will be closer to pure NaCl than pure MgCl₂.

ACKNOWLEDGMENTS

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REFERENCES

- (1) Nilssen, K., Klein-Paste, A., and Wählin, J. Accuracy of Ice Melting Capacity Tests: Review of Melting Data for Sodium Chloride. In *Transportation Research Record: Journal of the Transportation Research Board*, No. 2551, Transportation Research Board of National Academies, Washington, D.C, 2016, pp. 1–19.
- (2) Chappelow, C.C., McElroy, D.A., Blackburn, R.R., Darwin, D., Noyelles, F.G., and Locke Carl E. *Handbook of Test Methods for Evaluating Chemical Deicers*, SHRP-H-332nd ed. Strategic Highway Research Program. National Research Council, Washington DC. 1992
- (3) Koefod, S., R. Mackenize, and J. Adkins. *Effect of pre-wetting Brines on the Ice Melting Rate of Salt at Very Cold Temperatures*. Report number 15-4355. In: Transportation Research board 94th Annual Meeting, Washington D.C, 2015.
- (4) Gerbino-Bevins, B.M., C.Y. Tuan, and M. Mattison. Evaluation of Ice-Melting Capacities of Deicing Chemicals. In *Journal of testing and evaluation*, Volume 40, No 6, ASTM, 2012, pp. 1-9.
- (5) Fay, L., and X. Shi. Laboratory Investigation of Performance and Impacts of Snow and Ice Control Chemicals for Winter Road Service. In *Jornal of Cold Regions Engineering*. Vol 25, No 3, 2011, pp. 89–114.
- (6) Akin, M., and X. Shi. Development of Standardized Test Procedures for Evaluating Deicing Chemicals. Publication CR07-02 Project 0092-08-32. Western Transportation Institute. Montana State University, 2010.
- (7) Fay, L., Volkening, K., Gallaway, C., and Shi, X. *Performance and impacts of current deicing and anti-icing products: User perspective versus experimental data*. In: 87th Annual Meeting of Transportation Research Board. Transportation Research Board Washington, D.C., 2008, pp. 8–1382.
- (8) Svanekil, A. *Forsøk med varmbefuktet salt for å bedre friksjonen på vinterveger*. *Civil engineering theses dissertation, student research*. The Norwegian Public Roads Administration and the Norwegian University of Science and Technology, Trondheim, Norway, 2007.
- (9) Alger, R., and J. Haase. *Analysis of the Benefits of Bulk Pre-wetting Solid NaCl with Several Different Liquids*. Report no: RC-1473. Michigan Technological University, Michigan United States, 2006.

Nilssen, Klein-Paste, Wåhlin, Delapaz
Paper II. Measuring ice melting capacity using calorimetry

(10) Nixon, W.A., J. Qiu, L. Qiu, G. Kochumman, and J. Xiong. *Ice melting performance for ice-control chemicals* In: Proceedings: 84th Annual Meeting of the Transportation Research Board. Washington D.C., 2005.

(11) Hernes, I. *Use of magnesium chloride - solution as deicing agents*. Civil Engineering thesis, student research, The Norwegian University of Science and Technology, Trondheim Norway, 2004.

(12) Tuan, C.Y., and T. Albers. *Development of a Mechanical Rocker Test Procedure for Ice Melting Capacity Evaluation*. Project number: NDOR Project M322, University of Nebraska, United States, 2014.

(13) Koefod, S., J. Adkins, and M.R. Akin. *Alternative Approaches to Measuring Deicer Ice-Melting Capacity: Optimization of Test Accuracy and Precision*. In: Transportation Research E-Circular. Presented at the International Conference on Winter Maintenance and Surface Transportation Weather, Iowa United States, 2012, pp. 432-442

(14) Klein-Paste, A., and J. Potapova, Thermal Aspects of Melting Ice with Deicer Chemicals. In: *Transportation Research Record: Journal of the Transportation Research Board, No. 2440*, Washington D.C., 2014, pp 69–75.

(15) Haines, P.J. *Principles of Thermal Analysis and Calorimetry*. Royal Society of Chemistry, Inc., Surrey UK, 2002.

(16) Höhne, G., Hemminger, W., and Flammersheim, H.-J. *Differential Scanning Calorimetry*. Springer Science & Business Media, Inc., New York, 2003.

(17) Haynes, W.M., and T. Bruno. *CRC Handbook of Chemistry and Physics*. 95th edition Online. Taylor and Francis Group, LLC., California United States, 2014.

(18) Betten, L. *Measuring melting capacity with calorimetry*. *Civil engineering theses dissertation, student research*. The Norwegian Public Roads Administration and the Norwegian University of Science and Technology, Trondheim Norway, 2014.

(19) Melinder, Å. *Thermophysical Properties of Aqueous Solutions Used as Secondary Working Fluids*. *Doctoral theses*. School of Industrial Engineering and Management Royal Institute of Technology, KTH, Stockholm Sweden, 2007

APPENDIX C – Paper III

Nilssen, Kine; Klein-Paste, Alex; Wåhlin, Johan.

The effect of additives on the low temperature ice melting capacity of NaCl

(Paper submitted June 2017 TRR)

**THE EFFECT OF ADDITIVES ON THE LOW TEMPERATURE ICE MELTING
CAPACITY OF NaCl**

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ABSTRACT

Winter maintenance of high-traffic volume roads requires chemicals for the strategy of obtaining sufficient friction. Challenges often arise in very cold temperatures because the effect of the chemicals is reduced in low temperatures. The most commonly used chemical for winter maintenance operations is sodium chloride (NaCl), also called salt. NaCl has a eutectic point of -21°C , but its ability to melt snow and ice (ice-melting capacity) drastically decreases when passing temperatures as high as -10°C to -15°C . To improve performance of deicing chemicals, including increasing the ice-melting capacity in cold temperatures, additives to salt are often used. There is a lack of knowledge as to how these additives actually affect low temperature ice-melting capacity. Ice-melting capacity testing is often done using SHPR H-205.1 and 205.2; however, recent research has shown that the SHRP test produces inaccurate results.

Calorimetry has been used successfully to measure ice-melting capacity. This paper uses calorimetry to study the effect of additives on the low temperature ice-melting capacity of NaCl. MgCl_2 , CaCl_2 , KFo, CMA and sugar was added to NaCl in -18°C . The chemicals were also tested individually. The measures were done in a recently improved custom-made calorimeter described in the paper.

The results showed that solid chemicals had far higher melting capacity than solutions. In a solid state NaCl had the highest ice-melting capacity of the tested deicing chemicals. However, the results are different for solutions. For example, all of the tested chemicals had higher ice-melting capacity than NaCl when used both individually and as additives to NaCl, except KFo as additive and sugar. CaCl_2 had the highest ice-melting capacity of the solutions, melting 285% more than NaCl in -18.6°C . This was followed by MgCl_2 , KFO, Mix NaCl/ CaCl_2 , Mix NaCl/CMA, CMA, and mix NaCl/ MgCl_2 . Using chlorides as additives (MgCl_2 and CaCl_2) resulted in a melting capacity between that of NaCl and MgCl_2 and CaCl_2 ; the improvement depended on the amount of MgCl_2 or CaCl_2 . However, when KFo and CMA were used, the results were different. KFo had a destructive influence on melting capacity when mixed with NaCl, while mixing CMA with NaCl produced a higher melting capacity than what the two components had done individually. The sugar froze at -18°C .

Keywords: winter road maintenance, additives, NaCl, deicing, melting capacity, test procedures, calorimetry, cold temperatures

INTRODUCTION

Background

Winter road maintenance is challenging in cold temperatures. Sodium Chloride (NaCl) is the most frequently used chemical for deicing and anti-icing operations. While throughout most of the winter, NaCl is able to maintain ice-free roads, problems arise in areas where temperatures get very cold. The eutectic point of NaCl is -21.2°C (-6.2°F) with a eutectic concentration 23.2% (1); however, operators' many years of field experience has made them aware of the fact that NaCl abruptly – and disastrously - ceases to work at temperatures as high as -10°C to -15°C . NaCl's ability to melt ice, called its ice-melting capacity (gice/gdeicer), is drastically reduced with decreasing temperatures. In order to counteract this reduction, additives, e.g. other chemicals, have been used for many years to improve the performance of deicing and anti-icing chemicals, among other things to improve low-temperature performance (2). However, the degree to which additives can improve ice-melting capacity is not clear.

Research results are not unambiguous when it comes to the melting capacity of deicing/anti-icing chemicals and additives in cold temperatures. Several research results have shown that magnesium chloride (MgCl_2) solution (3) (4) (5) (6) and calcium chloride (CaCl_2) solution (4) (6) have a higher ice- melting capacity than NaCl in -18°C . Others have shown that CaCl_2 has very low melting capacity at

-18°C (7). Using MgCl_2 to pre-wet NaCl has shown increased melting capacity (8). The improvement of using MgCl_2 as an additive has shown to be supplemental to the total ice-melting capacity, meaning that the new level of ice-melting capacity is simply the sum of the ice-melting capacity of the individual components (9). Nonetheless, as regards other additives, it remains inconclusive if a synergistic boost (the result exceeds the sum of two components) can be possible. For instance, agro-based products and CCM products (Complex Chloride Minerals) are increasingly being employed in snow and ice operations (2), and manufacturers have claimed benefits for low-temperature performance. Adding corn-based derivatives to MgCl_2 has shown to improve and exceed the ice-melting capacity of MgCl_2 in -18°C (7). Others showing decreasing ice-melting capacity when glycerol was mixed in with MgCl_2 (10), and no increase in melting capacity for agro-based products compared to NaCl (4) (2). Interestingly, CCM products have not shown higher ice melting capacity in cold temperatures (2).

The reason for unambiguous results is the test methods used for measuring ice-melting capacity. These tests are usually performed using SHRP H-2051 and 205.2, which are still the standard method for measuring ice-melting capacity (2). However, recent research has shown these test methods' low level of accuracy (12), and the fact that the results found in literature are so inconsistent is just another indicator of this point. Ice-melting capacity is a physical property, and should provide consistent results independent of the test methods used.

There are many deicing/anti-icing chemicals with a lower eutectic point than NaCl, but this is not synonymous with having higher melting capacity in cold temperatures (14). Danilov et al. (2011) found low eutectic temperatures (as low as -30°C (15)), by mixing different ratios of magnesium and calcium nitrates, without having higher melting capacity than NaCl before exceeding the eutectic point of NaCl. Later on, they tested sodium acetate, potassium acetate, magnesium acetate, calcium acetate, ammonium acetate, sodium formate, potassium formate, sodium chloride and calcium chloride. Some

of these had a very low eutectic point and yet produced the result of NaCl having the highest melting capacity (down to -20°C). However, potassium acetate, ammonium acetate and potassium formate were able to melt ice down to -50°C and calcium chloride to -40°C (16). The tests were performed using VPA (Visual polythermal analysis).

Therefore, the deicer's melting capacity at a given temperature seems to be the result of complex compositions of several qualities. As more and more commercial products with mixed compositions are manufactured, the need to be able to measure their performance is increasing. For example, a new test method for measuring ice-melting capacity was published in 2016 (17), using calorimetry. An improved version of this calorimeter was built during this study and used to determine the ice-melting capacity of Sodium Chloride (NaCl) with additives at -18°C . Common deicers were used individually and as additives; Magnesium Chloride (MgCl_2), Calcium Chloride (CaCl_2), Potassium Formate (KFO), Calcium Magnesium Acetate (CMA) and Sucrose ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$). The goal of the study was to find if these chemicals had higher ice melting capacity than NaCl at low temperatures, both individually and as additives to NaCl.

METHOD

Design of the calorimeter

While the new calorimeter follows the same principal as an earlier version presented in Nilssen et al. 2017 (17), it has two new features to improve its accuracy. The mixing of ice and solution was performed vertically instead of horizontally because this produced a better blend of the ice and solution. The horizontal mixing process led to difficulties because the ice started floating to the top. Moreover, the heater was placed inside the deicing/ice mixture instead of underneath the reactor with the result that when the heater was placed under the reactor, it had to heat up the insulation, air and reactor bottom before penetrating the solution, which caused lost energy (heat).

The calorimeter is illustrated in figure 1 and consisted of the following:

- A cylindrical, insulated and hollow container separated into one bottom part and one lid. The insulation was a 15-centimetre thick extruded polystyrene layer covered with glass fibre to prevent water penetrating the insulation.
- A 0.5-litre volume plastic reactor inside the hollow container, which is where the mixing of ice and solution took place.
- One heater and two temperature sensors drawn through the insulated lid of the container and placed inside the plastic reactor. One temperature sensor monitored the heating element. It was attached inside a steel block along with the heating element and programmed to cut the power if the heater became overheated in order to prevent fire. The other temperature sensor measured the temperature inside the ice-solution mixture.
- A mixing table was fitted to the container and constructed to roll the entire container 180° back and forth. This movement ensured the proper mixing of the ice/solution blend.
- A 35-mm hole in the insulation was made for inserting a deicing solution during testing; otherwise, it remained closed.
- Wires connected the electrical elements of the heater, temperature sensors and mixing table to a power supplier and data program.

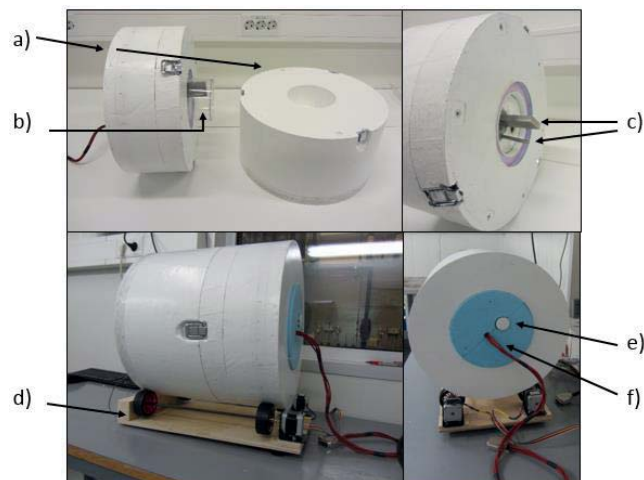


FIGURE 1 ILLUSTRATION OF THE CALORIMETER.

The calorimeter was tilted to one side by a few degrees. All the equipment was placed in a large walk-in cold storage room having temperature control ($\pm 1^\circ\text{C}$) to minimize heat flow through the insulation.

Ice was inserted in the plastic reactor b) and the ice was inserted through a hole in the lid e). When the deicer came in contact with the ice, the melting process began. This melting requires energy, which is normally taken from surrounding heat, causing the temperature to drop. Normally, heat quickly flows in, bringing the temperature back to its initial level: the concentration has then reached equilibrium. However, in this case, since the melting process was taking place inside an insulated calorimeter, no heat was flowing in after the temperature dropped. So in order to simulate this heat flow, a heater was inserted into the calorimeter, which supplied energy (heat) to bring the temperature back to the initial temperature. The calorimeter constantly monitored and logged the temperature and energy flow. As latent heat of fusion for ice is 334kJ/kg (1), the amount of melted ice could be calculated from the amount of energy added by the heater. Figure 2 illustrates the calorimeter, power supplier, control application from a computer (labview), and the data logger. The container was then removed between the addition of each chemical or mix. Prior to testing, a known quantity of ice was placed in the container and brought to the desired test temperature. The temperature sensors inside the container and insulation were used to determine if a constant temperature was reached. At the start of a test, the software stored the temperature of the ice as the initial/set point temperature. The solutions' mass and temperature were then entered manually to correct for differences between the temperature of the solution and the set point temperature. The control software kept the heating block at 0.5°C above the setpoint, until the melting process was almost finished. At the end of the procedure this reduced to 0.3°C .

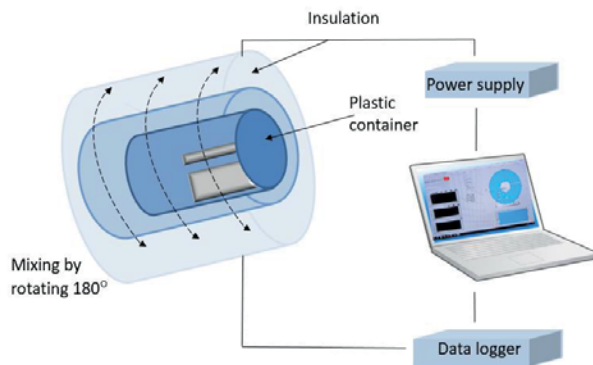


FIGURE 2 ILLUSTRATION OF THE CALORIMETER, POWER SUPPLIER, DATA LOGGER AND PC CONTROL SOFTWARE

Test procedure

A total of 63 tests were performed at approximately -18°C . Mixes of NaCl and Magnesium Chloride (MgCl_2), Calcium Chloride (CaCl_2), Potassium Formate (KFo), Calcium Magnesium Acetate (CMA) and sugar (sucrose/ $\text{C}_{12}\text{H}_{22}\text{O}_{11}$) were tested in the calorimeter. Each of the additives/deicing chemicals was also tested individually. Ice was cooled down inside the calorimeter and the deicing chemicals inserted through an opening at the start of each test. The ice was crushed ice cubes approximately size 2-6 mm in size.

Preparing additives/deicing chemicals

Different solutions were prepared by using the required amount of solutes dissolved in distilled water. A concentration representing a freezing point of -27°C was chosen for MgCl_2 , CaCl_2 , KFo and CMA. This was under the eutectic concentration to prevent precipitation, and was the lowest before reaching CMA's eutectic concentration. According to the literature, this was comprised of; 20w% for MgCl_2 (18), 25w% for CaCl_2 (18), 35w% for KFo (18) and 35w% for CMA (19). As regarded sugar, a freezing point of -19°C was chosen, as this was close to the test temperature and would not unnecessarily increase the concentration as it got very thick; this was to correspond to a 70w% solution (20). The eutectic point for NaCl (-21°C) was used with the corresponding and eutectic concentration of 23w%. Data for the tested deicers are shown in table 1. The NaCl, KFo, CMA and sugar had unknown water content and were therefore placed in a dryer at 70°C for 5 days to extract all water. No water content in the delivered NaCl and sugar was observed after drying. The 23w% NaCl solution was prepared by starting with 230g of solid NaCl and then adding distilled water until 1000 g of total weight was reached. The same procedure was done for the dried CMA, KFo and sugar. Solid MgCl_2 and CaCl_2 was (and is normally) delivered as hexahydrates ($\text{MgCl}_2\cdot 6\text{H}_2\text{O}$) and dihydrates ($\text{CaCl}_2\cdot 2\text{H}_2\text{O}$). This water content needs to be included. A MgCl_2 hexahydrate ($\text{MgCl}_2\cdot 6\text{H}_2\text{O}$) consists of 46.8% MgCl_2 and 53.2% H_2O . A CaCl_2 dihydrate consists of 75.5% CaCl_2 and 24.5% H_2O . In order to obtain the correct amount of solutes to make a 20w% MgCl_2 solution; 300g $\text{MgCl}_2\cdot 6\text{H}_2\text{O}$ was weighted, this equals 140.58g MgCl_2 , and 402.87g distilled water was added. In order to make the 25w% CaCl_2 solution, 300g $\text{CaCl}_2\cdot 2\text{H}_2\text{O}$, which equals to 226.53g CaCl_2 , was added to 606.12g distilled water.

Deicer	Chemical symbol	Eutectic temperature	Eutectic concentration	Freezing point concentration (-18°C)
Sodium Chloride	NaCl	-21°C	23.4%	21.5%
Magnesium Chloride	MgCl_2	-33°C	21.8%	16.5%
Calcium Chloride	CaCl_2	-50°C	30.5%	20.3%
Potassium Formate (KFo)	KCO_2H	-51°C	48%	27.5%
Calcium Magnesium Acetat	CMA	-27.5°C	32.5%	27.5%
Sucrose	$\text{C}_{12}\text{H}_{22}\text{O}_{11}$	-30°C	80%	70%

TABLE 1 DATA EUTECTIC POINT AND FREEZING POINT CONCENTRATION NaCl (18), MgCl_2 (18), CaCl_2 (18) KFo (18), CMA (19), SUCROSE (20)

Six repetitions were performed for each chemical or mix, 14 for NaCl and one for sugar, resulting in a total of 63 tests. Approximately 90g of ice were used in each test. The first test using a new chemical was performed with approximately 40g solution. The consecutive five tests using the same chemical were performed with the same ice and solution from previous test(s) by adding approximately 20g solution. This was done out of practical consideration for the purpose of achieving satisfactory mixing in the beginning and without surpassing the container's volume capacity at the test's conclusion. An overview of the tested solutions is presented in table 2.

Deicer	Initial concentration	Temperature	Freezing point	Number of repetitions
NaCl	23%	-17.3°C (0.9°F)	-21°C	14
MgCl ₂	20%	-18.9°C (-2°F)	-27°C	6
Mix 80/20 NaCl/MgCl ₂	23% NaCl + 20% MgCl ₂ (18.4w% NaCl + 4w% MgCl ₂)	-18.8°C (- 1.8°F)		6
CaCl ₂	25%	-18.6°C (- 1.5°F)	-27°C	6
Mix 80/20 NaCl/CaCl ₂	23% NaCl + 25% CaCl ₂ (18.4w% NaCl + 5w% CaCl ₂)	-19.4°C (- 2.9°F)		6
KFo	35%	-18°C (-0.4°F)	-27°C	6
Mix 80/20 NaCl/KFo	23% NaCl + 35% KFo (18.4w% NaCl + 7w% KFo)	-18.9°C (-2°F)		6
CMA	35%	-18.9°C (-2°F)	-27°C	6
Mix 80/20 NaCl/CMA	23% NaCl + 35% CMA (18.4w% NaCl + 7w% CMA)	-18.3°C (- 0.9°F)		6
Sucrose	70%	-18°C (-0.4°F)	-19°C	1

TABLE 2 PERFORMED ICE MELTING CAPACITY TESTS

Converting results from liquid to solid ice melting capacity

Although testing in the calorimeter was performed with deicing solutions, the result can be converted to represent solid chemicals by using equilibrium concentration (the freezing point concentration). Equation 1 describes how equilibrium concentration is calculated using the results from the calorimeter, and equation 2 how ice-melting capacity of solid chemicals is calculated

$$c_{eq} = \frac{m_{solid}}{m_{solid} + m_{melted\ ice} + m_{water\ in\ product}} \quad (1)$$

where:

c_{eq} = freezing point concentration (%)

m_{solid} = mass solid deicer (g)

$m_{melted\ ice}$ = mass melted ice and water in solution (g)

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$m_{\text{water in product}}$ = mass of water in solution or in product (g) = unrealized melting capacity
= the water used to dissolve the deicer (g) (17)

$$m_{\text{melted ice}} = \frac{m_{\text{solid}}}{c_{eq}} - m_{\text{solid}} - m_{\text{water in product}} \quad (2)$$

where:

$m_{\text{melted ice}}$ = mass melted ice (g). If $m_{\text{solid}} + m_{\text{water in product}} = 1$, is $m_{\text{melted ice}}$ = Ice melting capacity for solid chemical (IMC_{solid}) (g/g)

$m_{\text{water in product}}$ = mass water in solution = unrealized melting capacity = the water used to dissolve the deicer (g) (17)

m_{solid} = mass solid deicer (g)

RESULTS

Accuracy of the calorimeter

Accuracy was found by comparing measured data with calculated melting capacity. NaCl has a known phase diagram, which makes it possible to calculate the melting capacity (12). Fourteen tests were performed using 23% NaCl (brine) for the accuracy test. The scope of the testing involved cold temperatures, and the temperature range varied between -17.0°C and -17.7°C . The amount of ice used was approximately 100g per test, and the amount of solution approximately 20 - 40g (to test the practical challenges when varying the solution content).

Figure 3 shows a graphical illustration of the accuracy, measuring melted ice in grams. Red dots indicate the measured ice melt in the calorimeter, and the blue line represents the calculated melting capacity. The calorimeter is able to measure from 97% to 115% of the actual melted water; the average error was 104 %. The absolute error ranges between -0.001g to 0.016g per gram brine. When converted to solids by using equations 1 and 2, this equals an accuracy between 99.6% to 101.8%.

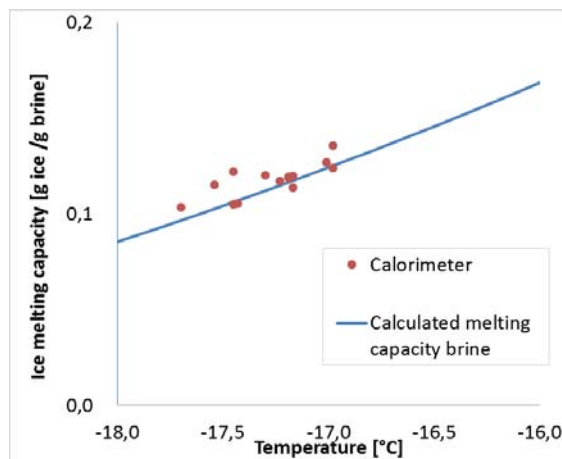


FIGURE 3 MELTING CAPACITY OF NAACL THEORETICAL AND MEASURED WITH THE CALORIMETER

Ice melting capacity of deicing solutions and additives

Figure 4 shows the ice melting capacity in gram-per-gram solution. Figure 4a) shows all data, and figure 4b) shows average data. Both are included because there are some differences in set point temperature as well as melting capacity. The blue line represents the calculated melting capacity of NaCl solution (brine) (12). MgCl₂ (20%), CaCl₂ (25%), Kfo (35%) had higher melting capacity than brine at -18°C. The sugar (70%) froze and had zero ice-melting capacity. Using MgCl₂ (20%), CaCl₂ (25%) and CMA (35%) as additives to brine in a 80/20 brine/additive-mix produced higher ice-melting capacity. Kfo (35%) as additive decreased the melting capacity of the brine.

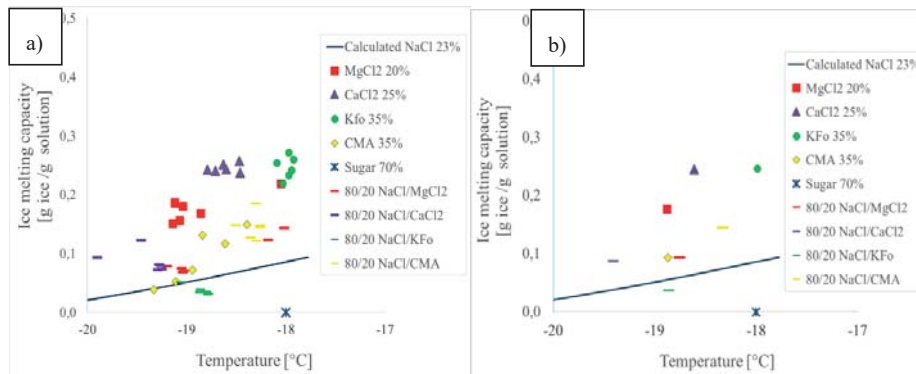


FIGURE 4 ICE MELTING CAPACITY OF DEICING SOLUTIONS. 4a) ALL DATA. 4b) AVERAGE DATA

A significant analysis was performed with a 95% confidence interval on the difference between measured ice melt for NaCl in the calorimeter and the calculated ice melt for NaCl, and the difference between measured ice melt with each chemical/additive and calculated ice melt for NaCl. See table 3. Table 3 also shows the improvement in ice-melting capacity compared to brine.

Deicer	Temperature °C	IMC (g/g)	More(+)/less (-) melted ice than brine		Statistically significant
			g	%	
MgCl ₂	-18.9	0.17	+0.12	+228	Yes
80/20 NaCl/MgCl ₂	-18.8	0.09	+0.03	+56	Yes
CaCl ₂	-18.6	0.24	+0.18	+285	Yes
80/20 NaCl/CaCl ₂	-19.4	0.09	+0.05	+144	Yes
KFo	-18.0	0.25	+0.16	+187	Yes
80/20 NaCl/KFo	-18.9	0.04	-0.02	-33	Yes
CMA	-18.9	0.09	+0.04	+61	No
80/20 NaCl/CMA	-18.3	0.14	+0.07	+97	Yes
Sugar	-18.0	0	-	-	-

TABLE 3. DIFFERENCE IN ICE MELTING CAPACITY BETWEEN DIFFERENT DEICERS AND BRINE

Ice melting capacity of solid chemicals and additives

Regarding a winter maintenance perspective, it is important to note that the melting capacity of solution (the numbers on the left side in figure 4), are low. The ice-melting capacity of solutions is lower compared to solid chemicals because of the water content. In figure 5, the ice-melting capacity has been converted to represent solid chemicals (the water content is subtracted), using equations 1 and 2. Note that the results for MgCl₂ are given in hexahydrate and results for CaCl₂ in dihydrates. The blue line represents calculated ice-melting capacity for solid NaCl (12).

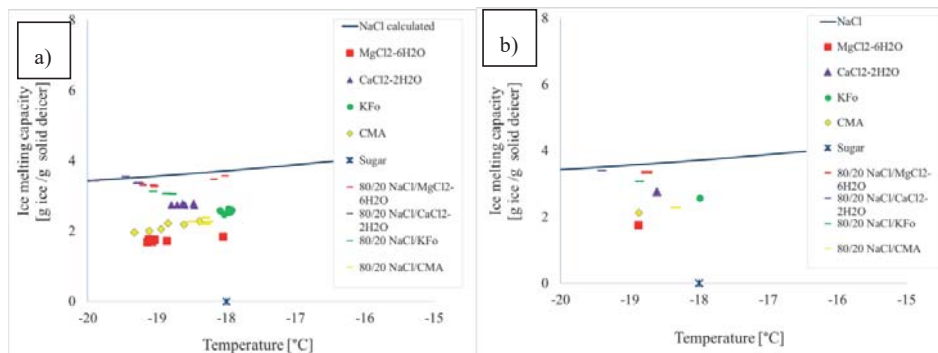


FIGURE 16. ICE MELTING CAPACITY SOLID CHEMICALS. 5a) ALL DATA 5b) AVERAGE DATA

All of the tested chemicals had in a solid state less melting capacity than NaCl as individual chemicals. The melting capacity of solid NaCl was also reduced if additives were used. A T-test was performed with a 95% confidence interval, and the observed lower melting capacity was significant. See table 4.

Deicer	Temperature °C	IMC (g/g)	More (+)/less(-) melted ice than NaCl		Statistically significant
			g	%	
MgCl ₂ -6H ₂ O	-18.9	1.75	-1.83	-51	Yes
80/20 NaCl/ MgCl ₂ -6H ₂ O	-18.8	3.36	-0.24	-7	Yes
CaCl ₂ -2H ₂ O	-18.6	2.76	-0.87	-24	Yes
80/20 NaCl/ CaCl ₂ -2H ₂ O	-19.4	3.42	-0.1	-3	Yes
KFo	-18.0	2.56	-1.16	-31	Yes
80/20 NaCl/ KFo	-18.9	3.08	-0.51	-14	Yes
CMA	-18.9	2.12	-1.46	-41	Yes
80/20 NaCl/ CMA	-18.3	2.27	-1.14	-38	Yes
Sugar	-18.0	0	-	-	-

TABLE 4. MELTED ICE COMPARED TO NACL

DISCUSSION

The calorimeter

The new calorimeter showed more accurate results than the earlier published version. The relative error for solutions was from 97% to 115% and for solid chemicals from 99.6% to 101.8%. One timesaving improvement was the ability to run a new test after the ice/deicer solution had come to equilibrium without taking the calorimeter out of the freezer. One negative point was the lack of the cryostat contained in the previous version which produced more accurate control of the set point temperature. It was difficult achieving the same set point temperature for each new test because the temperature in the walk-in cold storage room varied from day to day, which made it difficult to compare the deicers with each other. In this paper, the results were compared with calculated NaCl. In further research, the calorimeter can be used to draw complete phase diagrams, which will make comparisons easier.

Improving the ice melting capacity of NaCl by using additives

The improved test method “calorimetry”, was used to research the effect on ice-melting capacity using additives to NaCl in -18°C. The data showed that solid NaCl had high ice-melting capacity relative to other solid deicing chemicals in low temperatures, but lower than other chemicals used as brine. Of the individually chemicals tested in a solid state (MgCl₂, CaCl₂, KFo, CMA and sugar), NaCl had the highest ice-melting capacity. Using them as additives to solid NaCl will also decrease the melting capacity. MgCl₂ and CaCl₂ contain a high amount of water in a solid state, which contributes to low melting capacity in a solid state. The data also confirms that there is no linear correlation between freezing point and ice- melting capacity (14). The reason why NaCl has high melting capacity in -18°C is that it has low equilibrium concentration. This can be seen in equation 3 (12) (15). High initial concentration and low freezing concentration result in a high melting capacity.

$$IMC = \frac{C_i - C_{freeze}}{C_{freeze}} \quad (3)$$

Where:

IMC is the ice-melting capacity (g/g)

C_i is the initial concentration (chemical without water content). NaCl;100. MgCl₂; 46.2

C_{freeze} = concentration where a solution freezes (%)

In solutions the results are reversed. CaCl₂ , MgCl₂, KFO, Mix NaCl/CaCl₂, Mix NaCl/CMA, CMA, and mix NaCl/MgCl₂, had higher ice-melting capacity than NaCl (the CMA results were not significant). Using additives as brine increases the melting capacity, except sugar and KFo. The sugar froze, and the mix of NaCl with KFo had significantly lower melting capacity than NaCl. Regarding additives, the mix with CaCl₂ solution into brine gave the highest ice-melting capacity, increasing it by 144%. In solutions, the water content in solid MgCl₂ and CaCl₂ is a part of the solution, and they benefit from their combination of a low freezing concentration and high solubility at low temperatures and achieve a much higher ice-melting capacity relative to NaCl solution.

The test visualized the drastic decrease in ice-melting capacity when solutions were used instead of solid chemicals: brine only melts 2% of what solid NaCl in -18°C does. The other tested chemicals melted 4 - 12% in solution compared to solid form. The reason is naturally that solutions contain water, and water does not contribute to melting in

temperatures below 0°C. This is also the reason why pre-wetting results in lower melting capacity.

Previous studies (22) (17) have implied that the benefits of using MgCl₂ as an additive to NaCl are supplemental to the two compounds. This implication was not confirmed in this research; however, the results showed that there is an increase in melting capacity when MgCl₂ and CaCl₂ are added to brine, and that the melting capacity of the mix is situated somewhere between the melting capacity of the two compounds. Contrastingly, with respect to KFo and CMA, the picture was different. KFo had very high melting capacity individually at -18°C, and this might be because of a low eutectic point and high solubility in low temperatures. But when KFo was added to NaCl, the results were destructive. The ice melting capacity was reduced to a lower level, regarding not only for KFo but also for NaCl. While the reason why this happened is unknown, it might be that the quality of these two chemicals together makes them destructive to melting capacity. Mixing CMA and NaCl also produced an unexpected result. The mix increased the melting capacity to a higher level than the two components had individually. Danilov et al. 2012., found that mixing Potassium Acetate with Potassium Formate produced a doubling in ice-melting capacity than the two components had on their own. More research conducted on acetates would therefore be very interesting.

The solubility of MgCl₂ and CaCl₂ at -18°C is higher than used in this research. Solubility according to the extended UNIQUAC (23) model is 23.9% for NaCl at -17.3°C, 27.3% for MgCl₂ at -18.9°C and 34.5% for CaCl₂ at -18.6°C. Calculations were done, according to equation (2) in order to determine how the ice melting capacity would be if maximum solubility was used. C_{eq} was used from the calorimeter results.

$$\text{IMC}_{\text{NaCl (23.9\%)}}: 0.237/0.206 - 1 = \underline{0.15 \text{ g/g solution}}$$

$$\text{IMC}_{\text{MgCl}_2 \text{ (27.3\%)}}: 0.273/0.170 - 1 = \underline{0.61 \text{ g/g solution}}$$

$$\text{IMC}_{\text{CaCl}_2 \text{ (34.5\%)}}: 0.345/0.201 - 1 = \underline{0.72 \text{ g/g solution}}$$

NaCl used as 23.3% instead of 23% in -17.3°C increases the ice melting capacity from 0.11g/g to 0.15g/g (36%). The ice melting capacity of MgCl₂ will increase 258%, from 0.17g/g used as 20% solution at -18.9°C to 0.61g used as 27.6% solution, and the ice-melting capacity for CaCl₂ increases 200%, from 0.24g/g used as 25% solution at -18.6°C to 0.72 used as 34.5% solution. Using MgCl₂ and CaCl₂ as additives to 23% NaCl solution probably follows the same trend as with lower solubility, increasing the melting capacity of the brine. This calculation has not been done for CMA and KFo since we do not have data for maximum solubility at -18°C. However, the melting capacity for solutions is still low compared to solid chemicals, even with maximum solubility.

The experience with NaCl suggests that it is “ineffective” in cold temperatures; nevertheless, as this data points out, this is not due to the melting capacity, which is actually high, even when close to its eutectic point compared to other deicing chemicals. This confirms the findings from Koefod, 2012 (22). The experienced “ineffectiveness” is probably due to other mechanisms, such as low melting rate (that NaCl works very slowly) in cold temperatures (9).

CONCLUSIONS

In this study, improvements have been made to the previously described calorimeter (17), and it can now measure ice-melting capacity in cold temperatures with an accuracy between -0.001g to 0.016g, an absolute error from 97% to 115%. It was used in this paper to measure ice-melting capacity of deicing chemicals and additives to NaCl in cold temperatures. Additives were mixed with NaCl at -18°C in a 80/20-mix (80% NaCl with 20% additive). The additives were also tested individually. The calorimeter was built for testing liquid chemicals, but the results were also converted to solid chemicals.

Of all tests performed, solid NaCl had the highest ice-melting capacity, with 31% higher ice-melting capacity than the second best solid deicer, CaCl₂·2H₂O. Additives to solid NaCl, resulted in lower ice-melting capacity. The tests showed that ice-melting capacity is drastically reduced when solutions are used instead of solid chemicals. The solutions' ice-melting capacity was only 3% – 10% of the solid ice-melting capacity. But if solutions do need to be used, brine is the solution with the least ice-melting capacity at -18°C of the tested chemicals. Additives to brine therefore increased the ice-melting capacity, from 56% - 144% higher, except using KFo, which decreased the ice-melting capacity of brine and sugar, which froze. Using maximum solubility for MgCl₂ and CaCl₂ results in more than 200% higher ice-melting capacity for the solutions than the calorimeter showed; however, the ice-melting capacity is still low compared to solid chemicals.

The sugar froze and had zero melting capacity at -18°C.

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REFERENCES

- (1) Haynes, W.M., and T. Bruno. CRC Handbook of Chemistry and Physics. 95th edition Online. Taylor and Francis Group, LLC., California United States, 2014.
- (2) Muthumani, A. Fay, L. Bergner, D. Xiaming, S. *Understanding the effectiveness of non-chloride liquid agricultural by-products and solid complex chloride/mineral products*. Clear Roads Technical report CR13-12. Western Transportation Institute. Montana, USA. 2015.
- (3) Gerbino-Bevins, B.M., C.Y. Tuan, and M. Mattison. Evaluation of Ice-Melting Capacities of Deicing Chemicals. In *Journal of testing and evaluation, Volume 40*, No 6, ASTM, 2012, pp. 1-9.
- (4) Fay, L. and Shi, X. Laboratory Investigation of Performance and Impacts of Snow and Ice Control Chemicals for Winter Road Service. In: *Journal of Cold Regions Engineering, volume 25 (3)*. 2011, pp89-114.
- (5) Nixon, W.A., Kochumman, G. Qiu, J. Qiu, L. and Xiong, J. *Evaluation of deicing materials and corrosion reducing treatments for deicing salts*. Iowa Highway Research Board. IHR Technical report number 43. Iowa USA. 2007.
- (6) Druschel, S.J. *Salt Brine Blending to Optimize Deicing and Anti-Icing Performance*. Minnesota State University. DOT Technical report MN/RC 2012-20. Mankato, Minnesota, USA. 2012.
- (7) Bytnar S.C. De-icing composition and method. U.S Patent nr 7,563,386. 2009.
- (8) Alger, R. Haase, J. *Analysis of the Benefits of Bulk Pre-wetting Solid NaCl with Several Different Liquids*. DOT Technical report RC-1473. Michigan Tech University. Houghton, Michigan, USA. 2006
- (9) Koefod, S. Mackenzie, R. Adkins, J. Effect of Prewetting Brines on the Ice-Melting Rate of Salt at Very Cold Temperatures. In: *Transportation Research Record: Journal of the Transportation Research Board, Volume 2482*, 2015, pp 67-73.
- (10) Talor, P. Kasthurirangan, G. Verkade, J.G. Kuldeep, W. Sunghwan, K. *Development of an Improved Agricultural-Based Deicing Product*. InTrans Project report 09-310. Iowa State University, Institute of Transportation. Iowa, USA. 2010.
- (11) Chappelow, C.C., McElroy, D.A., Blackburn, R.R., Darwin, D., Noyelles, F.G., and Locke Carl E. *Handbook of Test Methods for Evaluating Chemical Deicers, SHRP-H-332nd ed*. Strategic Highway Research Program. National Research Council, Washington DC. 1992
- (12) Nilssen, K., Klein-Paste, A., and Wählin, J. Accuracy of Ice Melting Capacity Tests: Review of Melting Data for Sodium Chloride. In *Transportation Research Record: Journal of the Transportation Research Board, No. 2551*, Transportation Research Board of National Academies, Washington, D.C, 2016, pp. 1–19.

- (13) Koefod, S. *Journal of Transportation Research Record*. 2016
- (14) Koefod, S. *Eutectic Depressants. Relationship of eutectic, freezing point, and ice melting capacity in liquid deicers*. Transportation research circular. 4th National Conference on Surface Transportation Weather: Improving Transportation through Weather Information. Indianapolis, Indiana, USA. June 2008, pp 73-84
- (15) Danilov, V. P. Frolova, E. A. Kondakov, D. F. Avdyushkina, L. I. Orlava, V. T. Low-temperature anti-icing reagents in the $\text{Ca}(\text{NO}_3)_2\text{-Mg}(\text{NO}_3)_2\text{-CO}(\text{NH}_2)_2\text{-H}_2\text{O}$ system and their properties, *In: Theoretical Foundations of Chemical Engineering Volume 45*, No 5, 2011, pp 697-701.
- (16) Danilov, V. P. Frolova, E. A. Kondakov, D. F. Avdyushkina, L. I. Bykov, A.V. Orlava, V. T. Low-temperature anti-icing reagents in aqueous salt systems containing acetates and formiates, *In: Theoretical Foundations of Chemical Engineering, Volume 46*, No 5, 2012, pp 528-535.
- (17) Nilssen, K., Klein-Paste, A., Wählin, J. and Delapaz, M. Use of Calorimetry to Measure Ice-Melting Capacity. *In Transportation Research Record: Journal of the Transportation Research Board*, No. xxxx, Washington, D.C, 2017, pp. x-x.
- (18) Melinder, Å. *Thermophysical Properties of Aqueous Solutions Used as Secondary Working Fluids*. PhD thesis. ISBN 978-91-7178-707-1. Royal Institute of Technology, KTH. Department of Energy Technology. Stockholm, Sweden. 2007.
- (19) Ketcham, S., L. Minsk, R. Blackburn, and E. Fleege. *Manual of Practice an Effective Anti-Icing Program - A Guide for Highway Winter Maintenance Personnel*. Publication FHWA-RD-96-202. U.S Department of Transportation, 1996.
- (20) Young, F.E., Jones, F.T. Sucrose Hydrates. The Sucrose–Water Phase Diagram. *In: The journal of physical chemistry*. California, 1949, 53 (9), pp 1334–1350.
- (21) Koefod, S., R. Mackenize, and J. Adkins. *Effect of pre-wetting Brines on the Ice Melting Rate of Salt at Very Cold Temperatures*. Report number 15-4355. *In: Transportation Research board 94th Annual Meeting*, Washington D.C, 2015.
- (22) Koefod, S., J. Adkins, and M.R. Akin. *Alternative Approaches to Measuring Deicer Ice-Melting Capacity: Optimization of Test Accuracy and Precision*. *In: Transportation Research E-Circular*. Presented at the International Conference on Winter Maintenance and Surface Transportation Weather, Iowa United States, 2012, pp. 432-442
- (23) Thomsen, K. *Aqueous Electrolytes Model Parameters and Process Simulation*. PhD theses. Technical University of Denmark, Center for Energy Resources Engineering. Lyngby,