# Snow and Ice Treatment Products Evaluation

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The Missouri Department of Transportation (MoDOT) Maintenance Division uses different materials to reduce the negative impact of snow and ice on the friction performance of state travelways. These materials include abrasives (sand or cinders), rock salt (sodium chloride), and other chemical deicers that emerged in recent years. The use of chemicals and abrasives (in addition to plowing) for highway winter maintenance operations is an essential strategy for ensuring a reasonably high level of service, yet the performance of such materials has to be balanced with their cost effectiveness, and potentially detrimental effects on transportation infrastructure, the natural environment, and motor vehicles. Currently, there are considerable data gaps when it comes to the quantification of their performance and impacts and comprehensive assessment for decision making. This study conducted a comprehensive and quantitative evaluation of snow and ice control chemicals currently used by various MoDOT districts for highway maintenance operations based on laboratory tests. An evaluation matrix to assess the cost-effectiveness and potential impacts under a holistic and multi-criteria framework was developed. The results indicated that products #5 ("Clear Lane" Produce), #7 (Calcium Chloride (liquid) Treated Rock Salt) and #3 ("Snow Slicer" Treated Rock Salt) scored above 60 out of 100. Product #5 with a score of 67 is the first priority, then product #7 with a score of 66 is the second priority, and finally product #3 with a score of 64 is the third priority.

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# SNOW AND ICE TREATMENT PRODUCTS EVALUATION

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# ABSTRACT

The Missouri Department of Transportation (MoDOT) Maintenance Division uses different materials to reduce the negative impact of snow and ice on the friction performance of state travel ways. These materials include abrasives (sand or cinders), rock salt (sodium chloride), and other chemical deicers that emerged in recent years. The use of chemicals and abrasives (in addition to plowing) for highway winter maintenance operations is an essential strategy for ensuring a reasonably high level of service, yet the performance of such materials has to be balanced with their cost effectiveness, and potentially detrimental effects on transportation infrastructure, the natural environment, and motor vehicles. Currently, there are considerable data gaps when it comes to the quantification of their performance and impacts and comprehensive assessment for decision making. This study conducted a comprehensive and quantitative evaluation of snow and ice control chemicals currently used by various MoDOT districts for highway maintenance operations based on laboratory tests. The infrastructure impacts of products on pavement structures, and performance characteristics were assessed. An evaluation matrix to assess the cost-effectiveness and potential impacts under a holistic and multi-criteria framework was developed. The results indicated that products #5 (“Clear Lane” Produce), #7 (Calcium Chloride (liquid) Treated Rock Salt) and #3 (“Snow Slicer” Treated Rock Salt) scored above 60 out of 100. Product #5 with a score of 67 is the first priority, then product #7 with a score of 66 is the second priority, and finally product #3 with a score of 64 is the third priority.

# EXECUTIVE SUMMARY

The Missouri Department of Transportation (MoDOT) Maintenance Division uses different materials to reduce the negative impact of snow and ice on the friction performance of state travelways. These materials include abrasives (sand or cinders), rock salt (sodium chloride), and other chemical deicers that emerged in recent years. The use of chemicals and abrasives (in addition to plowing) for highway winter maintenance operations is an essential strategy for ensuring a reasonably high level of service, yet the performance of such materials has to be balanced with their cost effectiveness, and potentially detrimental effects on transportation infrastructure, the natural environment, and motor vehicles. Currently, there are considerable data gaps regarding the quantification of their performance and impacts and comprehensive assessment for decision making. Therefore, the objectives of this study are to: (1) evaluate the effective operational temperature ranges of designated products; (2) evaluate any infrastructure impacts of products on bridges and pavement structures; (3) evaluate the performance characteristics of the products; (4) evaluate cost effectiveness of various solid de-icing agents and liquid anti-icing and de-icing agents currently used by or proposed by MoDOT; and (5) provide a final report detailing testing and analysis results, findings of the evaluation, and recommendations for best practices.

Nine deicer products were collected in this study, including (1) rock salt – untreated; (2) rock salt – brine treated; (3) “Snow Slicer” treated rock salt; (4) “Ice Ban” treated rock salt; (5) “Clear Lane” product; (6) calcium chloride (flake/pellet) treated rock salt; (7) calcium chloride (liquid) treated rock salt; (8) beet juice treated rock salt; and (9) “Top Film” treated rock salt. Laboratorial tests were conducted to evaluate the performance, effectiveness, and infrastructure impacts of the collected deicer products. The ice-melting test was conducted to quantify the performance characteristics of deicers as a function of time, by measuring the amount of ice melted by each deicer over time. The thermal properties of deicers were quantified by measuring their characteristic temperature (Tc), and the enthalpy of fusion (H, integrated surface area of the peak). Eutectic phase diagrams were obtained to quantify the performance characteristics of deicers as a function of deicer concentration; the lower the freezing point temperature, the more thermodynamically powerful a deicer is. Snow–pavement bond and friction tests were carried out to quantify the performance characteristics of deicers for anti-icing strategy, i.e., prevention of the bond of compacted snow to the pavement (to facilitate subsequent mechanical removal). The corrosion rates of the carbon steel samples in diluted deicer solutions were measured to quantify the corrosive effect of deicers to carbon steel. Biological oxygen demand (BOD) measurements were conducted to quantify the environmental effects of deicers to species in soil and water bodies. Freeze-thaw test of concrete in the presence of deicer was conducted to quantify the negative effects of deicers to concrete. Low-temperature behavior of asphalt binder and mixture affected by deicer was quantified by asphalt binder bending beam rheometer (BBR) and asphalt mixture indirect tensile (IDT) tests.

When commercial deicer “Ice Ban” is added to rock salt, the lowest “characteristic temperature” can be achieved for this type of deicer, which would ultimately help the most in preventing black ice formation on roads. The treatment of rock salt with Ice Ban may also help the most in anti-icing, among all the other types on treated salts. The products #1 and #4 have the lowest BOD with values below 1 mg/L and product #9 has the highest BOD 49.53 mg/L. The lowest freezing

point is related to Snow Slicer Treated Rock Salt (product #3) at 3 wt.% (-2.03 °C), 10 wt.% (-7.25 °C) and 23 wt.% (-23.14 °C). However, rock salt (product #1) has the lowest freezing point at 5 wt.% (-3.44 °C), 10 wt.% (-7.25 °C) and 15 wt.% (-11.91 °C). On the other hand, Ice Ban Treated Rock Salt (product #4) has the lowest freezing point at 20 wt.% (-17.88 °C). It should be noted that in all the studied concentrations, deicers other than the control (NaCl reagent) have the lowest freezing point temperature. There were statistically significant differences between the ice bond strength onto the surface of pavements A and C. The differences between the ice/pavement bond strengths on the deiced pavements were notably higher than those between the control groups A and C. In addition, the products #7, #8, #9 (which are calcium chloride (liquid) treated rock salt, beet juice treated rock salt, and “Top Film” treated rock salt, respectively) showed better ice melting capacities than the other evaluated products. The product #6 which is the calcium chloride (flake/pellet) treated rock salt showed the lowest ice melting capacity. The product #7 (calcium chloride (liquid) treated rock salt) showed the best ice melting capacity among all the studied products.

The asphalt binder BBR test results indicated that some of the deicer products (#6 and #8) showed degrading effects on the low-temperature performance of asphalt binder, indicating by the increased stiffness and lowered m-value. However, the asphalt binder treated by the product #7 (calcium chloride (liquid) treated rock salt) showed improved low-temperature performance with low stiffness and high m-value. Although the asphalt binder treated by the product #3 (“Snow Slicer” treated rock salt) had higher stiffness than the controlled binder, it had higher m-value. The IDT creep compliance and strength of asphalt mixture results indicated products #2 (Rock salt – brine treated) and #9 (“Top Film” treated rock salt) had insignificant effects on the creep compliance of asphalt mixture, regardless of testing temperatures. The products #1, #2, #4, and #6 degraded the IDT strength of asphalt mixture at -10°C. The products #5, #7, #8, and #9 showed insignificant effects on the IDT strength of asphalt mixture. The product #3 (“Snow Slicer” treated rock salt) slightly increased the IDT strength as compared to the wet control sample.

All concrete beams with the presence of deicer products had durability factor (DF) values higher than 90% after freeze thaw cycles, which indicated that the concrete beams (with the selected typical Missouri mix design) had excellent durability even with the presence of deicer products. No significant difference (on DF) could be found between the concrete beams with the presence of water and deicer products. The deicer products had different scaling effects on concrete beams. The product #7 had little scaling effect on the concrete beams. The concrete beams with the presence of other deicer products (#2-#9) showed higher mass loss values (more significant scaling effect) than that of those with the presence of water. The concrete beams with the presence of product #2 showed the highest mass loss values. The PCM cylinder with the typical Missouri mix design was resistant to F-T damages, even with the presence of deicer solutions. The deicer products (especially product #9) had insignificant effect on the F-T resistance of PCM cylinders.

The single factor ANOVA revealed that there were statistically significant differences across the ice/pavement bond strengths of different deicer products (#1 to #9), given that the p-value of 7.52E-05 was considerably lower than 0.05. The single factor ANOVA revealed that there was no statistically significant difference across the friction coefficients of different Deicer products (#1 to #9). The product # 4 showed least corrosive behavior towards the carbon steel. Brine treated rock salt (product # 2) turned out to be the most corrosive deicer, relative to other chloride salt-based deicers. The single factor ANOVA revealed that there were statistically significant differences between the corrosion rates of steel in the different types of diluted deicer solutions, given that the p-value of 2.3E-06 was considerably lower than 0.05. In other words, a p-value of 0.05 or lower corresponds to a statistically significant difference between the two groups of data (with confidence level of 95% or higher).

In light of the findings from lab testing, the team developed an evaluation matrix to assess the cost-effectiveness and potential impacts (to the infrastructure, motor vehicles, and water bodies) under a holistic and multi-criteria framework. The results indicated that the product # 5 ("Clear Lane" Produce) showed the highest score with a score of 67 out of 100.

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# CHAPTER 1 INTRODUCTION

## 1.1 Problem Statement

The Missouri Department of Transportation (MoDOT) Maintenance Division uses different materials to reduce the negative impact of snow and ice on the friction performance of state travel ways. These materials include abrasives (sand or cinders), rock salt (sodium chloride), and other chemical deicers that emerged in recent years. The use of chemicals and abrasives (in addition to plowing) for highway winter maintenance operations is an essential strategy for ensuring a reasonably high level of service, yet the performance of such materials has to be balanced with their cost effectiveness, and potentially detrimental effects on transportation infrastructure, the natural environment, and motor vehicles. Currently, there are considerable data gaps when it comes to the quantification of their performance and impacts and comprehensive assessment for decision making.

A comprehensive evaluation to understand the performance characteristics and negative impacts of current chemical treatments is critical to effective and responsible winter maintenance operations. The research is urgently needed in light of the increasing reliance on chloride deicers for highway winter operations and the challenge of maintaining a state of good repair with limited bridge and pavement maintenance budgets. The findings from this study will be essential for MoDOT to establish a framework that would enable data-driven decision making, i.e., selecting products for snow and ice control with the right balance. The ultimate goal is to meet its multiple goals of winter road maintenance, including cost effectiveness, safety and mobility, environmental stewardship, and infrastructure preservation.

## 1.2 Background

Chloride-based salts are the most common chemicals used to serve as freezing-point depressants for winter road service applications (Blackburn et al. 2004) such as sodium chloride (NaCl), magnesium chloride ($MgCl_2$), and calcium chloride ($CaCl_2$). They are the most readily available and widely used, in either solid or liquid form (Fay and Shi 2011). They are effective over a wide range of temperatures (Cuelho et al. 2010), and their baseline performance and corrosivity have been reported (Shi et al. 2013). NaCl is the most widely used chemical owing to its abundance and low cost, and in the U.S., approximately 20 million tons of NaCl is used for every typical winter season. However, when air and pavement temperatures are below 10°F, NaCl-based deicers become much less effective and may cause snow to stick to the pavement. At cold temperatures, $MgCl_2$ brines are often used instead of NaCl because they exhibit better ice melting performance. However, recent studies revealed that the damage by $MgCl_2$ deicer may compromise the strengths of concrete without any visible surface distress, thus evading the traditional inspection methods (Xie et al. 2019). According to field studies, $CaCl_2$ is more effective than NaCl owing to its ability to attract moisture and stay on the roads. However, some agencies choose not to use $CaCl_2$ because it does not dry and can cause roads to become slippery (Perchanok et al. 1991). $MgCl_2$ is also hydroscopic and shares the same concern with $CaCl_2$. The chloride salts are persistent in the environment, posing a significant risk to infrastructure (Shi et al. 2010b; Farnam et al. 2015; Dang et al. 2016), motor vehicles (Li et al. 2013; Shi et al. 2013;

Nazari and Shi 2018), and the natural environment over time (Corsi et al. 2015; Pieper et al. 2018). Yet, the use of chloride-based deicers continues to rise.

In recent years, highway agencies have begun to voice a preference for organic salts because they tend to decompose quickly and do not contain chloride (Fay et al. 2008). For example, potassium acetate (KAc), while more expensive than chloride salts, is generally considered non-corrosive to carbon steel and environmentally benign (LaPerriere and Rea 1989; TRB 1991; D'Itri 1992; McFarland and O'Reilly 1992; Bang and Johnston1998). However, recent studies have found that KAc can be corrosive to galvanized steel (Hellstén et al. 2005; Hanslin 2011; Fay and Shi 2011; Harless et al. 2011; Mohiley et al. 2015), increase the emulsification risk of asphalt concrete (Pan et al. 2008), and chemically react with cement paste as well (Xie et al. 2017). In addition, potassium succinate (KSu) was found to perform as a deicer at warmer temperatures than salt brine, and may work well at or above 23°F, with slightly less ice-melting capacity and similar friction performance (Fay and Akin 2018).

Glycols are more expensive than chlorides, but are non-corrosive and more effective at colder temperatures (Kawasaki et al. 1983; Hartwell et al. 1995; EPA 2002; Corsi et al. 2006; Ramakrishna and Viraraghavan 2005). Since the late 1990s bio-based (or agro-based) deicers have been introduced to tackle the negative effects of chloride-based deicers and improve their performance. Some studies used commercial bio-based products with some unknown compounds, and other studies used either raw bio-based materials (e.g., beet juice), waste of industrial processes (e.g., desugared molasses), or commercial organic chemicals. These products are often blended with salt brine to reduce its corrosivity and improve its longevity on the pavement, thus enhancing its performance. By using less chlorides, this reduces the long-term environmental impacts from the cumulative use of chloride-based deicers (Corsi et al. 2012; Muthumani and Shi 2016; Shi et al. 2017; Muthumani et al. 2017; Nazari et al. 2017; Muthumani and Shi 2017).

A framework to enable a holistic approach to procurement or design of liquid deicers was proposed, which incorporated the experimental results of performance and impacts of various liquid deicer formulations to enable a comprehensive assessment of different options under the given set of decision weights (Shi and Akin 2012). In an Idaho Transportation Department (ITD) case study, Shi et al. (2014) further extended this framework for the evaluation of products to chemicals in solid form. In addition, friction coefficient measurements on the pavement before and after the anti-icing and deicing operations were incorporated into the characterization of product performance. The corrosive effects of products to steel rebars were incorporated into the characterization of risks, along with the damaging effects of products to asphalt and concrete pavements. The use of analytical hierarchy process (AHP) for the integration of test results, assisting winter maintenance agencies in the proper selection of a product depending on specific user priorities was also demonstrated (Jungwirth and Shi 2017). They found that all of the naturally sourced deicers featured higher scores than the salt brine control under the investigated conditions and given priorities.

## 1.3 Study Objectives

This study aims to a comprehensive and quantitative evaluation of snow and ice control chemicals (in liquid and solid forms) currently used by various MoDOT districts for highway maintenance operations based on laboratory tests. This includes the following objectives:

- Evaluate the effective operational temperature ranges of designated products;
- Evaluate any infrastructure impacts of products on bridges and pavement structures;
- Evaluate the performance characteristics of the products;
- Evaluate cost effectiveness of various solid de-icing agents and liquid anti-icing and de-icing agents currently used by or proposed by MoDOT; and
- Provide a final report detailing testing and analysis results, findings of the evaluation, and recommendations for best practices.

## 1.4 Research Methods

The objectives of the proposed project were achieved by conducting a number of research tasks as follows.

### *Task 1: Project Management*

The PI consulted with the research manager to establish the Technical Advisory Committee (TAC) of this project. The TAC provided the research team with guidance and technical feedback throughout this study. A kick-off meeting was conducted and involve the team and TAC members. The work plan, scope, and schedule of the project was reviewed in the kick-off meeting; a protocol for regular ongoing communication and coordination with the team was established.

### *Task 2: Obtain and Define Products List*

Under this task, a complete products list of recently employed de-icing/anti-icing products to review and evaluate for the project was finalized.

### *Task 3: Research/Literature Review*

The research team conducted a comprehensive search of documented (past and current) research as well as industry literature on performance and impacts of the chemical deicers identified in Task 2. In addition, the literature review covered any additional deicer “products that are not currently being utilized by MoDOT that should be considered for the product trials”, such as emerging anti-icing or deicing formulations that boost the effectiveness of salt brine while significantly reduce its negative impacts on metals and concretes. Concurrent to the literature review, a survey was designed and distributed to gather input from winter road operations professionals, in an effort to capture the experience of these practitioners in the selection and use of deicer products and fill the knowledge gaps that may not be addressed by a review of literature.

### *Task 4: Product Trials*

In this task, the research team conducted an array of laboratory trials of the proposed products selected by MoDOT in both laboratories of Missouri S&T and Washing State University (WSU). Laboratory data was then processed and analyzed to evaluate their suitability, performance, and impacts on infrastructure. Table 1.1 presents the test matrix.

### *Task 5: Evaluation*

In light of the findings from previous tasks, the team developed an evaluation matrix to assess the cost-effectiveness and potential impacts (to the infrastructure, motor vehicles, and water bodies) under a holistic and multi-criteria framework. By using the evaluation matrix, the “best” deicers for MoDOT districts could be selected.

### *Task 6: Develop Report*

Quarterly reports to timely update project progress were submitted during the above tasks. The research team also developed a final report and executive summary that detail the approaches taken in completing the research and deicer combinations tested, the analyses performed, the results of those analyses (e.g., evaluations of deicers), and recommendations based on the overall evaluation.

*Table 1.1 Test matrix of this project*

| **Test/Measurement** | **Purpose** | **Specification/Device** | **Parameters** |
|---|---|---|---|
| pH measurements | to ensure that the deicer products are not too basic or too acidic | none | pH value |
| Ice-melting test | to quantify the performance characteristics of deicers as a function of time | modified SHRP H-205.1 and H-205.2 | volume of ice melted over time |
| Thermal properties of deicers | to quantify the performance characteristics of deicers | Differential Scanning Calorimetry (DSC) | characteristic temperature (Tc); enthalpy of fusion (H) |
| Eutectic phase diagrams | to quantify the performance characteristics of deicers as a function of deicer concentration | ASTM D1177 | freezing point temperature |
| Snow–pavement bond and friction tests | to quantify the performance characteristics of deicers for anti-icing strategy | trafficking machine | shear force required to plow the snow from the pavement surface |
| Corrosion of deicer to carbon steel | to quantify the corrosive effect of deicers to carbon steel | ASTM C1010 | corrosion rate |
| BOD measurements | to quantify the environmental effects of deicers to species in soil and water bodies | spectrophotometer | chemical oxygen demand; biological oxygen demand |
| Freeze-thaw test of concrete in the presence of deicer | to quantify the negative effects of deicers to concrete | SHRP H205.8 F-T cyclic test for Portland cement mortar (PCM); ASTM C666 for Portland cement concrete (PCC) | length change; mass loss; relative dynamic modulus of elasticity; durability factor |
| Low-temperature behavior of asphalt binder and mixture affected by deicer | to quantify the negative effects of deicers to asphalt binder and mixture | AASHTO T 313 for asphalt binder bending beam rheometer (BBR) test; AASHTO T322-07 for asphalt mixture indirect tension (IDT) test | BBR: stiffness and m-value; IDT: creep compliance and strength |

# CHAPTER 2 LITERATURE REVIEW AND SURVEY

## 2.1 Introduction

Snow and ice control operations are essential to maintain roadway safety, mobility and productivity by providing safe driving surfaces in the winter season. The use of chemicals (deicing/anti-icing materials) and abrasives (in addition to plowing) for snow and ice control operations is an essential strategy for ensuring a reasonably high level of service. The deicing process involves applying deicing chemicals directly on the top of already accumulated snow (or ice) layers in order to destroy their bond with pavement surface and thus facilitate easier removal of these materials from the roads. The anti-icing treatment is defined as a snow and ice control method in which deicing chemicals are applied to the bare pavement surface hours before the expected precipitation to prevent bonding of ice and snow.

Transportation agencies' winter maintenance practices consume a large number of deicing/anti-icing materials. For example, during 2016~2017 winter, the Wisconsin department of transportation (WisDOT) used 526,199 tons of salt, 2,783,720 gallons salt brine for pre-wetting, 1,865,565 gallons salt brine for anti-icing (Xiao et al. 2018). The deicers used in Wisconsin including $CaCl_2$, $MgCl_2$, and some agricultural byproducts such as beet juice and cheese brine. For the winter of 2016-17, salt use was 32% higher than the previous year and sand use was 38% decreased from the average of the five previous winters (Xiao et al. 2018). During 2016~2017 winter, Minnesota DOT (MnDOT) used 46,000 tons of sand, 197,417 tons of salt, and 3.0 million gallons of salt brine to maintain its 30,517 lane miles of roads. The MoDOT Maintenance Division employs various tools to reduce the impact of snow and ice on State travelways. Rock salt (NaCl) has been used for decades as the primary snow and ice treatment solution, as both a spread solid and sprayed brine solution, to treat the pavement before and during inclement weather. In addition, abrasives such as sand or cinders are sometimes utilized in an attempt to provide a level of skid resistance in situations when temperatures render chloride treatment less effective. Both treatments have been deployed on state routes for many a winter, and are considered the standard. In recent years, some of the more urbanized MoDOT Districts have begun efforts to test and assess the other chemical deicers that emerged in recent years, such as $MgCl_2$, $CaCl_2$, and agro-based deicers such as beet juice, for their own winter operations. However, there are considerable data gaps when it comes to the quantification of their performance and impacts and comprehensive assessment for decision making. A comprehensive evaluation to understand the performance characteristics and negative impacts of the chemical treatments is critical to effective and responsible winter maintenance operations. This section presents a comprehensive literature review on performances and impacts of the chemical deicing/anti-icing materials. Concurrent to the literature review, a survey was also designed and distributed to gather input from winter road operations professionals, in an effort to capture the experience of these practitioners in the selection and use of deicer products. The survey questionnaire can be found at: https://wsu.co1.qualtrics.com/jfe/form/SV_9MsDAQpn9VmOMzH.

## 2.2 Literature Review

### 2.2.1. Performances of Commonly Used Deicers

Chloride-based snow and ice control materials are generally produced from the mining of surface or underground deposits, extracting and fractionating well brines, industrial by-products, or through solarizing saltwater. NaCl has a maximum solubility of 26 percent by weight (2.97 lb/gal) in water at a temperature of 32°F. In a laboratory setting, NaCl can lower the freezing point of water to -6°F (Blackburn et al. 2004). In the field, however, the lowest effective temperature at which snow and ice can be removed using NaCl is approximately 15°F (Blackburn et al. 2004). When air and pavement temperatures are below 10°F, NaCl-based deicers become much less effective and may cause snow to stick to the pavement (Fay and Shi 2010).

$CaCl_2$ is primarily produced from natural well brines and as a by-product of the Solvay process. The Solvay process involves combining sodium chloride and calcium carbonate ($CaCO_3$) to produce sodium carbonate ($Na_2CO_3$) and $CaCl_2$ (Blackburn et al. 2004). According to field studies, $CaCl_2$ is more effective than NaCl owing to its ability to attract moisture and stay on the roads. However, some agencies choose not to use $CaCl_2$ because it does not dry and can cause roads to become slippery (Fay and Shi 2010; Xie et al. 2017).

$MgCl_2$ is most commonly obtained through solarizing natural salt brines. $MgCl_2$ is highly soluble in water in both anhydrous and hydrate form and has a maximum solubility of 35.2 percent by weight (4.53 lb/gal) in anhydrous form and 61 percent by weight (13.1 lb/gal) in hydrate form at room temperature (NCHRP 2007). In a laboratory environment, a saturated solution of magnesium chloride has a freezing temperature of approximately -25°F although the lowest effective temperature for magnesium chloride when used as a deicer in the field is approximately -5°F (Blackburn et al. 2004). $MgCl_2$ brines are often used because they exhibit good ice melting performance. However, recent studies revealed that the damage by $MgCl_2$ deicer may compromise the strengths of concrete without any visible surface distress, thus evading the traditional inspection methods (Xie et al. 2019).

The performance of a snow and ice control chemical is measured by its ability to melt the ice, undercut and break the bond between the ice and the pavement, or prevent the ice–pavement bond from forming (Fay and Shi 2010; Pan et al. 2008; Xie et al. 2017). The effectiveness of each chemical can be evaluated by its eutectic temperature. Table 2.1 lists the general properties for chloride-based snow and ice control chemicals. The optimum eutectic temperature for a given product is the lowest temperature at which a product will freeze when at the optimum ratio of chemical to water.

***Table 2.1 General properties of chloride-based salts (Olek et al. 2013)***

| **Chemical** | **Eutectic Temperature °F (°C)** | **Eutectic Concentration %** | **Lowest Practical Melting Temperature °F (°C)** |
|---|---|---|---|
| NaCl | -6 (-21) | 23.3 | 21 (-6) |
| $CaCl_2$ | -60 (-51) | 29.8 | -25 (-32) |
| $MgCl_2$ | -28 (-33) | 21.6 | 5 (-15) |

Nixon et al. (2007) evaluated four tests (specific gravity, viscosity, ice melting capacity, and freeze point determination) to ensure deicer composition and performance. The results showed that these simple tests can be performed on every load of product delivered so agencies can have confidence in the performance of the ice-control products in three areas: temperature related performance, product consistency, and negative side effects (such as corrosion of vehicles and damage to concrete). The ice-melting capacity of deicers is usually measured by the SHRP Ice Melting Test (H-205.1 and H-205.2). Studies (Nixon et al. 2005; Alger and Haase 2006; Shi et al. 2009a; Shi and Akin 2012) indicated that $CaCl_2$ is a more effective chemical deicer than other products at lower temperatures because of its ability to attract moisture and stay on the road longer. Experience and lab tests showed that $MgCl_2$ melts ice more quickly and at colder temperatures than NaCl. Furthermore, less $MgCl_2$ is required than NaCl or $CaCl_2$ (Williams 2001). The Montana DOT found that $MgCl_2$ will keep 30 percent more water from freezing at -0.4°F (-18°C) than $CaCl_2$ (Williams 2001). Fay et al. (2008) performed lab tests on the ice melting capacity of various freeze-depressant chemicals and found that calcium magnesium acetate (CMA) was the only chemical still melting after 30 minutes. The field tests on asphalt and concrete pavements using NaCl, $CaCl_2$, $MgCl_2$, potassium acetate ($CH_3CO_2K$, abbreviated as KAc in this report) and an agro-based product showed that the NaCl and KAc deicers are most effective at reducing the bond strength between the pavement and snow (Cuelho et al. 2010). The $MgCl_2$ and the agro-based products are less effective, and the $CaCl_2$ deicer is the least effective. The highest bond strength between the snow and pavement was found on the test sections treated with $CaCl_2$ (Cuelho et al. 2010).

According to a survey by Fay et al. (2008), the agro-based deicers were one of the "most advantageous" snow and ice control chemical and performed well at low temperatures. Lab tests found agro-based products effective at 23°F (-5°C) (Fay et al. 2008). Another study indicated that such products melt snow faster at lower temperatures and provide more consistent, longer-lasting residuals than $MgCl_2$ (Fischel 2001). Fu et al. (2012) compared the performance of regular salt brine with two beet juice–based organic deicers. A significant increase in performance of organic materials for pre-wetting under low temperatures was not observed, and the two beet juice–based organic deicers showed similar performance in terms of pre-wetting.

Fay and Shi (2010) evaluated the ice melting, ice penetration, and ice undercutting capabilities of the seven deicers, including CMA, two types of NaCl deicers, $MgCl_2$, a sodium acetate/formate blend, KAc, and an agro-based deicer. They found that the KAc-based deicer had the coldest effective temperature, followed by the $MgCl_2$-based deicer, and the agro-based deicer led to the lowest friction coefficients on both the ice and the deiced concrete, whereas the NaCl-based solid deicer had the greatest variance of friction coefficients on the ice. The ice-melting capacity test by Xie et al. (2017) also showed that KAc had a higher deicing capability than NaCl.

A study for MnDOT (Druschel 2012) evaluated the ice melt capacity and field performance factors (i.e., deicers' bounce, penetration, undercut, and grain size) of 24 deicers with the main components consisting of NaCl, $MgCl_2$, $CaCl_2$, KAc, sodium acetate, sugar beet, and corn salt. The results indicated that the units of ice melt capacity depended upon whether the deicer is applied as a solid (units of mL brine created/g of deicer applied) or liquid (units of mL brine created/mL of deicer brine applied) and were generally found to be strongly associated with temperature. In terms of the factors that influence the filed performance of the deicers, the results revealed that only grain size was found to be statistically significant in providing performance differences, among these evaluated four factors.

### 2.2.2 Deicers' Impacts on Pavement Infrastructure

#### ***Concrete Pavements***

Both chloride-based and non-chloride-based deicers may pose detrimental effects on concrete infrastructure and thus reduce concrete integrity (as indicated by expansion, mass change and loss in the dynamic modulus of elasticity) and strength. Such risks of deicers on the durability of Portland Cement Concrete (PCC) structures and pavements exist through three main pathways (Shi et al. 2010a, b; Olek et al. 2013; Xie et al. 2017): 1) physical deterioration of the concrete through such effects as salt scaling; 2) chemical reactions between deicers and cement paste; and 3) deicers aggravating aggregate-cement reactions.

The process of physical deterioration of concrete initiates when saturated concrete freezes and, as a result, is subjected to internal stress and volumetric expansions. The repeated freezing and thawing cycles can subject concrete to scaling. Research by Lee et al. (2000) used concrete pavement cores collected from the field and immersed them in three types of chlorides, including NaCl and CMA with different molar ratios of Ca- and Mg-acetate. After the samples were exposed to wet/dry and freeze/thaw experiments, of the chemicals investigated, the NaCl samples were the least deleterious to the concrete samples, with only slightly more deleterious effects than water on the concrete. Shi et al. (2010a) investigated the effect of different diluted deicers, such as NaCl, K-formate, NaCl-based deicer, K-acetate-based deicer, Na-acetate/Na-formate blend deicer, CMA deicer, and $MgCl_2$ liquid deicer, on the deterioration of PCC samples which were exposed to freeze-thaw cycles while being submerged in dilutions of the different deicers. The results revealed that the CMA solid deicer and the $MgCl_2$ liquid deicer were benign to the concrete durability, whereas K-formate and the Na-acetate/Na-formate blend deicer showed moderate amount of weight loss and noticeable deterioration of the concrete. NaCl, the NaCl-based deicer, and the K-acetate-based deicer were the most deleterious to the PCC samples. The SHRP freeze-thaw test conducted by Fay and Shi (2010) also indicated that the $MgCl_2$-based product and CMA based deicers had the least impact on PCC.

Dang et al. (2016) investigated how a film forming sealer applied to a concrete surface would protect the concrete structure from deicer scaling. When the film forming sealer applied to concrete samples exposed to a 2.5% $MgCl_2$ solution, there was no substantial change in scaling, but the splitting tensile strength was reduced. Xie et al. (2019) conducted laboratory investigations, including the exposure of concrete samples to freeze/thaw and wet/dry samples, to understand the effect of using $MgCl_2$ deicers on the concrete structure in comparison to NaCl deicers. The exposure of samples to $MgCl_2$ was found to significantly reduce splitting tensile strength and reduce micro-hardness. The authors noted that visual inspections of concretes exposed to $MgCl_2$ may not be sufficient for assessing a concrete structure. Lead by Iowa DOT, a pool fund study was conducted to evaluate deicer scaling resistance of concrete pavements, bridge decks and other structures containing slag (Schlorholtz and Hooton 2008). The results indicated that only cores extracted from one site exhibited scaling mass loss values that exceeded 1.5 lbs/yd$^2$, which implied the $CaCl_2$ solution showed little effect on the deicer scaling resistance of concrete pavements, bridge decks and other structures containing slag evaluated in the study.

Chemical attack is caused by reactions with cement hydrates and results in the deterioration of the matrix (Shi et al. 2010a). It has been suggested that repetition of the application of deicers combined with freezing/thawing cycles is more damaging to PCC than any of these actions separately (Shi et al. 2010a; Olek et al. 2013). According to Olek et al. (2013), both, an increase in the porosity of exposed surfaces and the increase in permeability lead to an increase in the amount of water available and thus increased probability of ice formation, which is usually caused by the dissolution of calcium hydroxide ($Ca(OH)_2$). Research (Shi et al. 2010a; Olek et al. 2013) indicated NaCl is not harmful to plain concrete unless reactive aggregate is present. However, if reactive aggregate is present, the reaction between NaCl and PCC is a process of dissolution of $Ca(OH)_2$, which leads to an increase in porosity near the exposed surface. Farnam et al. (2015) investigated the effects of $CaCl_2$-based deicing salts on concrete pavements. These effects include a chemical reaction between the calcium hydroxide, $CaCl_2$ and water forming calcium oxychloride. When calcium oxychloride is formed, it expands, which can then cause durability issues in concrete including damage to the concrete when exposed to temperatures above freezing and introduction of fluids entering concrete (Farnam et al. 2015). Similar conclusions were reached by Olek et al. (2013) that indicated that $CaCl_2$ reacts with $Ca(OH)_2$ to form hydrated calcium oxychloride ($3CaO.CaCl_2.15H_2O$). Numerous research studies have shown that $MgCl_2$, when used as a deicer, causes much more severe deterioration to concrete than NaCl or $CaCl_2$. This is due to the reaction between $Mg^{2+}$ and the hydrated products in cement paste (Lee et al. 2000; Shi et al. 2010a; Olek et al. 2013; Xie et al. 2017). Lee et al. (2000) indicated that the $MgCl_2$ can cause significant crumbling after freeze/thaw and wet/dry cycles. This phenomenon was partially because of the conversion of calcium silica hydrates (CSH), a strength-contributing component of cement, to the non-cementitious magnesium silicate hydrate (MSH) gel. Muthumani et al. (2017) investigated the performance of four agro-based deicers and two complex chlorides/mineral (CCM) based deicers. Investigations using the gravimetric method found that CCM-based deicers had lower corrosivity to carbon steel over that of NaCl while the agro-based deicers reduced the corrosivity further.

Alkali silica reaction (ASR) is a deleterious process caused by the chemical reaction between available alkalis from the cement paste and reactive silica in the aggregate of PCC. Studies indicated that NaCl can initiate and/or accelerate ASR by supplying additional alkalis to concrete (Lee et al. 2000; Shi et al. 2010a; Farnam et al. 2015). $CaCl_2$ and $MgCl_2$ do not have as obvious an effect on ASR as NaCl (Shi et al. 2010a). As the effect $CaCl_2$ has on the aggregates within concrete was investigated, it was found that when coarse aggregate consisted of dolomite, concrete deteriorates due to the dolomite reacting with the magnesium to produce brucite and additional MSH (Lee et al. 2000). Xie et al (2017) investigated the effects of NaCl and KAc deicers on properties of concrete samples obtained from the field bridge deck coring and those prepared in the laboratory. The mechanical properties, including splitting tensile strength, compressive strength, and microhardness of were tested to evaluate the deterioration of concrete samples after exposure to KAc and NaCl. The results revealed that KAc deicer resulted in more damage to the concrete over that of NaCl in terms of compressive strength, splitting tensile strength, and microhardness.

A study recently completed by Purdue University and Indiana DOT investigated how mixtures of deicers can damage the joints in concrete pavement (Suraneni et al. 2016). The investigation was completed by using low temperature differential scanning calorimetry (LTDSC) to detect a reaction between the deicer and the cement matrix and investigated the potentially sources of calcium oxychloride from the blended salt deicers. The results from this study showed deterioration at the joints from increased saturation from deicers and a chemical reaction between deicing salt and the cement matrix. Also, there was a direct relationship between the increase of calcium hydroxide in the paste and increase of calcium oxychloride formation. Another study in Indiana (Olek et al. 2013) investigated the interaction between concrete and deicers such as NaCl, $CaCl_2$, $MgCl_2$, and Ice Ban. The results indicated that NaCl had the least impact on concrete comparing to other deicer chemicals. Fly ash modified concrete performed better than plain concrete when exposed to deicing chemicals.

### ***Asphalt Pavements***

The effects of deicer application to asphalt pavements is not as severe as its application on PCC, but when adding deicing salts a loss of skid resistance is usually noted. This is due in part to the high chemical resistance of asphalt binders when exposed to chloride deicers (Shi et al., 2009a). To improve the degradation of asphalt pavements when exposed to deicers it is recommended to have a low void content, use aggregates with a high pH, and use harder bitumen (Shi et al., 2009a). Ozgan et al. (2013) performed the Marshall Stability test on asphalt samples submerged in plain water, as well as three different NaCl dilutions and one $CaCl_2$ dilution. Interestingly, the largest reduction in the Marshall Stability was of the samples in the plain water at 15%.

Goh et al. (2011) exposed asphalt samples containing nanoclay and/or carbon microfibers to deicers including NaCl, $MgCl_2$, and $CaCl_2$ for seven freeze-thaw cycles. Overall it was found the addition of the nanoclay and carbon microfibers improved the asphalt samples susceptibility to degradation from deicer exposure. Hassan et al. (2002) investigated the effects of various deicers including KAc, urea, and sodium formate, as well as NaCl, on the durability of aggregates and asphalt during freeze-thaw cycles when submerged in a solution of different deicers was determined based on mass loss. Of the aggregates investigated deicers had a larger negative impact on quartzite aggregate over that of limestone. Urea was found to cause the most damage to samples submerged in urea dilutions and exposed to freeze-thaw cycles while the damage from placing samples in a dilution of NaCl, KAc or sodium formate, provided results similar to those if samples were submerged in water.

Martinez and Poecker (2006) investigated the effects of applying $MgCl_2$ liquid deicer on skid resistance of open-graded pavements. Four sections on two different highways in Oregon were selected to be skid tested under three conditions: 1) No deicer application; 2) after a deicer application rate of 15 gallons/lane mile; and 3) after a deicer application rate of 30 gallons/lane mile. It was found that the application of deicer on either type of pavement at either application rate appeared to have little if any effect on the Friction Number (FN). However, the authors did not come up a clear conclusion about the effect of $MgCl_2$ liquid deicer on skid resistance of open-graded pavements because of the difficulty in controlling variables.

Hossain et al. (2015) investigated the performance of different salts when applied to Canadian asphalt pavements. Effectiveness was measured via the change in snow cover with time and the bare pavement regain time. Deicers investigated included rock salt and other alternative salts such as blue salt (NaCl treated with $MgCl_2$), Slicer (78% NaCl, 9% $MgCl_2$, 2%-3% proprietary ingredients), green salt (treated sodium formate), and jet blue (treated NaCl). It was found that the alternative salts such as blue salt, slicer, green salt, and Jet blue outperformed the rock salt and that lower application rates of the alternatives performed the same as higher rates of rock salt.

Hosseini et al. (2016) investigated how using bio-based deicers affects friction on asphalt pavements during the wintertime in Canada. Bio-based deicers investigated included brine, Snowmelt, Fusion, and Caliber M100. The use of the bio-based deicers was found to improve pavement friction by 10-40% in comparison to no deicer application.

### 2.2.3. Deicers' Impacts on Environment

There are growing concerns over the impact of deicers on the environment (Shi et al. 2009 a, b, c). Abundant evidence demonstrates that chloride salts accumulate in aquatic systems (Mason et al. 1999; Kaushall et al. 2005), cause damage to terrestrial vegetation (Bryson and Barker 2002), and alter the composition of plant communities (Miklovic and Galatowitsch 2005). Furthermore, the use of chloride salts may liberate mercury and other heavy metals from lake sediments or soil through ion exchange processes (Fay and Shi 2012).

The effects of deicers on the quality of groundwater in northwestern Indiana was investigated by Watson et al. (2002). The areas with large quantities of applied deicers; high snowfall rates; presence of a high-traffic highway; a known groundwater-flow direction; and minimal potential for other sources of Na and Cl to complicate source interpretation; a homogeneous, permeable, and unconfined aquifer; a shallow water table was selected to study. The results indicated that the Na and Cl was accumulated in the aquifer throughout the year, and the concentrations reached highest during spring and summer times. The quality of water in New York area was also evaluated by Albright (2005). High chloride concentrations were found in many areas such as streams and lakes. The periodic monitor results indicated that the annularly incensement in chloride concentration in Otsego Lake is about 1.0 mg/L. The underground water neat the lake showed highest chloride concentration with a number of 40 to 60 mg/L.

Pieper et al. (2018) found that using road deicers poses a potential threat to drinking water safety due to corrosion of potable water infrastructure. Investigations in the chloride concentrations in groundwater and the effect on private wells was conducted in New York. Private wells located down gradient of a storage building for road salts had the highest chloride levels. 70% of those surveyed had stopped drinking their well water. Increasing the chloride content in the water, during lab investigations, was found to increase metal leaching and cause a thinning of the pipe wall. Their analysis estimated almost a quarter of private well users in New York (24%) could be affected by the storage facilities housing the salt deicers.

Langen et al. (2006) investigated the effect of sodium chloride deicers on the environment at the Cascade Lakes and Chapel Road in New York. Investigations found that 168 and 226 US tons (152 and 205 metric tons) of sodium chloride deicers were deposited into the upper and lower Cascade Lakes, respectively. This has resulted in the soil being low in nutrients and likely to erode. Within five years there was a 250% increase in chloride concentration within the lakes studied, due to the increase in chloride deicer applications. Godwin et al. (2003) studied the change in the ionic composition and solute flux of water from a New York State basin was investigated from the 1950s to the late 1990s. Over that time there was a 140% and 243% increase in sodium and chloride ions, respectively, primarily due to the application of road salts.

Langen et al. (2006) also indicated that due to the use of sodium chloride deicers and sand during the winter the soil nearby the roads has been physically and chemically altered. The effects of the deicers on the salt concentrations in roadside soils was investigated by Cunningham et al. (2008). Their results showed that the magnesium cation was the most abundant cation in soils adjacent to roadways which were frequently deicers treated. They also found that the effect of sodium cation from the deicer on water is more significant than that on soil.

Czerniawska-Kusza et al. (2004) evaluated the effect of deicers on the urban soil properties and the health of roadside trees in the Opole region. Their results indicated that content of $Na^+$ and $Cl^-$ of the soil nearby the roadway increased significantly after deicing treatments. They reported that the protozoa was significantly affected when the $Na^+$ and $Cl^-$ concentrations exceeded 26.0 mg /100 g and 12.0 mg /100 g, respectively. The chlorosis and necrosis of the edge of leaf blades showed up in plants when the $Na^+$ and $Cl^-$ concentrations exceeded 13.2 mg /100 g and 3.9 mg /100 g. The effects of deicers on the vegetation along a mountain pass in the Adirondack Park, New York in which the salt application rate ranged from 50 to 140 tonnes per centerline-km in the last decades was investigated by Willmert et al. (2018). The results indicated that Roadside soils and vegetation were significantly impacted by salt deposition compared to soils and vegetation 30 to 150 m from the road. The number of the paper birch trees (Betula papyrifera) and other woody vegetation along the roadside decreased significantly in last decades, which suggested that survival and recruitment of paper birch trees was impacted by degradation of soil fertility and deposition and aerosolization of road salt.

Cui et al. (2015) found that chloride-based deicers have various negative environmental impacts when applied on roads. These include negative effects to soil located near the road, nearby water, aquatic life, and nearby vegetation. When implementing a water monitoring program to monitor the effects of deicing salts have on nearby water bodies, soils, and vegetation, it is important to keep records of the water temperature, flow rate, pH, water hardness, sulfates, sample timing, and monitoring the ecological health of the water system.

Maintenance yards have a high likelihood of causing a high rate of chloride solution runoff, and are a potential point source of pollution (Nazari et al. 2015). Stormwater runoff from roads where deicers have been applied have a lower likelihood of being a point source of pollution due to the dilution of rainwater, but may be a non-point source pollution. Chloride concentrations of water systems near roads are usually highest during annual spring snowmelt. Mapping the road density, sensitive areas, and precipitation rates can help management determine areas where deicer application should be limited or alternatives should be investigated. The review by Fay and Shi (2012) indicated that one concern over using agro-based deicers would be their use may lead to a decrease in the dissolved oxygen content of aquatic ecosystems. The use of deicers containing particular cations, including calcium and magnesium, can also lead to an increase in heavy metal content in aggregate near roadways.

Investigations into the effect of various deicers, including urea, sodium chloride, magnesium chloride, potassium acetate, calcium chloride, and CMA, on larval wood frogs was investigated by Harless et al. (2011). Mortality rates of larvae were lowest in larvae exposed to urea, sodium chloride, and magnesium chloride, whereas the highest mortality rates were found in larvae exposed to CMA, potassium acetate and calcium chloride.

Mohiley et al. (2015) investigated the performance of aircraft deicing fluids, in comparison to wastewater, was determined using two bio-tests. Aircraft deicing fluids investigated included sodium formate, and a deicer named A-3, which consists of 40% glycerol along with sodium acetate, potassium acetate, and additional unknown ingredients. The results found that the aquatic plants and marine bacteria had a higher sensitivity to the aircraft deicing fluids than the wastewater.

### 2.2.4. Decision Making of Deicers Selection

Snow and ice control chemicals (in liquid and solid forms) have been used (or considered) by various MoDOT districts, understanding the performance characteristics and negative impacts of deicers is critical to effective and responsible winter maintenance operations. When choosing materials for snow and ice treatment several factors need to be considered, such as safety, mobility, environmental stewardship, infrastructure preservation, and economics (Olek et al. 2013; Shi et al. 2013). Shi and Akin (2012) demonstrated a framework to enable a holistic approach to procurement or design of liquid deicers, which incorporated the experimental results of performance and impacts of various liquid deicer formulations to enable a comprehensive assessment of different options under the given set of decision weights.

In an Idaho Transportation Department (ITD) case study, Shi et al. (2014) further extended the framework developed in Shi and Akin (2012) for the evaluation of products to chemicals in solid form. In addition, friction coefficient measurements on the pavement before and after the anti-icing and deicing operations were incorporated into the characterization of product performance. The corrosive effects of products to steel rebars were incorporated into the characterization of risks, along with the damaging effects of products to asphalt and concrete pavements. In addition, Jungwirth and Shi (2017) demonstrated the use of analytical hierarchy process (AHP) for the integration of test results, assisting winter maintenance agencies in the proper selection of a product depending on specific user priorities. The AHP was generally used to create a matrix to determine a scoring system based on prioritizing the test results. An example of AHP results is provided in Table 2 (Shi and Jungwirth 2018).

***Table 2.2 Normalized assessment of deicers (and sand) by the selected four dimensions and the composite indices calculated from them (Shi and Jungwirth 2018). For each index, the normalization process makes the best 100 and the worst 0.***

| Product of Interest | Direct Cost Index | Performance Index | Infrastructure/ Vehicle Index | Environmental Index | Composite Index |
|---|---|---|---|---|---|
| Solid Salt | 100 | 51 | 9 | 44 | 41 |
| Salt Brine | 100 | 66 | 51 | 68 | 65 |
| Product I | 46 | 67 | 60 | 50 | 60 |
| Product B | 27 | 73 | 65 | 50 | 63 |
| I20-SB80 | 89 | 64 | 40 | 49 | 57 |
| B20-SB80 | 85 | 66 | 49 | 49 | 60 |
| Product A | 60 | 64 | 61 | 68 | 63 |
| Product C | 33 | 68 | 86 | 39 | 67 |
| Product F | 0 | 67 | 80 | 34 | 61 |
| Sand | 27 | 15 | 68 | 42 | 37 |

### 2.3. Summary of Survey Results

The survey was conducted to gather input from winter road operations professionals, in an effort to capture the experience of these practitioners in the selection and use of deicer products and fill the knowledge gaps that may not be addressed by a review of literature. Survey questions were developed based on knowledge learned from the literature review and included the following important research questions: how the application of deicer products have evolved over time, which type of deicer product was most used, the details of this deicer product, and whether they have tested or evaluated deicer products for decision-making. The detailed questionnaire can be found in the Appendix.

#### 2.3.1. Respondents

A total of 28 respondents participated in the survey with three from Canada, one from Russia, and the rest representing 18 different U.S. states and agencies (Figure 2.1). In some responses of the survey, the answer to some questions was blank since the lack of available data or experience from the respondents. Therefore, the summaries in these cases used the information provided by fewer than 28 respondents.

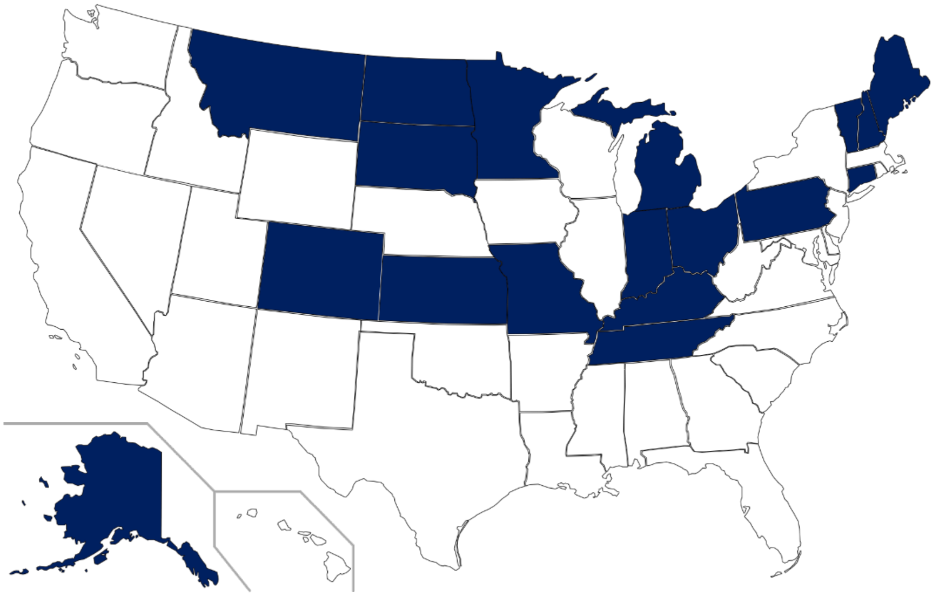


***Figure 2.1 Map of the U.S. with 21 surveyed states highlighted in blue***

#### 2.3.2. Deicer products for Anti-icing, Deicing, or Pre-wetting

The most mentioned change during the last decade is the expanding use of liquids in snow and ice control. Using liquids for anti-icing becomes popular in most agencies, especially in the severely cold climates, where deicing is not an appropriate option. Salt brine is the most commonly used deicer product for anti-icing. Liquid magnesium chloride is also used, but the associated issue of creating an icy location on the road surface by attracting moisture from the air should be aware. In some cases, the corrosion inhibitor is blended into the salt brine to make it stick to the road better and exhibit less harmful effects on the equipment and infrastructure. The results of applying liquid deicers for anti-icing usually vary according to the treating timing and traffic conditions. As a comparison, anti-icing with pre-wetted salt provides more consistent results. Potassium acetate is only used in the automated bridge deck sprayers.

The crews in many agencies have also learned that pre-wetted salt (or called slurry) is more effective than solid salt. The most commonly used liquid for pre-wetting solid deicer is salt brine. Compared with the amount of salt used directly in operation, pre-wetting allows for the reduction use of salt by 20%. Many agencies mentioned that pre-wetting operation helps keep material on the roadway and works fast. When the temperature is dropped to 15°F, magnesium chloride can be used as an effective pre-wetting liquid with rock salt. For the agencies that adopt pre-wetting operations, many of them use the plow trucks that equipped the rear-mounted spray bars, enabling pre-wetting salt at the spinners.

For deicing, the combination of salt and sand works better than salt alone. Although rock salt is the most commonly used deicer product for deicing, some agencies have also used the liquid deicers for deicing. The operation of using liquid magnesium chloride can allow for better road conditions and the clearing of the road within 6 hours after the snow event has stopped. At very low temperatures, the salt brine can be blended with calcium chloride at different ratios to remove ice from the road surface successfully. Some agencies also noted that there exists a challenge in the liquid only routes since the temperature extremes and variation in snow events. The successful story for the effective direct liquid application (DLA) is using this aggressive operation when the temperature is above 20°F.

From the survey responses, the most frequently used deicer product is salt brine, following by other deicer products, as shown in Figure 2.

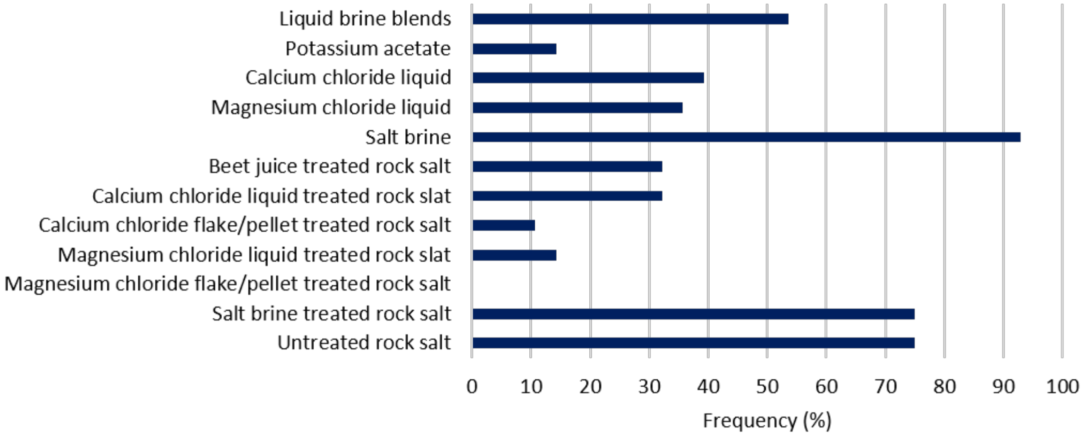


***Figure 2.2 Frequency of different deicer products mentioned by the survey respondents***

### 2.3.3. Details of the Deicer Products

There are many brand names for the deicer products mentioned by the survey respondents. Besides, some agencies make their own deicers due to their local conditions. For anti-icing operations, the deicer products include:

- Salt brine + inhibitor
- 80% salt brine + 20% beet juice for moderately low temperature
- 50% salt brine + 50% beet juice for extremely cold weather
- Salt brine + Amp (90% + 10%)
- Rock salt: Category 8B
- Magnesium chloride: Caliber, M2000, IceBan 305, Torch, Dustbusters
- Potassium acetate: Nuchurs Alpine Solutions
- Calcium chloride: Beet Heet
- Tiger Calcium Road Guard Plus 8
- Salt brine + Beet 55
- Apex
- For deicing operations, the deicer products include:
- 80% salt brine + 20% beet juice for moderately low temperature
- 50% salt brine + 50% beet juice for extremely cold weather
- Salt brine + inhibitor
- Ice Slicer
- Salt + Ice Slicer (50% + 50%)
- Magnesium chloride: Caliber, M2000, IceBan 305, Torch
- Liquid magnesium chloride: ProMelt, Dustbusters
- Magnesium treated rock salt: Morton
- Rock salt: Cargill, Morton, Drvn, Category 8B
- Potassium acetate: Nuchurs Alpine Solutions
- Bionord
- Tiger Calcium Road Guard Plus 8
- Salt brine + Beet 55
- Apex
- Rapid Thaw
- Ice Kicker

For pre-wetting operations, the deicer products include:

- Salt brine + inhibitor
- 80% salt brine + 20% beet juice for moderately low temperature
- 50% salt brine + 50% beet juice for extremely cold weather
- Salt brine + Amp (90% + 10%)
- Salt brine + Beet Heet
- Magic Zero
- Liquid magnesium chloride: ProMelt, Dustbusters
- Salt brine: Category 8B
- Tiger Calcium Road Guard Plus 8
- Salt brine + Beet 55

The most commonly mentioned advantage by agencies who using rock salt or salt brine is their low costs. Most respondents claimed that they will keep using what they have until another product can come along at a lower price or work more effectively for the cost. Other deicer products, such as magnesium chloride- or calcium chloride-based deicers, are mainly applied directly or acting as additives to mix with rock salt or salt brine because of their effectiveness at low temperatures and fast action in facilitating snow/ice removal.

The main disadvantage of applying salt brine is its corrosion to metals. Since it is very tough on equipment, equipment must be washed after each use. In the cases of using magnesium chloride- or calcium chloride-based deicers, they are corrosive to metals on the vehicles, especially in high humidity as they draw moisture from the air. What’s worse, if sugar-based materials are added in the chloride deicers, they will enhance the adhesion between chloride and metals. In most agencies, the inhibitor has to be added to salt brine to reduce the corrosive effects of the brine.

### 2.3.4. Current Evaluation and Future Suggestions

Some agencies have done side by side comparisons to evaluate the effectiveness of deicer products. The Clear Roads QPL is also used. For the timing to anti-ice, a decision-making tree can be used. As most agencies are moving more and more toward liquids due to their fast action and low waste, people are seeking a non-chloride alternative that is both environmentally friendly and cost-effective. Some organics, such as beet products, may be the option for the future.

# CHAPTER 3 PRODUCT TRIALS

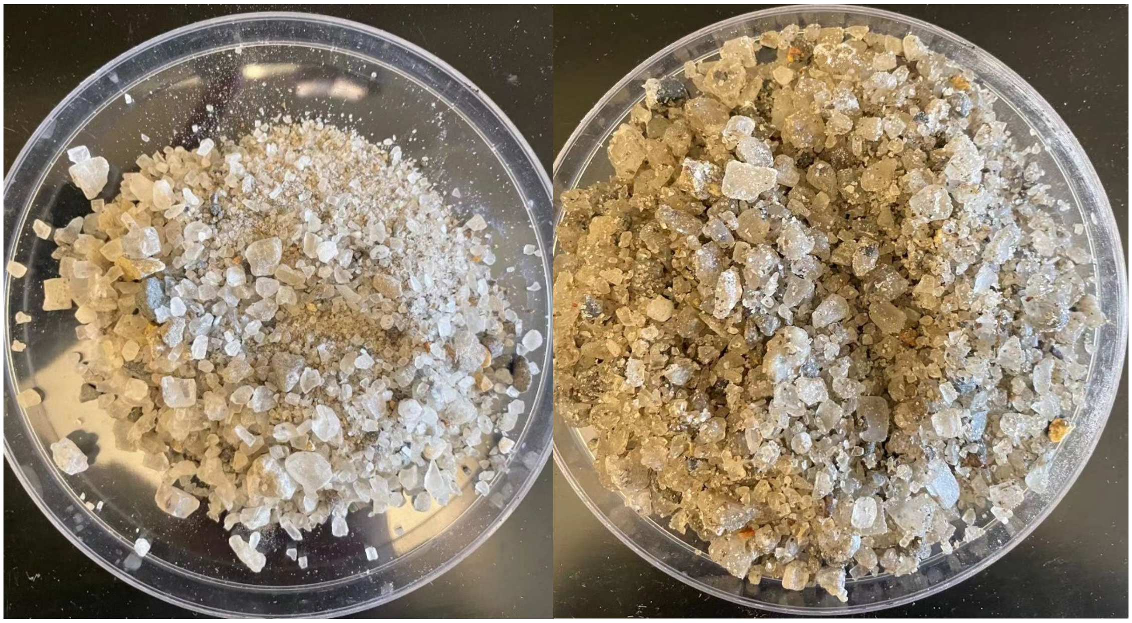
In this task, the research team conducted an array of laboratory trials of currently utilized products and product combinations, in addition to any proposed products selected by MoDOT in both laboratories of Missouri S&T and Washing State University (WSU). Laboratory data was processed and analyzed to evaluate their suitability, performance and impacts on infrastructure.

## 3.1. Materials

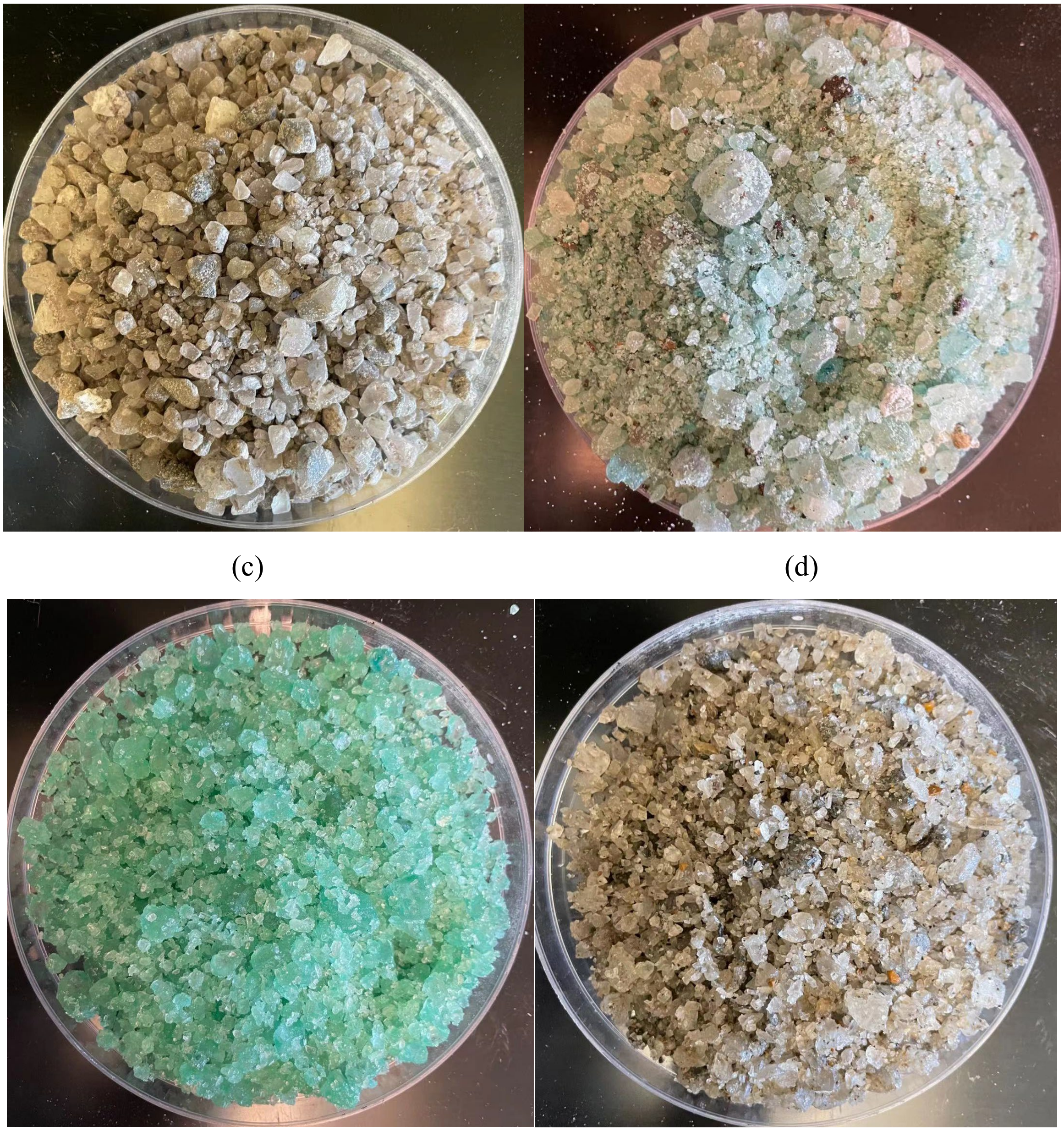
A total of nine de-icing/anti-icing products were collected from MoDOT. Table 3.1 lists the collected products. Figure 3.1 shows the photos of the products.

***Table 3.1 List of evaluated de-icing/anti-icing products***

| No. (#) | Products |
|---|---|
| 1 | Rock salt – untreated [baseline] |
| 2 | Rock salt – brine treated |
| 3 | "Snow Slicer" treated rock salt (Magnesium treated #1); from the Marshfield Maintenance Building |
| 4 | "Ice Ban" treated rock salt (Magnesium treated #2); from St. Louis |
| 5 | "Clear Lane" product (Magnesium treated #3-delivered as a pre-mixed product); from St. Louis |
| 6 | Calcium chloride (flake/pellet) treated rock salt |
| 7 | Calcium chloride (liquid) treated rock salt |
| 8 | Beet juice treated rock salt |
| 9 | "Top Film" treated rock salt |



(a) (b)

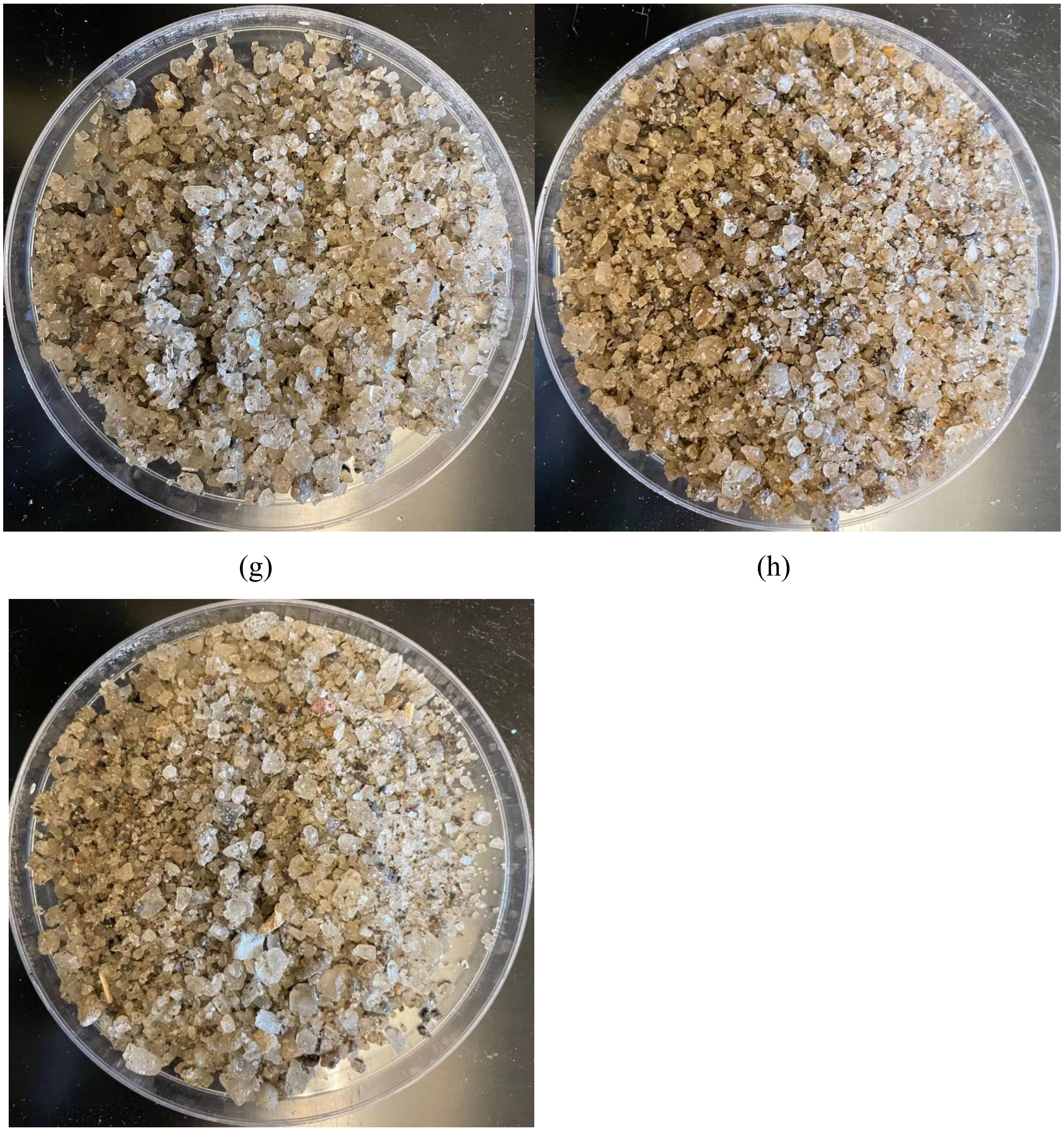


(c)

(d)

(e)

(f)



(g) (h)

(i)

***Figure 3.1 Photos of the evaluated deicer products: (a) Rock salt – untreated; (b) Rock salt – brine treated; (c) "Snow Slicer" treated rock salt; (d) "Ice Ban" treated rock salt; (e) "Clear Lane" product; (f) Calcium chloride (flake/pellet) treated rock salt; (g) Calcium chloride (liquid) treated rock salt; (h) Beet juice treated rock salt; and (i) "Top Film" treated rock salt***

## 3.2. Laboratory Tests

### 3.2.1 pH Measurement

A pH meter with 0.01 pH resolution will be used for measuring the pH of liquid deicer solutions (Figure 3.2). This is to ensure that the deicer products evaluated are not too basic or too acidic.

Table 3.2 presents the pH values of collected deicer solutions (with concentration of 9% by weight). As shown, all the products have pH values around 8. Product #1 which is untreated road salt had the lower pH value of 7.84, while the product #8 (beet juice treated rock salt) had the highest pH value of 8.57. Overall, the deicer products (solution, 9% by weight) evaluated are not too basic or too acidic with pH values ranged from 7.84 to 8.57.

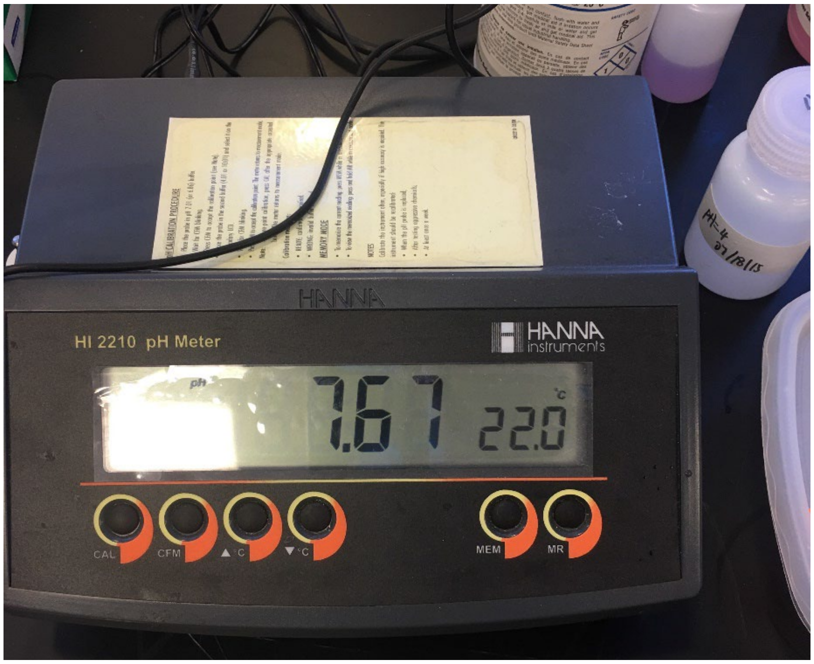


***Figure 3.2 pH meter used in this study***

***Table 3.2 pH values of deicer solutions (9%wt)***

| **Products** | **#1** | **#2** | **#3** | **#4** | **#5** | **#6** | **#7** | **#8** | **#9** |
|---|---|---|---|---|---|---|---|---|---|
| **pH value** | 7.84 | 7.91 | 8.03 | 8.06 | 7.93 | 7.84 | 8.3 | 8.57 | 8.19 |

### 3.2.2 Ice-Melting Test

Ice melting performance of the collected solid deicers was evaluated following a modified Strategic Highway Research Program (SHRP) ice-melting test (H-205.1) method. The purpose of this test is to quantify the performance characteristics of deicers as a function of time, by measuring the ice melted by each deicer over time. First, 48 mL of distilled water is frozen in a 150 × 20 mm petri dish and then the ice surface is melted and re-frozen using a flat glass disk to ensure a smooth surface (Figure 3.3). A weight of 1.5g of solid deicer (Figure 3.4) was applied to the ice surface and at 10, 20, 30, 40, 50, and 60 min after application the dish was titled, and the melted brine is collected with a syringe and the volume was recorded. The brine is returned to the ice sample after each measurement. The procedures were completed at a temperature chamber at 25°F (-4°C). The tests were triplicated to ensure statistical reliability.

*Figure 3.3 Ice in the flat glass trays*

*Figure 3.4 Example of deicer samples*

Ice melting test results for sample measurements during the 60 min test are shown in Figure 3.5. Ice melted (IMC), (mL/g) at a time point was calculated based on Eq. 3.1. As shown in Figure 3.5, the ice melt of all products tended to increase over time, and the increasing rate almost kept constant. The scenarios are consistent with the ice melting results from the other research (Hossain et al. 2015; Koefod et al. 2015). The products #7, #8, #9 (which are calcium chloride (liquid) treated rock salt, beet juice treated rock salt, and "Top Film" treated rock salt, respectively) showed better ice melting capacities than the other evaluated products. The product #6 which is the calcium chloride (flake/pellet) treated rock salt showed the lowest IMC values at each specific time. A summary of all accumulated volume of the melted ice results at the 20- and 60-min measurements are shown in Figure 3.6, which present similar scenarios. The product #7 (calcium chloride (liquid) treated rock salt) showed the best ice melting capacity among all the studied products.

$$IMC = \frac{A}{B} \qquad [3.1]$$

where A is the volume of melted ice (mL) at a specific time and B is the initial mass of solid salt (g).

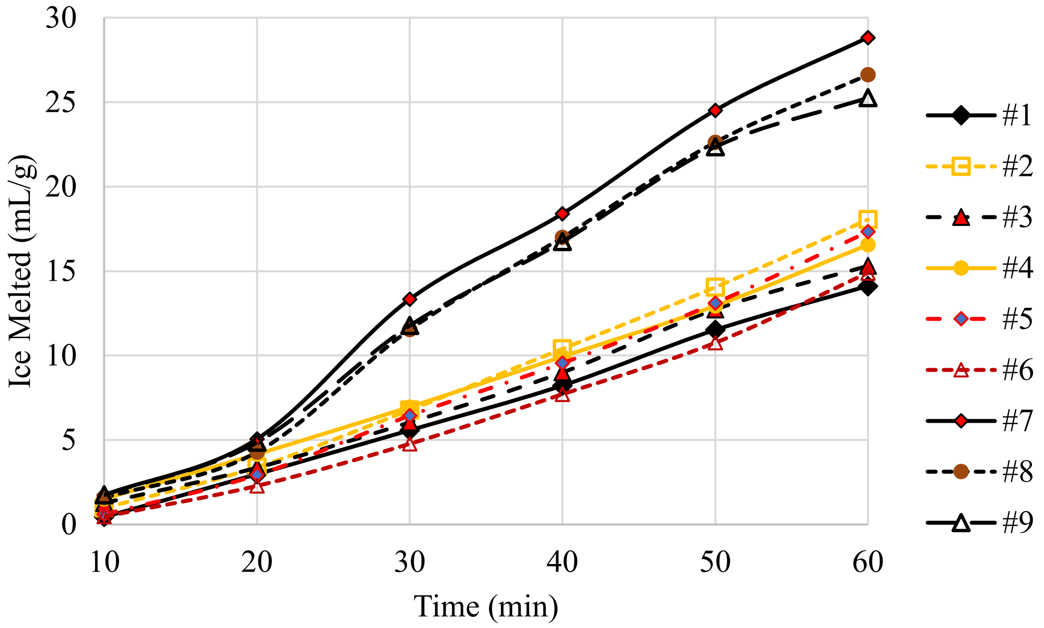
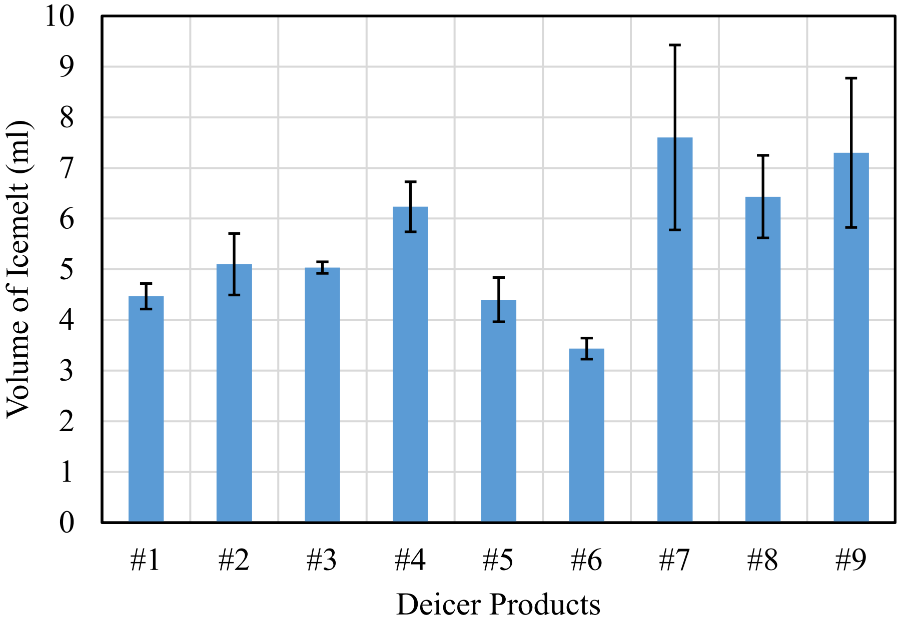
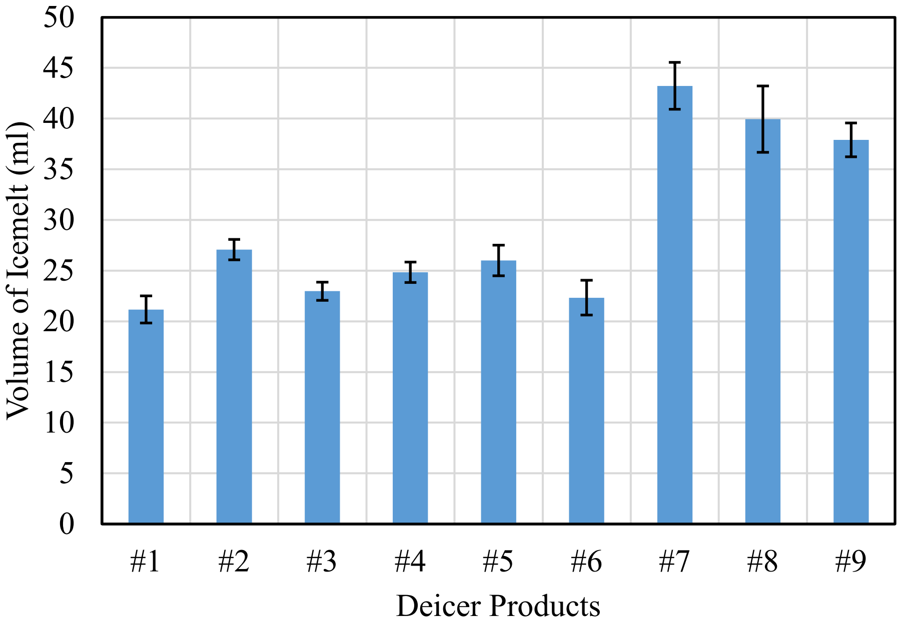


*Figure 3.5 Ice melting test results at −4°C*



(a)



(b)

***Figure 3.6 Summary of the accumulated volume of melted ice at different time: (a) 20 min and (b) 60 min***

### 3.2.3 Thermal Properties of Deicers

The purpose of this test was to quantify the performance characteristics of deicers: the lower the characteristic temperature ($T_c$), and the lower the enthalpy of fusion ($H$, integrated surface area of the peak), the more thermally effective a deicer would be. Laboratory testing was conducted using a Differential Scanning Calorimetry (DSC), set to run from +77 to -76°F with cooling/heating rates at 3.6°F per minute. Samples were first diluted at 3:2 deicer/water volume ratio, and then were separated in triplicate. The use of DSC to quantify deicer performance was relatively new (Akin and Shi, 2012) even though it had been widely employed to rapidly and consistently characterize the thermal properties of materials. The first peak at the warmer end of the heating cycle thermogram was used to derive the $T_c$. The $T_c$ along with the $H$ could be used to estimate the ice melting capacity (*IMC*) of the deicer at 60 minutes, at 15°F and 30°F, respectively. In addition, $T_c$ was an indicator of effective temperature of different products. Differential Scanning Calorimetry (DSC) was used for determining the characteristic temperature ($T_c$) for each deicer under study. It measured the thermal energy within a deicer during its solid and liquid phase transition. The process is briefly described below.

#### ***DSC Method of Quantifying $T_c$***

For this method, 3wt. % solutions for each deicer were prepared. For each test only 10μL (approximately 10 mg) of a deicer solution was used. To collect such a small quantity for each test, micropipette was used. Roughly, 10 μL of deicer solution was placed on a small Aluminum pan for weigh measurements in a digital weight balance. After weighing it, the pan was hermetically sealed to ensure that it could be safely used in DSC measurement.

For DSC test the lower limit for temperature was set as -60°C and upper limit as 25°C. The aluminum pan (holding the deicer liquid) was held in a closed chamber in DSC equipment (shown as (a) in Figure 3.7), through which gas flowed to control the heat contents of the sample. A computer with the designated software program was attached to the calorimeter, to record the measurements (shown as (b) in Figure 3.7). The test lasted for about 40 minutes and, during the test, the heat contents of sample were analyzed.

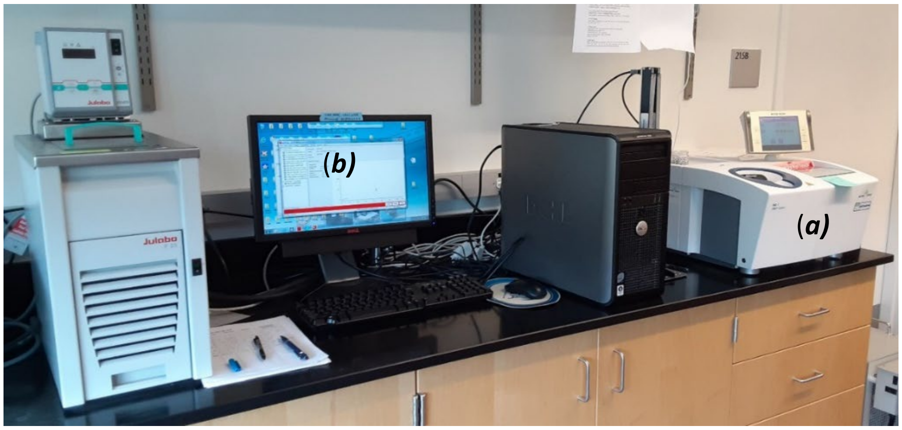


*Figure 3.7 The DSC setup used for testing thermal behaviors of Deicers*

The initial thermograms were obtained after measuring the heat contents in a deicer in milliwatts (mW). As an example, initial thermogram of 3wt.% Beet Juice solution is shown in Figure 3.8 (wt.% stands for percentage by weight). The final thermograms were plotted against the changing temperature (°C) on x-axis and heat flow in watt per gram (W/g) on y-axis. Initial Thermograms were obtained at a temperature range of -25 to 60 °C at a heating/cooling rate of 2.78 °C per minute.

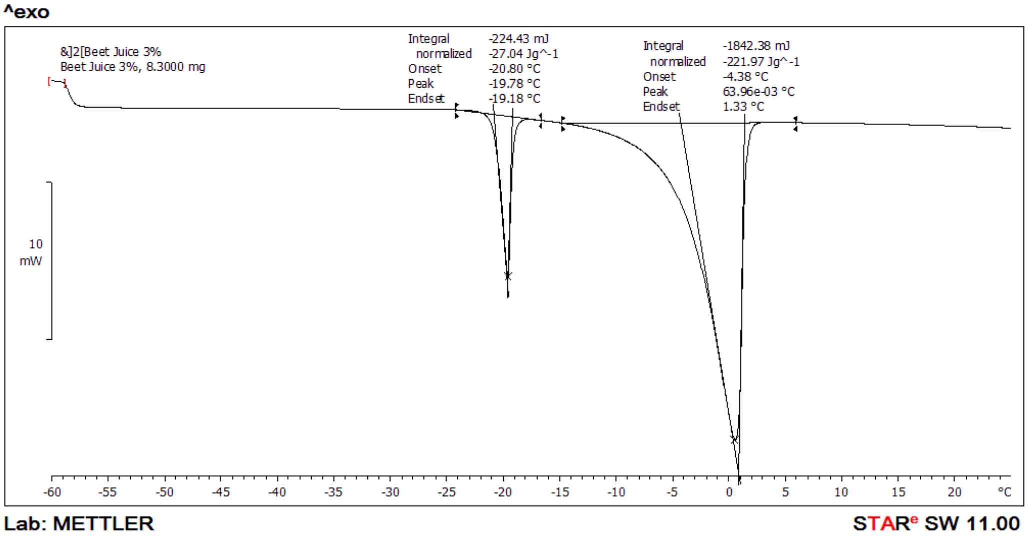


***Figure 3.8 Initial Thermogram obtained directly from the DSC software (Beet Juice Treated Rock Salt at 3wt. %)***

The first peak at the warmer end of thermogram indicates towards the characteristic temperature which defines the temperature below which ice crystals start to form in the deicer solution. From the thermograms it can be noticed that this peak likely corresponded to the phase transition of water because most of the 3 wt.% solutions start to exhibit this phase transition around 0 °C. The results of all deicers plotted as thermograms are shown in Figure 3.9.

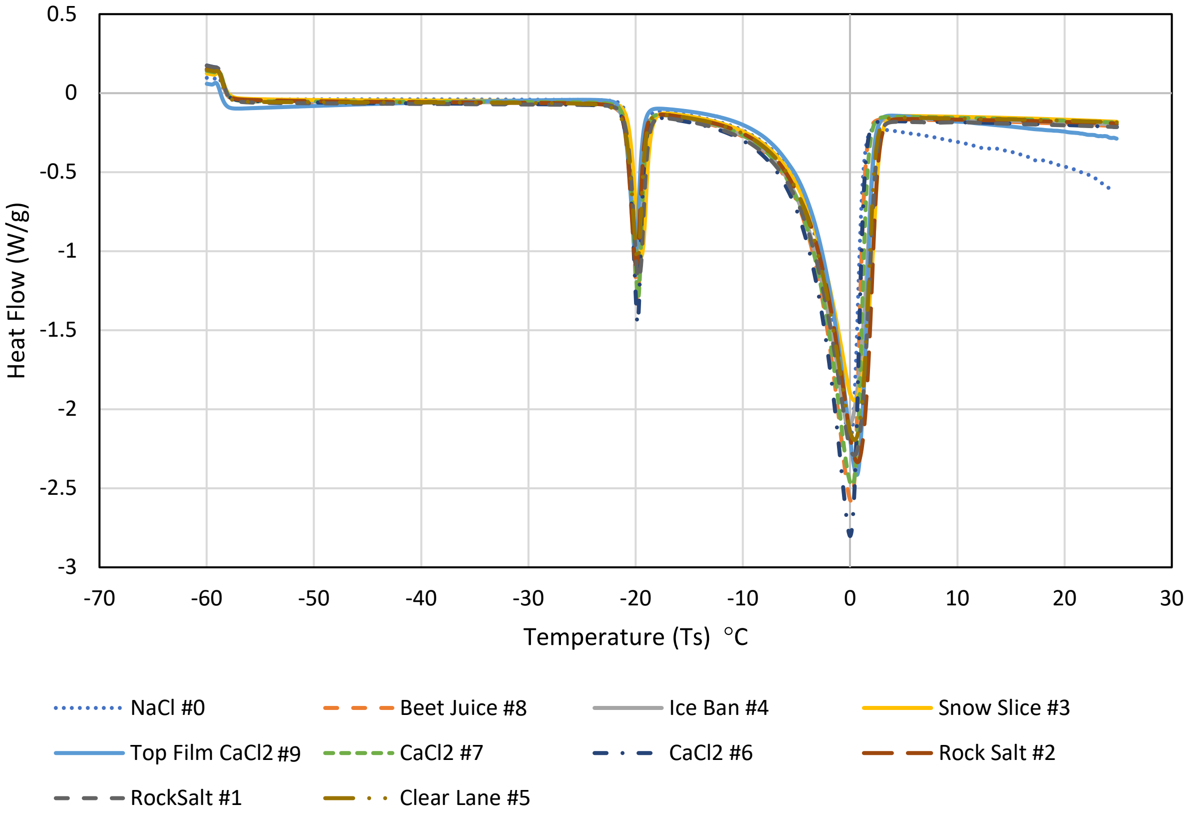


***Figure 3.9 Thermograms obtained from DSC measurements of all deicers***

Since, the compositions of all the deicers were mostly based on rock salt (NaCl) and the control itself was pure NaCl (crystal form), the temperature at which liquid to solid phase change occurred were almost similar for all samples. The difference could better be seen in the tabulated data. Temperatures for 1st peak and 2nd peak (from the warmer end of thermograms – right to left) for each deicer samples, are recorded and shown in Table 3.3. From this table it can be noticed that when commercial deicer "Ice Ban" was added to rock salt, the lowest "characteristic temperature" could be achieved for this type of deicer, which would ultimately help the most in preventing black ice formation on roads. The treatment of rock salt with Ice Ban could also help the most in anti-icing, among all the other types on treated salts listed in Table 3.1.

### 3.2.4 Eutectic Phase Diagrams

The purpose of this test was to quantify the performance characteristics of deicers as a function of deicer concentration; the lower the freezing point temperature, the more thermodynamically powerful a deicer would be. The Freezing point determination for all 9 deicer samples was done by following the ASTM D1177 standard process, "*Standard Test Method for Freezing Point of Aqueous Engine Coolants*". The purpose of finding the freezing points for various compositions by weight, was to form eutectic phase diagrams for each deicer. The compositions that were tested for this experiment for each deicer was: 3 wt. %, 5 wt. %, 10 wt. %, 15 wt. %, 20 wt. %, and 23 wt. %. The process D1177 is shortly explained in this section and the modifications needed accordingly are also illustrated.

***Table 3.3 Characteristic temperatures of deicers***

| **Deicer No.** | **Diluted Deicers (3 wt. %)** | **1st Peak Temp. (°C), $T_c$** | **2nd Peak Temp. (°C)** |
|---|---|---|---|
| #0 | NaCl Crystals | -0.048 | -19.73 |
| #1 | Rock Salt (baseline) | 0.38 | -19.74 |
| #2 | Brine Treated Rock Salt | 0.70 | -19.95 |
| #3 | "Snow Slicer" Treated Rock Salt | 0.38 | -20.66 |
| #4 | "Ice Ban" Treated Rock Salt | -0.14 | -19.83 |
| #5 | "Clear Lane" Produce | 0.42 | -19.80 |
| #6 | Calcium Chloride (pellets) Treated Rock Salt | -0.0034 | -19.84 |
| #7 | Calcium Chloride (liquid) Treated Rock Salt | 0.16 | -19.76 |
| #8 | Beet Juice Treated Rock Salt | 0.0639 | -19.78 |
| #9 | "Top Film" with Calcium Chloride Treated Rock Salt | 0.63 | -20.02 |

***<u>Experiment Details – ASTM</u>* <u>D1177</u>**

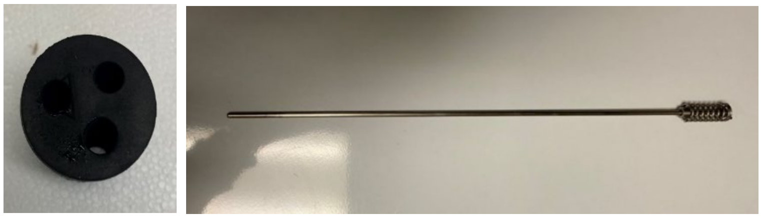
The Experimental setup was consisting of one 2100 mL Dewar flask (silvered and closed in a fitting container as shown in Figure 3.10). This Dewar flask has no cover as in the experiment it is supposed to be without cover; however, there were some modifications made which allowed covering the top of 2100 mL Dewar flask. Another un-silvered and un-evacuated Dewar flask (200 mL in capacity, shown in Figure 3.11) was used with a cork with three holes (Figure 3.12a), to close the mouth of this flask. Figure 3.11 presents the freezing tube (Figure 3.11) in which deicer solution was added in roughly 75 to 100 mL of volume, for each experiment.

***Figure 3.10 Dewar flask (2100 mL, silvered and evacuated) to be used for cooling bath***

A driving motor (shown in Figure 3.11b) was used to rotate a stainless- steel stirrer (Figure 3.12b), to stir the deicer solution constantly between 60 to 80 rpm. A platinum resistance thermometer with data logging facility was used to measure the temperature and record it whenever needed during experiment. This thermometer was capable to measure 0.1ºC of temperature and to take readings every second if needed during the experiment.

(a) (b)

***Figure 3.11 Dewar flask (200 mL, un-silvered and un-evacuated) to be used as freezing tube***



(a) (b)

***Figure 3.12(a) A rubber cork with three holes and (b) stainless steel five coil stirrer***

The thermometer’s probe had to be long enough to reach the deicer inside the freezing tube and measure the temperature effectively; as shown in the Figure 3.13b. The whole arrangement is also shown in the Figure 3.14.

(a) (b)

*Figure 3.13 Data Logger (a) & Platinum resistant thermometer probe (b).*

The following describes the step-by-step process for the testing of freezing point temperature of each given deicer solution.

1. Cooling bath was prepared in the 2100 mL Dewar flask, 30 minutes before the experiment was started. A cooling bath was consisting of dry ice cubes and ethanol (190 proof). Ethanol had a very low freezing point (-114ºC) and therefore upon adding dry ice in it (having a temperature of -78ºC) it would not freeze.
2. The freezing tube was dipped inside the cooling bath (almost 3/4th of the tube was dipped inside the cooling bath). A modification made on the freezing tube (as shown in Figure 3.11a), allowed it to rest nicely on the top of the bigger Dewar flask, which also closed the mouth of the bigger Dewar flask and heat losses in the cooling bath were somewhat avoided. Notice that the bigger Dewar flask had dry ice inside and therefore was never closed airtight, to allow the escape of carbon dioxide. The whole arrangement was kept in a fume hood, making sure that the tester does not inhale any $CO_2$ and it should mostly be vacuumed by the hood. Freezing tube was dipped in the cooling bath for 15 minutes to allow the temperature of the freezing tube drop below at least 10ºC (depending on the composition of deicer solution, it can be dipped for longer period of times as well).
3. The Deicer solution was poured into the freezing tube carefully. The deicer solution can be pre-cooled to a temperature of 8 ºC to 1 ºC, depending on the composition of the solution. The higher compositions (10 wt. % to 23 wt. %) tend to freeze at lower temperatures, like between -10ºC and -21ºC. To save time the deicer solution can therefore be pre-cooled accordingly.
4. Clean thermometer probe and stirrer were added to the freezing tube. It was made sure that the stirrer head (five-coiled stainless steel) was fully immersed in the deicer solution inside the freezing tube. The cork with holes bored according to the diameters of the probe and stirrer rod, was then placed on the top of the freezing tube and its mouth was firmly closed. A third hole in the cork was machined according to the seeding tube diameter. A seeding tube is a hollow steel tube (internal diameter of

around 2 to 3mm), which was normally used during freezing point experiment to avoid the supercooling. A frozen deicer sample was inserted inside the freezing tube near the approximate freezing point of deicer solution, which allowed the solution to freeze on time. Delayed freezing is referred to as supercooling and may be avoided by the use of seeding tube. The different graphs obtained with or without supercooling are shown later**.**

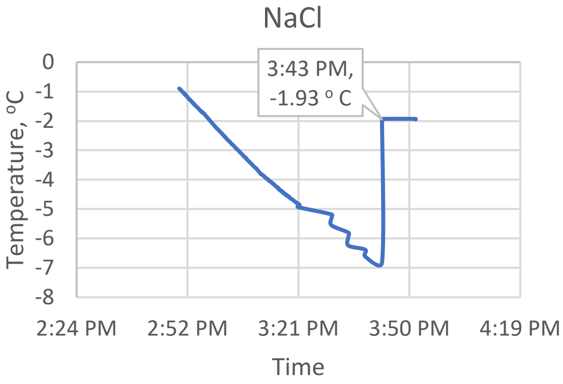
5. Thermometer was turned on and temperature was monitored every minute in the start of the cooling process. Dry ice cubes were added time to time to make sure the temperature of the cooling bath was at least -45°C and the cooling rate was at least -0.3°C /min. Too fast cooling rate (e.g., -1°C /min) should not be reached, if the cooling rate was that fast the test should be repeated.
6. Stirrer was turned on, and the rotations per minute (rpm) was set between 60 and 80 rpm.
7. The freezing points for the compositions mentioned above, for pure NaCl crystals, should already be known. If not, then the experiments against all those compositions for NaCl should be done before any other deicer solutions. This would help the tester to identify the expected freezing points of deicer solutions since they were all rock salt. Around the expected freezing point, the thermometer recorder settings should be set to at least every 10 seconds. For better results and graphs it was recommended to record the temperature near the expected freezing points, every 2 seconds. This would allow to notice minute changes in temperature, and freezing point could be effectively determined.
8. If undercooling or supercooling had occurred, the temperature would sharply rise back to freezing point upon the birth of first frozen (dendrite) deicer particle. Temperature would then again start to drop evenly. Stirring should be continued from this point onwards for another 10 minutes, to ensure the freezing point was reached. During these 10 minutes, no further dry ice addition was necessary.
9. Graph against the temperature and time of each experiment was generated and transformed to excel file, as added to this section.

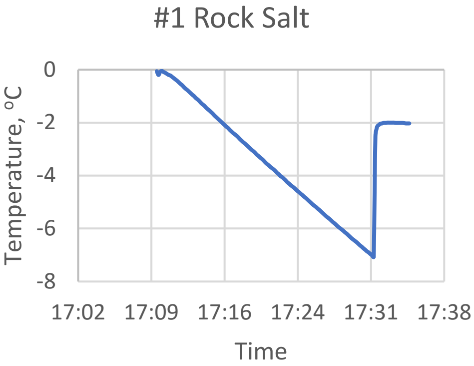
The cooling bath can be kept for as long as the experiments are still performed. If necessary, ethanol was added to it, as it evaporated with time. When cooling bath was not in use, the flask could be covered with a wooden cover to avoid any contamination. The freezing tube must be washed with DI water and dried fully, in between each experiment.

***Figure 3.14 Complete arrangement of the equipment used in freezing point determination.***

***Plotted Data for Freezing Points***

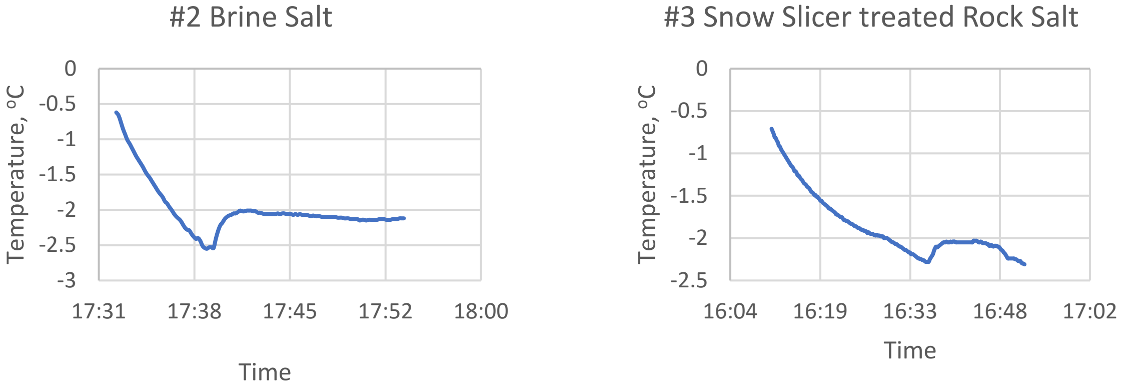
The graphs of some of the compositions for each deicer are shown in Figure 3.15. The measured freezing points for 3–23 wt.% deicers are presented in Table 3.4. As can be seen, the freezing point decrease with increasing concentration for all deicers. The lowest freezing point was related to Snow Slicer Treated Rock Salt (Deicer #3) at 3 wt.% (-2.03 °C), 10 wt.% (-7.25 °C) and 23 wt.% (-23.14 °C). However, rock salt (Deicer #1) had the lowest freezing point at 5 wt.% (-3.44 °C), 10 wt.% (-7.25 °C) and 15 wt.% (-11.91 °C). On the other hand, Ice Ban Treated Rock Salt (Deicer #4) had the lowest freezing point at 20 wt.% (-17.88 °C). It should be noted that in all concentrations studied, deicers other than control (NaCl reagent) had the lowest freezing point temperature.





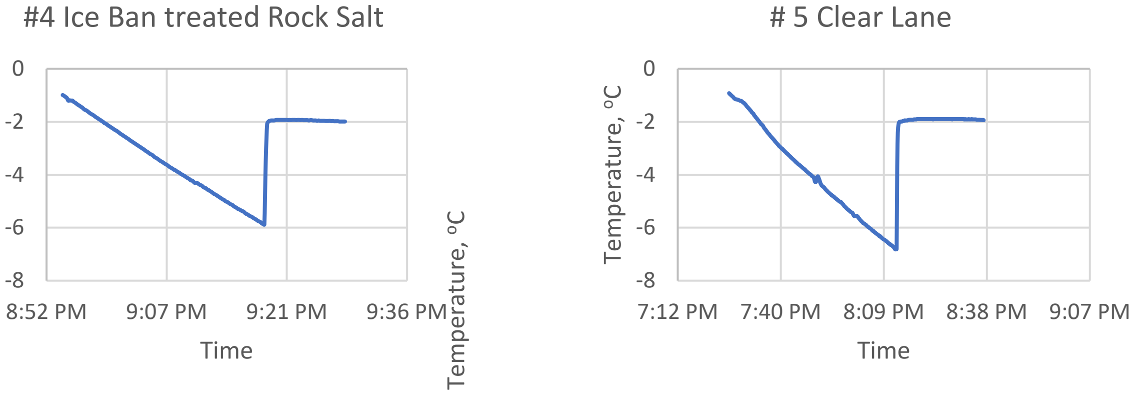
(a) NaCl

(b) #1 Rock salt



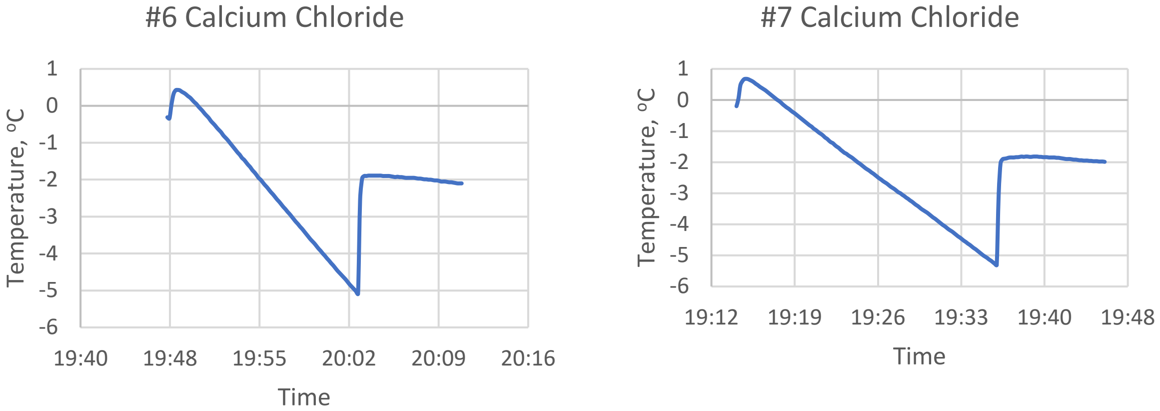
(c) #2 Brine salt

(d) #3 Snow Slicer treated Rock Salt



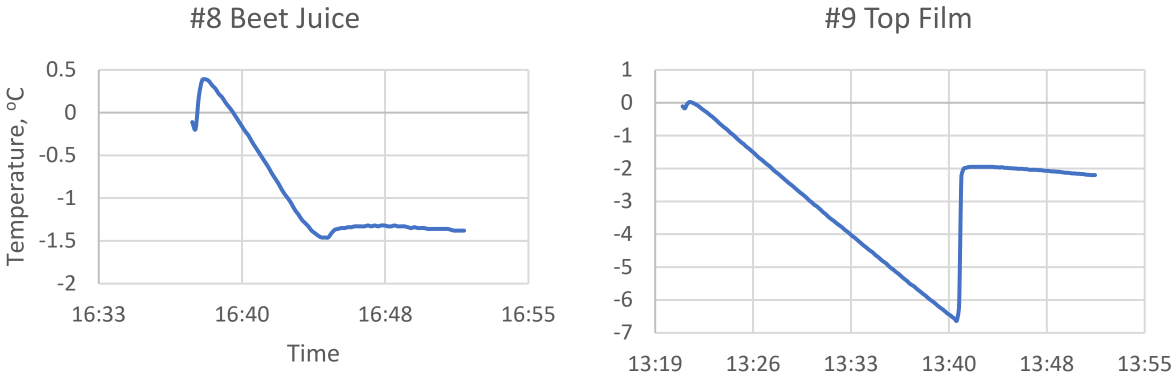
(e) #4 Ice Bean

(f) #5 Clear Lane



(g) #6 Calcium chloride

(h) #7 Calcium chloride



(i) #8 Beet Juice (j) #9 Top Film

***Figure 3.15 Freezing point curves for 3 wt.% of different deicers (see Appendix B for more information): (a)NaCl; (b) Rock salt – untreated; (c) Rock salt – brine treated; (d) "Snow Slicer" treated rock salt; (e) "Ice Ban" treated rock salt; (f) "Clear Lane" product; (g) Calcium chloride (flake/pellet) treated rock salt; (h) Calcium chloride (liquid) treated rock salt; (i) Beet juice treated rock salt; and (j) "Top Film" treated rock salt***

***Table 3.4 Freezing points for all nine deicers at the selected concentrations (°C)***

| **ID** | **Deicer Salts** | **3 wt.%** | **5 wt.%** | **10 wt.%** | **15 wt.%** | **20 wt.%** | **23 wt.%** |
|---|---|---|---|---|---|---|---|
| #1 | Rock Salt | -2.01 | -3.44 | -7.25 | -11.91 | -17.62 | -20.47 |
| #2 | Brine Treated Rock Salt | -2.02 | -3.41 | -6.61 | -11.49 | -16.08 | -19.61 |
| #3 | Snow Slicer Treated Rock Salt | -2.03 | -2.66 | -7.25 | -11.32 | -16.63 | -23.14 |
| #4 | Ice Ban Treated Rock Salt | -1.93 | -3.13 | -6.9 | -11.26 | -17.88 | -21.5 |
| #5 | Clear Lane Produce | -1.9 | -3.3 | -6.87 | -11.30 | -17.40 | -21.5 |
| #6 | Calcium Chloride pellets Treated Rock Salt | -1.91 | -3.32 | -6.94 | -11.6 | -15.35 | -22.79 |
| #7 | Calcium Chloride liquid Rock Salt | -1.84 | -3.36 | -6.7 | -11.82 | -17.3 | -22.42 |
| #8 | Beet Juice Treated Rock Salt | -1.33 | -2.52 | -6.26 | -10.69 | -15.92 | -20.71 |
| #9 | Top Film with Calcium Chloride Treated Rock Salt | -1.98 | -3.09 | -6.72 | -11.24 | -17.12 | -20.22 |
| #0 | NaCl (Control) | -1.93 | -3.38 | -6.95 | -11.65 | -17.66 | -21.98 |

### 3.2.5 Snow–Pavement Bond and Friction Tests

Laboratory tests were conducted at the Subzero Science and Engineering Research Facility (SSERF) at Montana State University (MSU), in the Cold Structures Testing Chamber (Klein-Paste and Dalen, 2018), to inspect the behavior of deicer samples on two different types of pavements. In this section the friction coefficient and bonding strength results, as received from MSU, for deicer samples (mentioned in Table 3.1) are shared.  The brief description of the process used and the four different types of testing protocols adopted for these field operational tests (FOTs) are illustrated.

#### ***General Details of Field Operational Tests by MSU***

The procedure of the FOTs involves the measurement of bond strength of ice with the pavements, after the application of solid deicers. Friction between the pavement surface and tire surface, was also measured to evaluate each deicer's effect on the road. Mainly, the tests were performed using a trafficking machine, artificial snow conditions and two different pavement types (prepared in the lab by the MSU team). The various steps are explained shortly below:

#### *Pavement Types*

MSU prepared the pavements using the material they received from S&T. Two pavement material types were developed, broadly one was concrete and other was asphalt, as shown in the Figure 3.16. Pavement temperatures had to be maintained for some time before any test had to be started. For this cold room facility was utilized.

(a) (b)

***Figure 3.16 Examples of test samples for different types of pavements: (a) concrete pavement, (b) asphalt pavement.***

#### *Application of Snow*

Snow was artificially made in the Cold Hydrodynamics Chamber at MSU using a constructed system with a high humidity cold- temperature chute. The air temperature during snow-making was -13°F (-25°C) and in storage was 5°F (-15°C), which produces "drier" snow. The snow was sieved through a 0.04 in. (1 mm) mesh which breaks the bonds between the individual snow particles and encourages sintering and bonding of the snow to the pavement surface. Before each test, the snow had to be equilibrated to 25ºF. Snow was also compacted after the application on the pavement surface and before application of deicers. Further details can be found in Klein - Paste and Dalen (2018).

### *Application of Deicers*

As the sequence of steps shows (Table 3.5), application of solid deicers (dry salt only) was done after the snow application and compaction on the pavement types. This indicates that only deicing was performed at MSU or at least at this stage.

### *Trafficking and Post Compaction*

To simulate vehicle traffic in the laboratory, the pavement samples were trafficked using a custom built automated trafficking machine, as shown in the Figure 3.17. The trafficking includes 500 passes of the tire, over one pavement surface for the purpose of post-compaction; which took just over 26 minutes. Post compaction refers to the compaction performed second time after the application of deicers on the pavement surface.

***Figure 3.17 Automated trafficking machine used in this research.***

### *Sequence of steps involved during FOTs*

During the FOTs the steps that were followed in general are tabulated and are shown in Table 3.5.

***Table 3.5 Sequence of steps for the FOTs performed by MSU***

| **Sr. No.** | **Deicer Type → Solid** |
|---|---|
| 1 | Application of Snow, over the pavements |
| 2 | Pre-Compaction of snow to 0.5" depth |
| 3 | Application of Deicer – at 200 lbs/ln-mi |
| 4 | Post-Compaction - Trafficking done for 500 times (~26 minutes) |
| 5 | Bond measurements were done – After small square pieces of snow were cut (Figure 3.18) |
| 6 | Plowing was done over the pavements to ***remove the all the removable*** snow/ice, as shown in Figure 3.19 |
| 7 | Friction measurements were done by dragging a constant weight across the pavement – 6 readings were taken for each friction force |

*Same steps were followed for the control (#ND: no deicer).*

All tests were performed in conditions of snow, where the snow density varied from 0.2786 g/mL to 0.354 g/mL during the testing days. Humidity levels were recorded to be from 12% to as high as 22%, as the tests were performed on 5 different days.

**(a)** **(b)**

***Figure 3.18 Squares cut for Bond measurements, over the pavement: (a) Concrete and (b) Asphalt***

**(a)** **(b)**

***Figure 3.19 Plowing was done on the pavements to remove all detachable snow/ice: (a) Concrete and (b) Asphalt.***

***Plowing was done on the sidewalks to remove all detachable snow / ice***

*Process for Friction and Bond Strength Measurement*

The process for the friction and bond strength measurement is already summarized in Table 3.5. However, some details are added here. About 1 inch of snow was applied to the pavements before the pre-compaction (first trafficking) was done. The temperature of the pavement was kept at 25ºF during the entire testing. During the cutting of squares of the post-compacted snow, area only under trafficking was considered (as the size of the tire was smaller in width than the pavement). Once all the measurements were taken, the sample was removed from the cold lab, washed off with water, dried, and then returned to the cold lab so the sample can adjust to the cold room temperature (25ºF).

***Results of FOTs***

The results from the FOTs performed by MSU are compiled in Table 3.6. Bar graphs, showing the values of bond strength and friction magnitude over each pavement type are also shown later on.

***Table 3.6 Friction and bond strength testing results for various deicer types (FOTs)***

(a) Friction coefficients and testing conditions for various deicer types (FOTs), (Unit: °C).

| **Deicer Type** | **Pavement Type** | **Friction Coefficient (μ)** | **Snow Density (g/mL)** | **Humidity (%)** | **Avg. Compacted Snow Depth (mm)** |
|---|---|---|---|---|---|
| #ND | Asphalt | 0.61 | 0.3546 | 12 | 13.7 |
| #1 | Asphalt | 0.35 | 0.2945 | 13 | 12.3 |
| #2 | Asphalt | 0.51 | 0.2895 | 14 | 15.3 |
| #3 | Asphalt | 0.56 | 0.2895 | 15 | 14.3 |
| #4 | Asphalt | 0..28 | 0.2895 | 21 | 13.7 |
| #5 | Asphalt | 0.55 | 0.2973 | 21 | 14.3 |
| #6 | Asphalt | 0.50 | 0.2786 | 14 | 14 |
| #7 | Asphalt | 0.35 | 0.3369 | 12 | 14 |
| #8 | Asphalt | 0.33 | 0.352 | 16 | 15 |
| #9 | Asphalt | 0.54 | 0.352 | 16 | 15 |
| #ND | Concrete | 0.70 | 0.3546 | 12 | 14.7 |
| #1 | Concrete | 0.59 | 0.2945 | 13 | 14.7 |
| #2 | Concrete | 0.51 | 0.2895 | 15 | 14.7 |
| #3 | Concrete | 0.33 | 0.2895 | 14 | 14.7 |
| #4 | Concrete | 0.57 | 0.2895 | 20 | 15 |
| #5 | Concrete | 0.46 | 0.2973 | 20 | 13.7 |
| #6 | Concrete | 0.41 | 0.2786 | 14 | 14.7 |
| #7 | Concrete | 0.49 | 0.3369 | 14 | 15 |
| #8 | Concrete | 0.44 | 0.352 | 16 | 14.3 |
| #9 | Concrete | 0.38 | 0.352 | 22 | 15.3 |

(b) Bond Strengths and testing conditions for various deicer types (FOTs)

| Deicer Type | Pavement Type | Bond Strength | Snow Density (g/mL) | Humidity (%) | Avg. Compacted Snow Depth (mm) |
|---|---|---|---|---|---|
| #ND | Asphalt | 22.43 | 0.3546 | 12 | 13.7 |
| #1 | Asphalt | 6.07 | 0.2945 | 13 | 12.3 |
| #2 | Asphalt | 9.15 | 0.2895 | 14 | 15.3 |
| #3 | Asphalt | 5.59 | 0.2895 | 15 | 14.3 |
| #4 | Asphalt | 8.91 | 0.2895 | 21 | 13.7 |
| #5 | Asphalt | 8.56 | 0.2973 | 21 | 14.3 |
| #6 | Asphalt | 6.35 | 0.2786 | 14 | 14 |
| #7 | Asphalt | 5.23 | 0.3369 | 12 | 14 |
| #8 | Asphalt | 12.57 | 0.352 | 16 | 15 |
| #9 | Asphalt | 4.57 | 0.352 | 16 | 15 |
| #ND | Concrete | 23.81 | 0.3546 | 12 | 14.7 |
| #1 | Concrete | 10.28 | 0.2945 | 13 | 14.7 |
| #2 | Concrete | 12.93 | 0.2895 | 15 | 14.7 |
| #3 | Concrete | 8.78 | 0.2895 | 14 | 14.7 |
| #4 | Concrete | 12.35 | 0.2895 | 20 | 15 |
| #5 | Concrete | 10.59 | 0.2973 | 20 | 13.7 |
| #6 | Concrete | 13.22 | 0.2786 | 14 | 14.7 |
| #7 | Concrete | 16.01 | 0.3369 | 14 | 15 |
| #8 | Concrete | 10.84 | 0.352 | 16 | 14.3 |
| #9 | Concrete | 13.30 | 0.352 | 22 | 15.3 |

These results were used to generate the bar graphs as shown in Figures 3.20 and 3.21**.** The bar graphs representing the values for friction coefficients and bond strengths on two types of pavements (with standard deviation displayed in each graph).

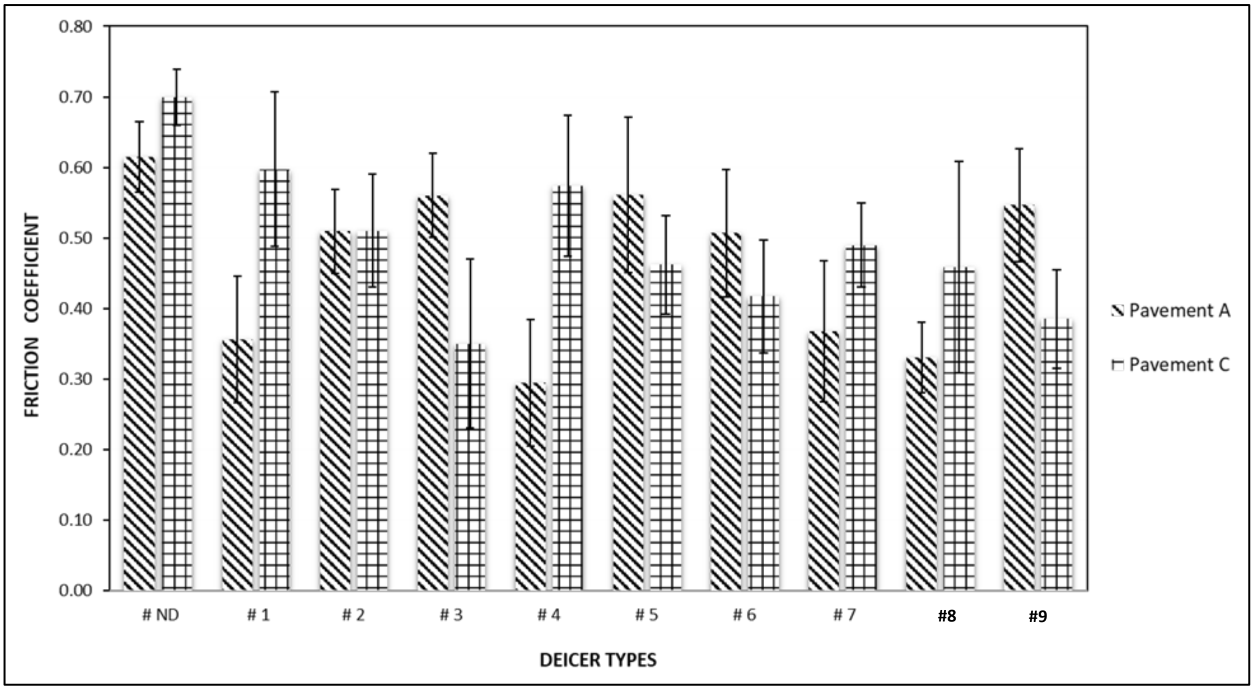


*Figure 3.20 Friction coefficients for all deicer samples on two different pavement types*

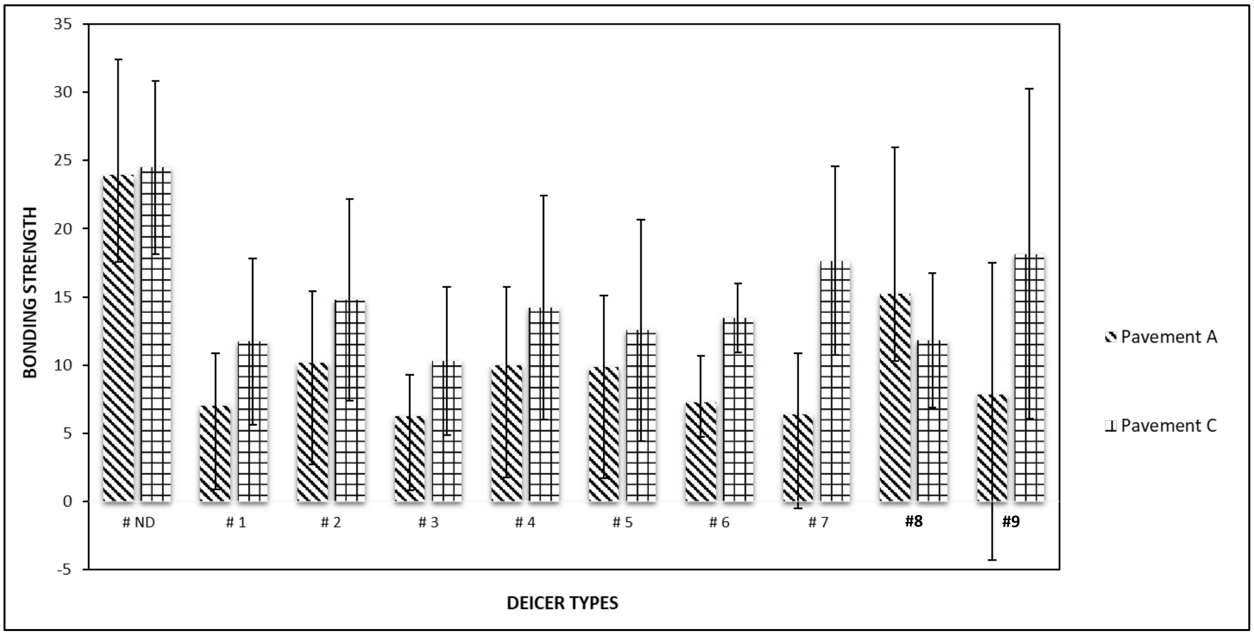


*Figure 3.21 Bond Strength, for all deicer samples on two different pavement types*

***Difference of Bond Strength between Two Types of Pavement***

The single factor ANOVA revealed that there were statistically significant differences between ice bond strength on pavement surfaces A and C; given that, the p-value of 0.03128 was lower than 0.05 (Table 3.7). It is interesting to note that once we remove the control group (#ND: no deicer), the p-value was reduced to 0.001055. This much lower p-value suggests that the differences between the ice/pavement bond strengths on the deiced pavements were notably

***Table 3.7 Statistical analysis for ice bond strength on pavement surfaces A and C: (a) summary of the experiment results; and (b) ANOVA analysis results***

(a)

| *Groups* | *Count* | *Sum* | *Average* | *Variance* |
|---|---|---|---|---|
| A | 10 | 83 | 8.3 | 24.9594 |
| A | 10 | 96.48 | 9.648 | 101.276 |
| A | 10 | 96.75 | 9.675 | 53.3961 |
| A | 10 | 103.09 | 10.309 | 81.4951 |
| A | 10 | 136.62 | 13.662 | 84.446 |
| A | 10 | 107.25 | 10.725 | 50.8074 |
| C | 10 | 208.29 | 20.829 | 86.8177 |
| C | 10 | 154.45 | 15.445 | 47.8708 |
| C | 10 | 109.9 | 10.99 | 27.6813 |
| C | 10 | 122.85 | 12.285 | 48.1471 |
| C | 10 | 155.4 | 15.54 | 100.699 |
| C | 10 | 143.56 | 14.356 | 19.2185 |

(b)

| *Source of Variation* | *SS* | *df* | *MS* | *F* | ***p-value*** | *Fcrit* |
|---|---|---|---|---|---|---|
| Between Groups | 1358.55 | 11 | 123.504 | 2.0391 | **0.03128** | 1.87839 |
| Within Groups | 6541.33 | 108 | 60.5679 | | | |
| | | | | | | |
| Total | 7899.87 | 119 | | | | |

***Difference of Bond Strength between Different Deicers***

The single factor ANOVA revealed that there were statistically significant differences across the ice/pavement bond strengths of different ND and deicer groups (#ND to #9), given that the p-value of 7.52E-05 was considerably lower than 0.05 (Table 3.8). It is interesting to note that once we remove the control group (#ND: no deicer), the p-value was considerably increased to 0.708331. This considerably higher p-value suggests that the differences between the ice/pavement bond strengths on the deiced pavements were actually statistically insignificant.

***Table 3.8 Statistical analysis for ice bond strength of different deicers: (a) summary of the experiment results; and (b) ANOVA analysis results***

(a)

| *Groups* | *Count* | *Sum* | *Average* | *Variance* |
|---|---|---|---|---|
| #ND | 12 | 290.39 | 24.1992 | 51.3659 |
| #1 | 12 | 112.33 | 9.36083 | 29.9081 |
| #2 | 12 | 149.55 | 12.4625 | 43.4104 |
| #3 | 12 | 99.28 | 8.27333 | 21.9975 |
| #4 | 12 | 145.12 | 12.0933 | 50.3282 |
| #5 | 12 | 134.33 | 11.1942 | 44.4308 |
| #6 | 12 | 124.15 | 10.3458 | 18.825 |
| #7 | 12 | 144.32 | 12.0267 | 65.4167 |
| #8 | 12 | 162.14 | 13.5117 | 66.4495 |
| #9 | 12 | 156.03 | 13.0025 | 137.981 |

(b)

| *Source of Variation* | *SS* | *df* | *MS* | *F* | ***p-value*** | *F crit* |
|---|---|---|---|---|---|---|
| Between Groups | 2068.63 | 9 | 229.848 | 4.33583 | **7.52E-05** | 1.96605 |
| Within Groups | 5831.24 | 110 | 53.0113 | | | |
| | | | | | | |
| Total | 7899.87 | 119 | | | | |

### ***Difference of Friction Coefficient between Two Types of Pavement***

The single factor ANOVA revealed that there was no statistically significant difference between the friction coefficients on the surface of pavements A and C, given that the p-value of 0.366915 was much higher than 0.05 (Table 3.9). It is interesting to note that once we remove the control group (#ND: no deicer), the p-value was reduced to 0.184574. This lower p-value suggests that even though the differences between the friction coefficients on the deiced pavements A and C remained statistically insignificant, these differences were slightly higher than those between the control groups A and C.

***Table 3.9 Statistical analysis of friction coefficient data for different pavements: (a) summary of the experiment results; and (b) ANOVA analysis results***

(a)

| *Groups* | *Count* | *Sum* | *Average* | *Variance* |
|---|---|---|---|---|
| A | 10 | 4.83048 | 0.48305 | 0.01779 |
| A | 10 | 5.07571 | 0.50757 | 0.02127 |
| A | 10 | 4.70929 | 0.47093 | 0.01553 |
| A | 10 | 4.10904 | 0.4109 | 0.01336 |
| A | 10 | 4.27728 | 0.42773 | 0.02968 |
| A | 10 | 4.88893 | 0.48889 | 0.01112 |
| C | 10 | 5.28672 | 0.52867 | 0.0125 |
| C | 10 | 5.70732 | 0.57073 | 0.01095 |
| C | 10 | 4.97876 | 0.49788 | 0.02661 |
| C | 10 | 4.6765 | 0.46765 | 0.01786 |
| C | 10 | 4.60663 | 0.46066 | 0.01885 |
| C | 10 | 4.4056 | 0.44056 | 0.01676 |

(b)

| *Source of Variation* | *SS* | *df* | *MS* | *F* | ***p-value*** | *Fcrit* |
|---|---|---|---|---|---|---|
| Between Groups | 0.21438 | 11 | 0.01949 | 1.10181 | **0.36692** | 1.87839 |
| Within Groups | 1.91035 | 108 | 0.01769 | | | |
| | | | | | | |
| Total | 2.12473 | 119 | | | | |

### ***Difference of Friction Coefficient between different deicers***

The single factor ANOVA revealed that there was no statistically significant difference across the friction coefficients of different deicer groups (#1 to #9), given that the p-value of 0.361466 was much higher than 0.05 (Table 3.10). However, if we add in the control group (#ND), the p-value was sharply reduced to 7.68E-05. This very low p-value suggests that the friction coefficients on pavements differed considerably between those treated by the deicers and those not treated by any chemical.

***Table 3.10 Statistical analysis of friction coefficient for different deicers: (a) summary of the experiment results; and (b) ANOVA analysis results***

(a)

| *Groups* | *Count* | *Sum* | *Average* | *Variance* |
|---|---|---|---|---|
| #1 | 12 | 5.71873 | 0.47656 | 0.0259 |
| #2 | 12 | 6.11509 | 0.50959 | 0.00436 |
| #3 | 12 | 5.46209 | 0.45517 | 0.01978 |
| #4 | 12 | 5.21401 | 0.4345 | 0.02946 |
| #5 | 12 | 6.13933 | 0.51161 | 0.00997 |
| #6 | 12 | 5.54336 | 0.46195 | 0.00858 |
| #7 | 12 | 5.147 | 0.42892 | 0.01058 |
| #8 | 12 | 4.7378 | 0.39482 | 0.0162 |
| #9 | 12 | 5.59041 | 0.46587 | 0.0126 |

(b)

| *Source of Variation* | *SS* | *df* | *MS* | *F* | ***p-value*** | *Fcrit* |
|---|---|---|---|---|---|---|
| Between Groups | 0.13589 | 8 | 0.01699 | 1.11252 | **0.36147** | 2.0333 |
| Within Groups | 1.5115 | 99 | 0.01527 | | | |
| | | | | | | |
| Total | 1.64739 | 107 | | | | |

Figures 3.20 and 3.21 reveal that**,** for both pavement A and pavement C, the no-deicer pavement surfaces achieved the highest friction between the pavement surface and tires (~26 minutes after deicer application and then thorough removal of compacted snow and ice by plowing). This differs from the scenario in the field environment, where the deiced pavement surfaces tend to result in higher (instead of lower) friction coefficients. *One possible reason* is that the deicer application rate of 200 lbs per lane-mile for a pavement temperature of 25°F was somewhat low and the amount of time the deicer was allowed to work (approximately 30 minutes) was insufficient, both of which resulted in the refreezing (i.e., presence of residual ice) on the pavement surface. *Another possible reason* is that the last step of the FOT, plowing, aimed to remove all the removable snow/ice from the pavement, instead of implementing a consistent plowing force and frequency. In the field operations, due to the higher ice/pavement bond strength in the case of no-deicer pavements, the plowing operation generally fails to remove all the removable snow/ice from the pavement and thus results in a significantly lower friction coefficient. Arguably, the FOT in this study simulated a scenario not yet common in the field operations, where the mechanical removal is highly effective (due to the use of higher force and

frequency). In this scenario, even though the application of the deicers effectively reduced the ice/pavement bond strength, it ended up reducing the friction on the pavement surface (possibly due to refreezing or the presence of organic compounds).

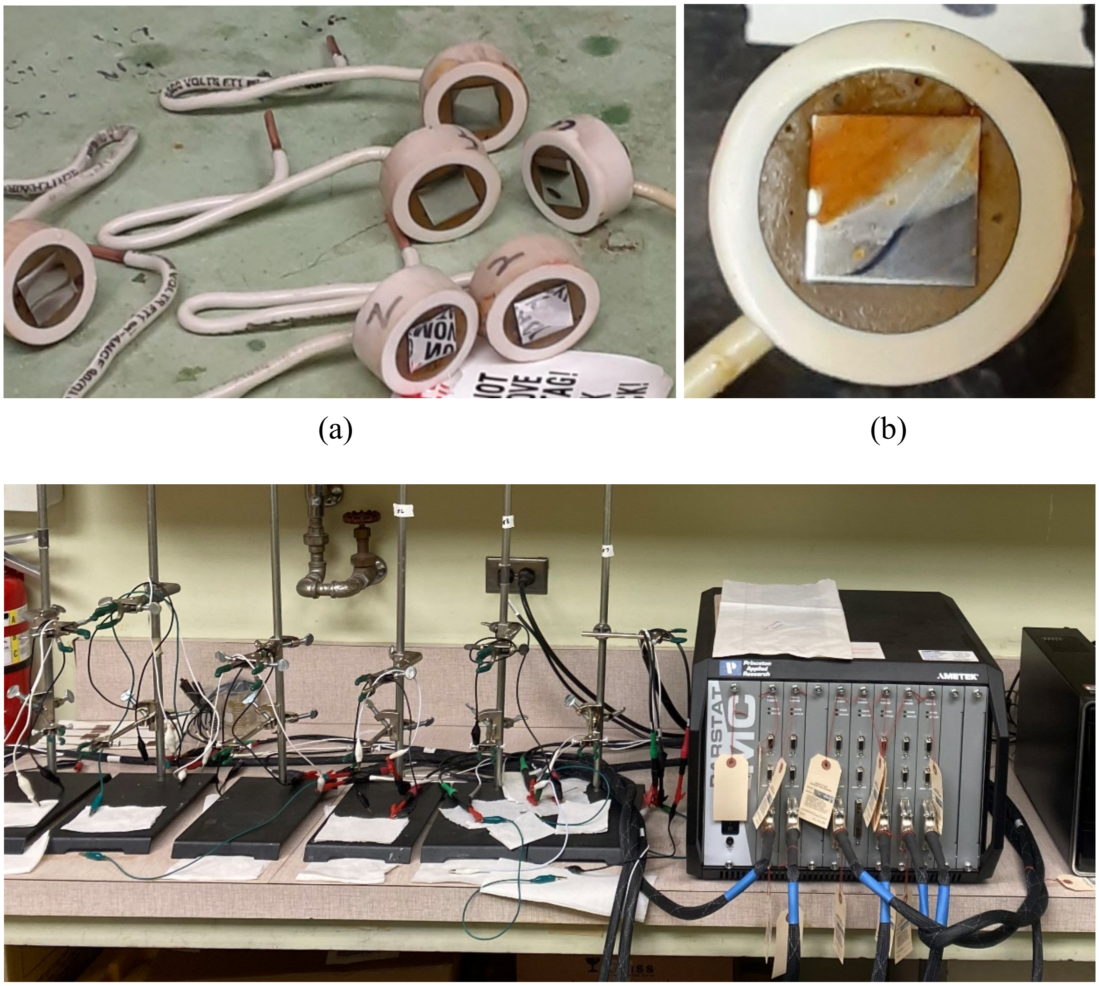
### 3.2.6 Corrosion of Deicer to Carbon Steel

The purpose of this test is to quantify the corrosive effect of deicers to carbon steel; the higher the corrosion rate, the less desirable a deicer is. Specifically, the corrosion rate of the carbon steel samples in diluted deicer solution is measured according to ASTM C1010, using linear polarization resistance (LPR) method via a multichannel potentiostat. In this method steel (AISI C1010) samples/coupons of size 1 x 1 $cm^2$ were soldered to a conductive wire (copper wire) and then transformed into metallography samples after filling of silicon gel (hardened) within a plastic ring mold; as shown in Figure 3.22. These samples were then ground from 400 to 1200 and polished from 1500 to 3000 grit size SiC papers. In some instances, the samples needed less hard griding and therefore only 800 and above grit size papers were used. Grinding and polishing was conducted manually by hand using good quality SiC waterproof papers, as shown in Figure 3.23. Samples had almost mirror like surfaces after the final stage of polishing in which 3000 grit size paper was used, as shown in Figure 3.24a. After the polishing stage, samples were swabbed with cotton using ethyl alcohol and finally washed with deionized (DI) water followed by air-drying.

***Figure 3.22 Steel coupons (soldered) encased within a polymer ring using epoxy adhesive***

Depending on the desired accuracy of results, test was run either as triplicate or even with 6 samples at a time for a single deicer’s corrosion rate measurements. Right after the sample preparation (grinding & polishing + drying), they left fully dipped in 100 mL of 3 wt. % solutions of deicers under consideration, for 24 hours.

*Figure 3.23 Grinding Papers – grit sizes from 600 to 3000 were used for sample preparations*



(a)

(b)

(c)

***Figure 3.24 Experimental details for corrosion of deicer to carbon steel: (a) The mirrorlike surface of steel coupons after wet fine grinding; (b) sample after LPR; and (c) multichannel potentiostat.***

After 24 hours of immersion in solution, electrodes (Ag/AgCl reference electrode, platinum counter electrode and samples as working electrode) were put in the beakers while samples still dipped in. The samples and electrodes were then connected to the circuits one by one to run the triplicate LPR test. The data obtained from the LPR test was directly recorded in computer via software program. The sample for deicer #9 looked like as shown in Figure 3.19b, after the LPR process was completed using a multichannel potentiostat (Figure 3.19c).

Based on the LPR and open circuit potential (OCP) measurements, the software program was able to calculate the corrosion rate (CR) for specific deicers on steel surface. Based on the CRs for several deicers used, compiled results are shown in Table 3.11. As it can be seen from results, deicer sample # 4 showed least corrosive behavior towards the carbon steel. Moreover, Brine treated rock salt (# 2) turned out to be the most corrosive deicer, relative to other chloride salt-based deicers.

***Table 3.11 The corrosion rates in mils per year (mpy) and OCP-values for deicers tested***

| **Deicer No.** | **Deicers (3 wt.%)** | **OCP, mean** | **Corrosion Rates, (mpy)** |
|---|---|---|---|
| #1 | Rock Salt (baseline) | -635.66 | 8.848 |
| #2 | Brine Treated Rock Salt | -641.85 | 11.426 |
| #3 | “Snow Slicer” Treated Rock Salt | -648.77 | 9.872 |
| #4 | “Ice Ban” Treated Rock Salt | -623.10 | 6.90 |
| #5 | “Clear Lane” Produce | -640.65 | 8.164 |
| #6 | Calcium Chloride (pellets) Treated Rock Salt | -644.69 | 8.673 |
| #7 | Calcium Chloride (liquid) Treated Rock Salt | -616.78 | 8.779 |
| #8 | Beet Juice Treated Rock Salt | -635.67 | 9.849 |
| #9 | “Top Film” with Calcium Chloride Treated Rock Salt | -602.27 | 7.646 |

The single factor ANOVA (i.e., analysis of variance) revealed that there were statistically significant differences between the corrosion rates of steel in the different types of diluted deicer solutions, given that the p-value of 2.3E-06 was considerably lower than 0.05 (Table 3.12). In other words, a p-value of 0.05 or lower corresponds to a statistically significant difference between the two groups of data (with confidence level of 95% or higher).

*Table 3.12 Statistical analysis of corrosion rate for different deicers: (a) summary of the experiment results; and (b) ANOVA analysis results*

(a)

| *Groups* | *Count* | *Sum* | *Average* | *Variance* |
|---|---|---|---|---|
| #1 | 3 | 26.544 | 8.848 | 0.947173 |
| #2 | 5 | 57.134 | 11.4268 | 1.723801 |
| #3 | 6 | 59.232 | 9.872 | 1.1573 |
| #4 | 3 | 20.7 | 6.9 | 0.957936 |
| #5 | 6 | 48.9851 | 8.164183 | 0.967411 |
| #6 | 6 | 52.039 | 8.673167 | 0.582364 |
| #7 | 3 | 26.337 | 8.779 | 0.895921 |
| #8 | 3 | 29.546 | 9.848667 | 0.938008 |
| #9 | 6 | 45.877 | 7.646167 | 0.234379 |

(b)

| *Source of Variation* | *SS* | *df* | *MS* | *F* | ***p-value*** | *Fcrit* |
|---|---|---|---|---|---|---|
| Between Groups | 65.27965 | 8 | 8.159957 | 8.97915 | **2.3E-06** | 2.244396 |
| Within Groups | 29.08055 | 32 | 0.908767 | | | |
| Total | 94.3602 | 40 | | | | |

### 3.2.7 BOD Measurements

The purpose of this test was to quantify the environmental effects of deicers to species in soil and water bodies; the higher the BOD (biological oxygen demand), the less desirable a deicer was. WSU used BOD to quantify the difference in depleted oxygen levels in various diluted deicers (3 wt. % solutions made from each solid deicer), from day 0 to day 5. Each deicer (3 wt. % solution) was diluted with aerated DI water, already having chlorides and sulfates and phosphates (chemical compounds) and then left in the incubator for five days; after its dissolved oxygen was measured manually using specific equipment. Dissolved oxygen was measured again after the five days period was completed. Details of the procedure are further explained in this section.

BOD test was conducted to determine whether a certain discharge of a product (mostly chemical products) would be harmful to marine life in streams, rivers and oceans or not. This test quantified the amount of oxygen that was depleted from a sample in five days of incubation time, with the sample tightly contained in a bottle. The higher the amount of depleted oxygen, the greater the risk a deicer sample would pose to aquatic species in water bodies adjacent to the road, after the deicer was applied onto the road surface for the benefit of safety and mobility. It is known that deicers would reach the underground water, to rivers or may even to oceans, after their use on roads and pavements. The following provides a brief description of the BOD measurement procedure:

1. Deionized (DI) water should be used in BOD testing procedure, and the first step is to aerate the DI water for good amount of time, to make sure plenty of oxygen is added to the clean DI water.
2. Chloride, Sulfate based chemicals with a certain weight/volume percentage are to be added in the aerated DI water. Phosphate buffer is also added to it. These chemicals and their compositions are given below in the Table 3.13.
3. Add 1mL/L of each Calcium Chloride ($CaCl_2$), Ferric Chloride ($FeCl_3$), Magnesium Sulfate ($MgSO_4$) and Phosphate buffer solution to the aerated DI water. Shake the container after adding all chemicals to DI water to make sure adequate mixing of oxygen and chemicals in water.
4. Make a control of 300 mL aerated DI water, mixed with all the chemicals in it. The temperature of control, the samples that are needed to be tested, and the surrounding (lab temperature) must all be around $22 \pm 1^{o}C$. Temperature of the incubator should also be same.
5. Use a dilution ratio for the samples to be tested. In this case, there were 9 solid based deicers (as mentioned in the Table 3.1). Each deicer had a 3 wt. % composition (3 g of deicer in 97 g of DI water) and was further diluted at a dilution rate of 45mL of 3 wt. % deicer solution / 300mL of prepared DI water (aerated and chemically infused). This gives a dilution ratio value of 0.15.
6. Prepare three samples of each diluted deicer solution in three different bottles. For 9 deicers, 27 samples would be required in total. As an approximation, 8100 mL (8.1 L) of DI water would be required for testing all 9 deicers.
7. Clean the probe of dissolved oxygen (DO) meter (as shown in Figure 3.25) with normal DI water and calibrate it well before the testing begins.
8. Measure the DO for the control first, while stirring it at a constant speed of 9 (magnetic stirring). Label the bottle and close it tightly with least amounts of bubbles in it. To make sure least bubble formation, fill the bottle a little extra and then insert the cap to make the sample flow out a little, making it filled all the way to the top with diluted deicer solution. Also, to avoid faulty readings for DO, make sure there are no bubble formation right in front of the testing probe of the meter (inserted fully in the sample being stirred).

*Figure 3.25 DO Meter used in BOD measurements*

9. Next measure the DO for each sample (3 for one deicer solution) by using same method as listed above. If all samples are even and have same dilution ratios, the reading should match quite a bit for all three samples of each deicer solution. Label each sample bottle for one deicer solution as $A_0$, $B_0$ and $C_0$.
10. Repeat the procedure with all the samples of all the deicer solutions. Label all properly and make sure all the bottles ate tightly closed with least amounts of bubbles trapped inside.
11. Place a plastic cap on the top of each bottle before placing them all in the incubator.
12. Check the temperature of the incubator before placing all the samples in it. It should be 22 ± 1 $^{o}$C. Place all samples in the incubator for 5 days ± 4 hours.
13. After incubation time, take the samples out of incubator and measure the DO for all the samples again and record the readings as $A_5$, $B_5$ and $C_5$ for 3 samples of each deicer solution.
14. The aim is to find the depleted oxygen from the samples after 5 days of time. This is done by subtracting $A_5$ from $A_0$. BOD is calculated by dividing the depleted oxygen with dilution ratio (in this case 0.15).
15. Tabulated results as show in Table 3.14. As can be seen, mixes #1 and #4 have the lowest BOD with values below 1 mg/L and Mix #9 has the highest BOD 49.53 mg/L.

*Table 3.13 The weight/volume percentages and amounts of chemicals added to aerated DI water.*

| Chemicals Used | Compositions / Dilution percentages |
|---|---|
| Ferric Chloride ($FeCl_3.6H_2O$) | 0.25 g in 1L of DI water (0.025 w/v %) |
| Calcium Chloride ($CaCl_2$) | 27.5 g in 1L DI water (2.75 w/v %) |
| Magnesium Sulfate ($MgSO_4.7H_2O$) | 22.5 g in 1L of DI water (2.25 w/v%) |
| Phosphate Buffer | Dissolve 8.5 g of $KH_2PO_4$, 21.8 g of $KH_PO_4$, 33.4 g of $Na_2HPO_4 \cdot 7H_2O$, and 1.7 g of $NH_4Cl$ in about 500 mL of deionized water. Dilute to 1L |

*Table 3.14 The results from BOD tests for all deicer samples*

(a) DI water blanks/control

| Sample No. | Initial DO readings for three samples ($A_0$) (mg/L) | Final DO readings for three samples ($A_5$) (mg/L) | BOD* (mean) ($A_0$-$A_5$), (mg/L) | S.D.* | Standard Error |
|---|---|---|---|---|---|
| | $A_0$ | $A_5$ | | | |
| 1 | 8.16 | 7.95 | 0.21 | --- | --- |
| 2 | 7.79 | 7.19 | 0.6 | --- | --- |
| 3 | 8.40 | 8.14 | 0.26 | --- | --- |

(b) Deicer Solutions (3 wt. %) - Diluted Samples (deicer sample numbers used from Table 3.1)

| Sample No. | Initial Reading ($A_0$) (mg/L) | Initial readings ($B_0$) (mg/L) | Initial readings ($C_0$) (mg/L) | Final reading ($A_5$) (mg/L) | Final readings ($C_5$) (mg/L) | Final readings ($A_5$) (mg/L) | BOD (mean) ($A_0$-$A_5$) / 0.15 (mg/L) | S.D.** | Std. Error |
|---|---|---|---|---|---|---|---|---|---|
| #1 | 8.07 | 8.05 | 8.11 | 8.03 | 7.92 | 7.89 | 0.87 | 0.6 | 0.35 |
| #2 | 7.57 | 7.57 | 7.6 | 7.18 | 7.19 | 7.16 | 2.7 | 0.21 | 0.12 |
| #3 | 7.97 | 8.04 | 8.11 | 7.06 | 6.55 | 6.53 | 8.84 | 2.42 | 1.40 |
| #4 | 8.07 | 8.14 | 8.12 | 7.95 | 7.91 | 8.05 | 0.93 | 0.54 | 0.31 |
| #5 | 8.15 | 8.06 | 8.11 | 7.43 | 7.66 | 7.74 | 3.31 | 1.29 | 0.74 |
| #6 | 8.03 | 8.03 | 8.04 | 7.78 | 7.77 | 7.75 | 1.78 | 0.14 | 0.08 |
| #7 | 8.08 | 8.1 | 8.11 | 7.73 | 7.77 | 7.76 | 2.29 | 0.07 | 0.04 |
| #8 | 7.61 | 7.58 | 7.6 | 3.83 | 3.77 | 3.82 | 25.27 | 0.11 | 0.06 |
| #9 | 7.57 | 7.55 | 7.57 | 0.17 | 0.12 | 0.11 | 49.53 | 0.2 | 0.11 |
| a*** | 7.57 | 7.5 | 7.57 | 7.15 | 7.15 | 7.16 | 2.76 | 0.038 | 0.02 |

**BOD measurement for control does not has any division by the dilution factor.*
***S.D. is the standard deviation.*
****a is NaCl crystals (3 wt. %) solution.*

*Note that results of #9 was significantly different from those of the other deicers. But even after repeating for all three duplicates twice, similar results were obtained. This could be because of the composition of the commercial deicer (Top Film) added to the rock salt, which likely consists of organic compounds that cause more oxygen depletion the BOD test.*

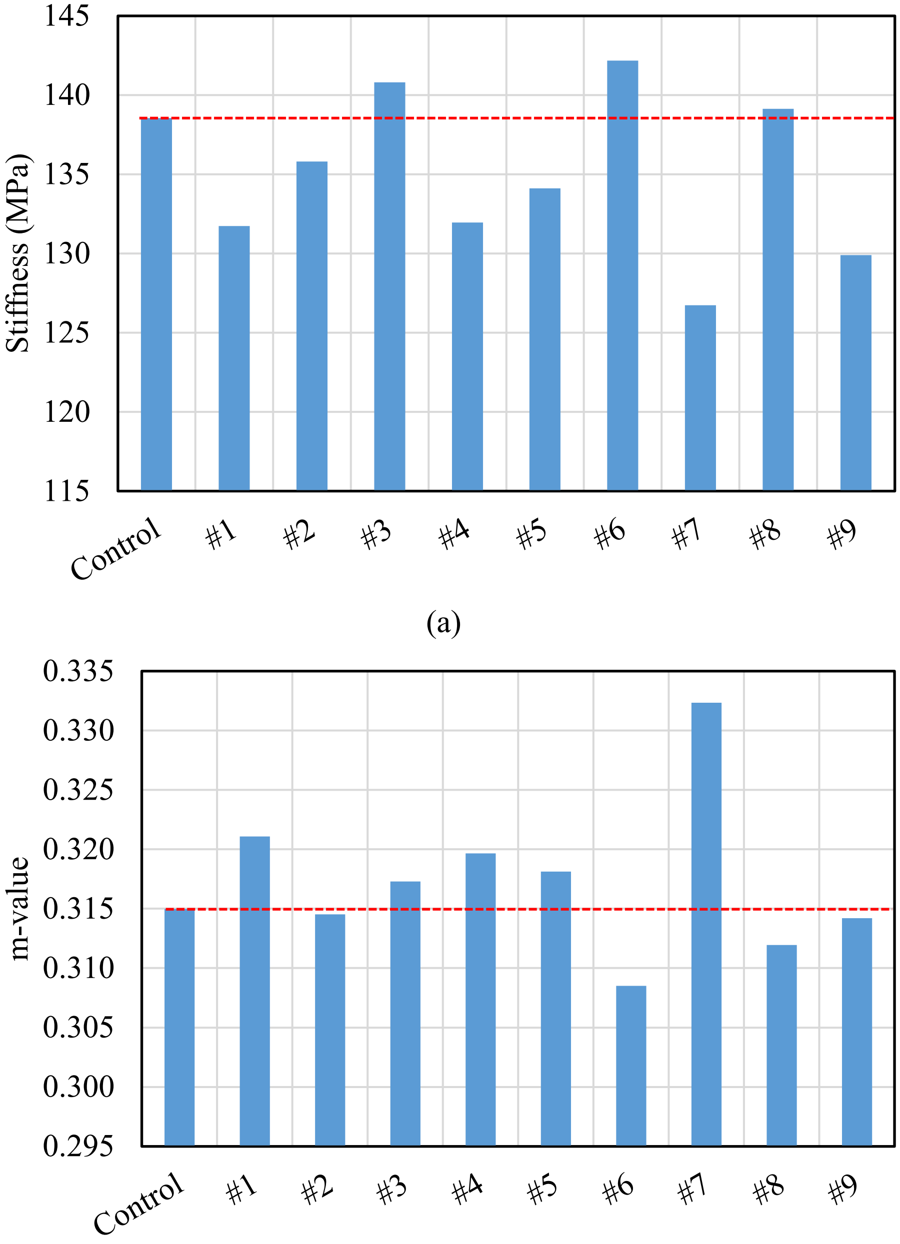
### 3.2.8 Low-Temperature Behavior of Asphalt Binder and Mixture Affected by Deicer

#### ***Asphalt Binder***

The purpose of this test was to quantify the effects of deicers on the low-temperature performance of asphalt binder. A typical asphalt binder PG 64-24 used in Missouri was studied. The rolling thin film oven (RTFO) test was conducted to simulate the effect of short-term aging during mixing and construction, according to AASHTO T 240. The pressure-aging vessel (PAV) test was conducted to simulate the effect of long-term aging. The PAV aging tests were conducted on RTFO residues at elevated temperature of 100°C and pressure of 2070 kPa for 20 hours according to AASHTO R28.

10 mL of deicer solution (9% by weight) was added to each 30 g of the PAV aged PG 64-40 binder. The mix (deicer solution and aged binder) was heated in a vacuum oven at 80°C for 1 h, and 150°C for 2 h in atmospheric pressure. The processed binder was then be used for BBR test. The BBR tests were conducted on deicer solution treated PAV aged PG 64-24 at -12°C to obtain stiffness (S) and m-value, which was defined as the rate of change of stiffness with time, according to AASHTO T 313. Superpave specified that the measured S value at 60 seconds must be less than 300 MPa and the m-value at this time of loading must be at least 0.30. For the test, a sample of asphalt binder was molded into a beam measuring 6.25 x 12.5 x 127 mm. This sample was then simply supported at two points 102 mm apart in a controlled temperature fluid bath. The beam was then loaded at the midpoint by a 100 g load that, under normal gravity conditions, produces 0.98 N of force. By using the Simple Beam theory, the stiffness and m-value were determined. The BBR tests were done on two beam samples.

Figure 3.26 presents the BBR stiffness and m-value results of the asphalt binders treated by various deicer solutions (9% by weight). As shown in Figure 3.26 (a), the stiffness of the asphalt binder at low temperature decreased after treating with deicer solutions (except for products #3 ("Snow Slicer" treated rock salt), #6 (calcium chloride (flake/pellet) treated rock salt), and #8 (beet juice treated rock salt)). This is beneficial to the low-temperature performance of asphalt binder. However, the asphalt binders treated by the products #3, #6, and #8 showed higher stiffness than the control binder (without treated) at low-temperature. As shown in Figure 3.26 (b), the asphalt binders treated by the products #2, #6, #8, and #9 showed lower m-value than the control binder, while the asphalt binders treated by the other products showed higher m-value than the control binder. Among all the studied deicer solutions, the asphalt binder treated by the product #6 (calcium chloride (flake/pellet) treated rock salt) showed higher stiffness while lower m-value than the control binder at low temperature, indicating the product #6 could bring negative effects on the low-temperature performance of asphalt binder. In sum, some of the deicer products (#6 and #8) showed degrading effects on the low-temperature performance of asphalt binder, indicating by the increased stiffness and lowered m-value. However, the asphalt binder treated by the product #7 (calcium chloride (liquid) treated rock salt) showed improved low-temperature performance with low stiffness and high m-value. Although the asphalt binder treated by the product #3 had higher stiffness than the controlled binder, it had higher m-value. Therefore, the effects of the product #3 on low-temperature performance of asphalt binder could not be identified by this test.



(a)

(b)

***Figure 3.26 The BBR results of asphalt binders treated by various deicer solutions: (a) Stiffness and (b) m-value***

***<u>Asphalt Mixture</u>***

*Creep Compliance Test*

For low-temperature performance of asphalt mixtures in the presence of liquid deicer, indirect tension test (IDT) was conducted according to AASHTO T322-07. Loose mixtures with PG 64-24 used in Missouri was collected. The IDT test specimens were fabricated using the Superpave gyratory compactor (SGC) according to AASHTO PP 60. The target air voids of testing specimens was 4.0 ± 0.5%. In order to produce the specimens for IDT tests, samples were compacted into gyratory cylinder with a diameter of 150 mm and a height of 70 mm, and then they were cut into 50 mm thick pieces using a masonry saw. Both ends were cut to ensure a more consistent air void distribution along the height of the test specimens. Studs for mounting linear variable differential transformers (LVDTs) were then attached to the IDT specimens using a gauge point fixing jig (Figure 3.27). Owing to the IDT creep compliance test was a non-destructive test, the specimens were firstly used for the creep compliance test, and then used for IDT tensile strength test which is a destructive test. The specimens were placed in the container with deicer solutions (9% by weight) for 48 hours before conducting IDT test.

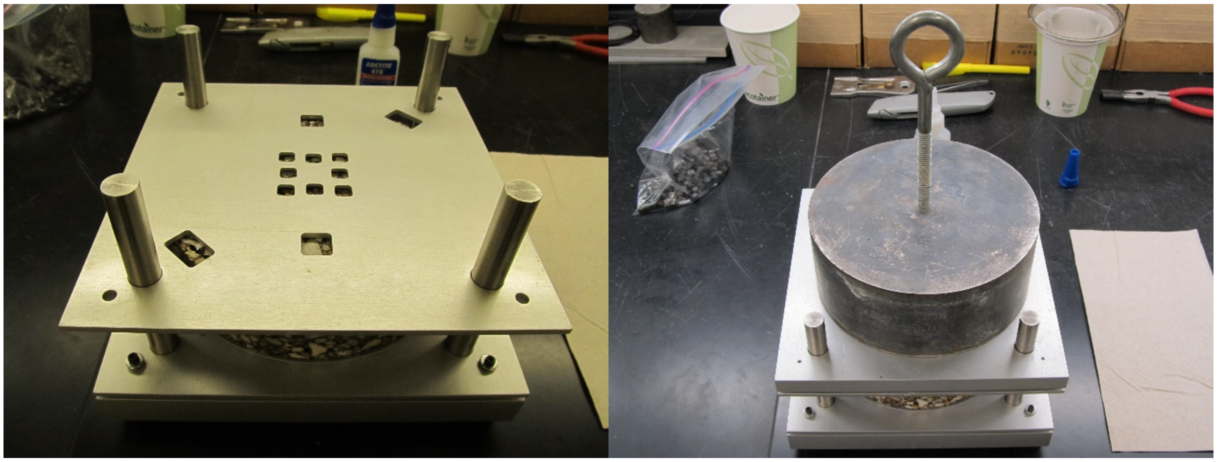


***Figure 3.27 Gauge point fixing jig***

Figure 3.28 shows the main equipment for IDT tests. The temperature chamber was MTS model 651.34. The temperature was controllable from -30 to +100°C, ±0.2°C. A programmed data acquisition system was used to record the load and deformation of the specimens during testing. The definition of creep compliance in AASHTO T 322 was “the time-dependent strain divided by the applied stress”. The test was conducted by imposing a static compressive load along a diametral axis of the cylindrical specimen at the target test temperature for about 100 seconds. Creep compliance testing was non-destructive, so each specimen could be tested at several temperatures. In this study, tests were conducted at three different temperatures (i.e., -20, -10, and 0°C). During the loading period, vertical and horizontal deformations were measured on the two parallel faces of the specimen using two LVDTs per specimen face. Three replicates were applied. The creep compliance of each mixture was calculated according to the function (Eq. 3.2) from AASHTO T 322.

$$D_t = \frac{\Delta X \times D_{avg} \times b_{avg}}{P_{avg} \times GL} \times C_{cmpl} \tag{3.2}$$

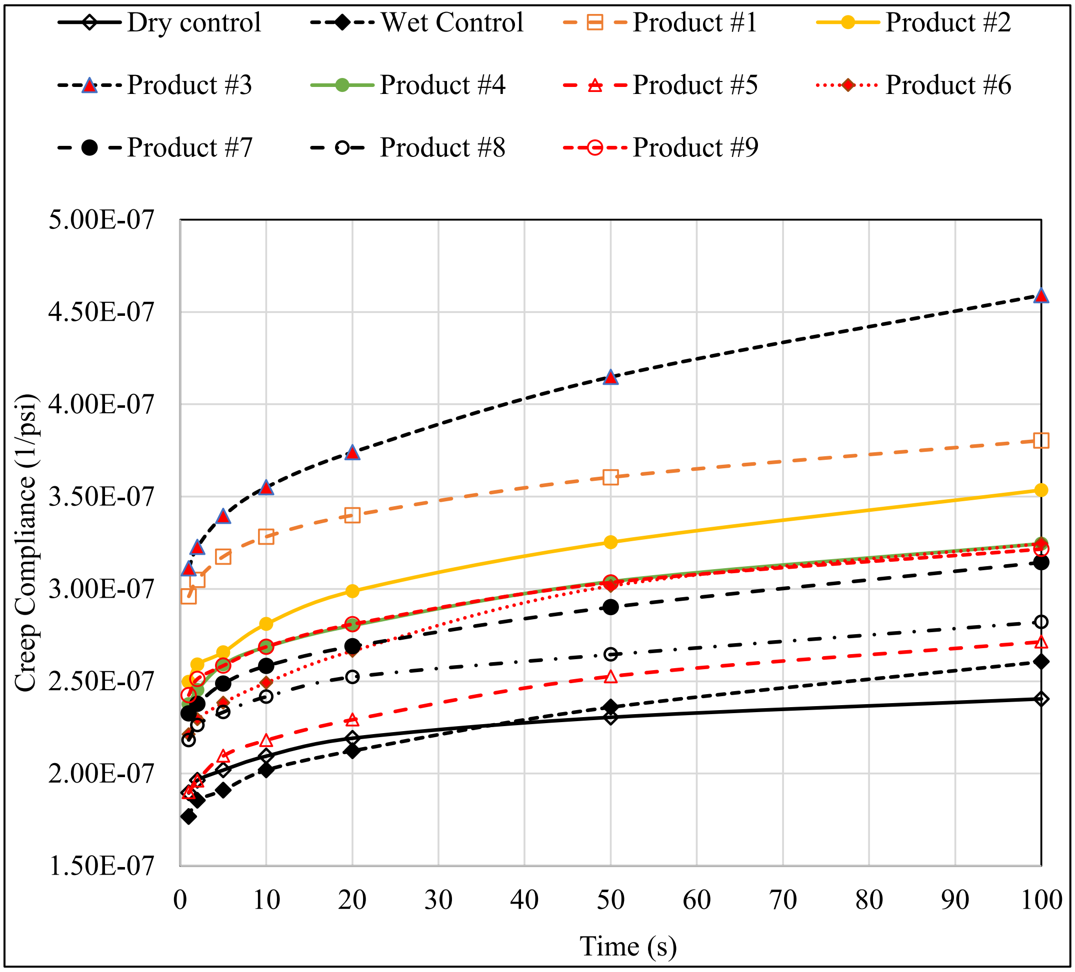
where, $D_t$ = creep compliance (1/kPa); $\Delta X$ = trimmed mean of the horizontal deformations (m), $D_{avg}$ = average specimen diameters (m); $b_{avg}$ = average specimen thickness (m); $P_{avg}$ = average force during the test (kN); GL = gage length (38mm); and $C_{cmpl}$ = creep compliance parameter at any given time, computed as:

$$C_{cmpl} = 0.6354 \times \left(\frac{X}{Y}\right)^{-1} - 0.332 \tag{3.3}$$

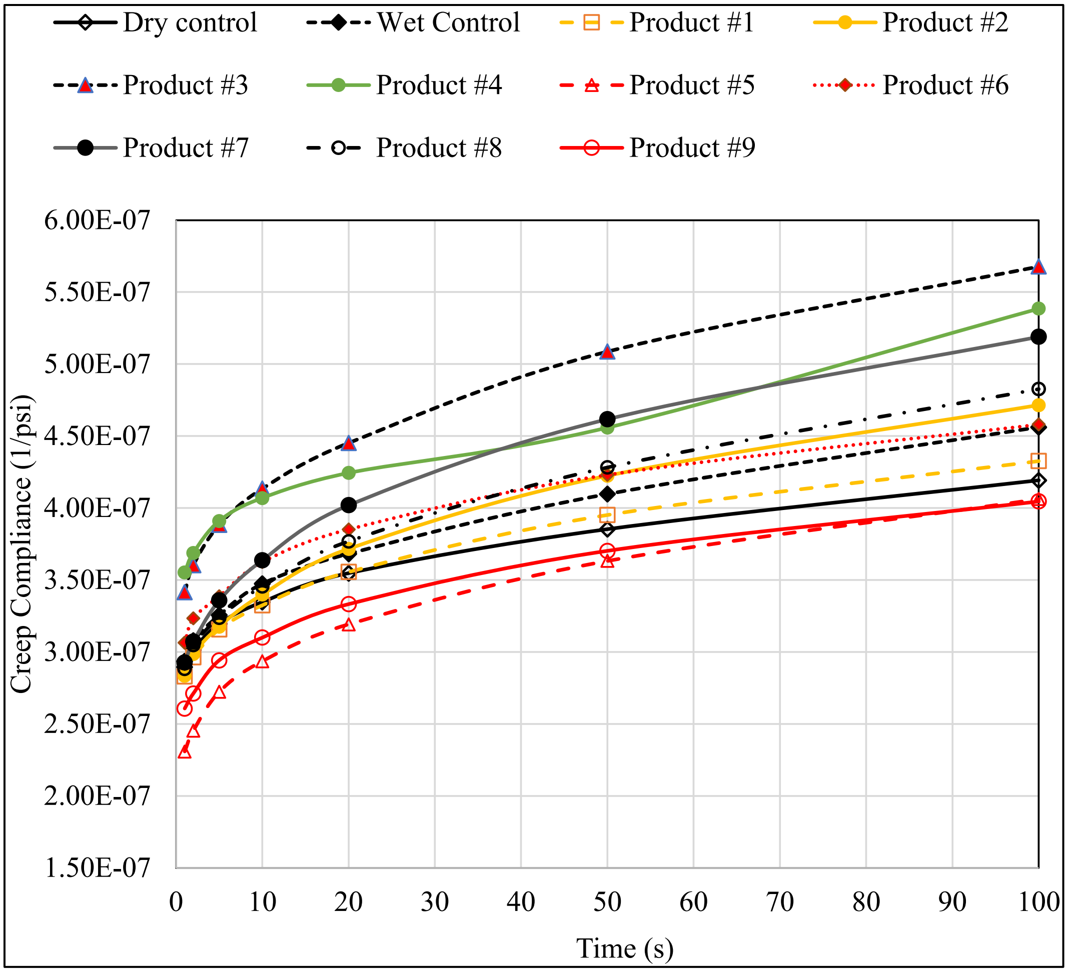
where, $\frac{X}{Y}$ = the ratio of the horizontal to vertical deformations.

*Figure 3.28 MTS for asphalt mixture IDT tests*

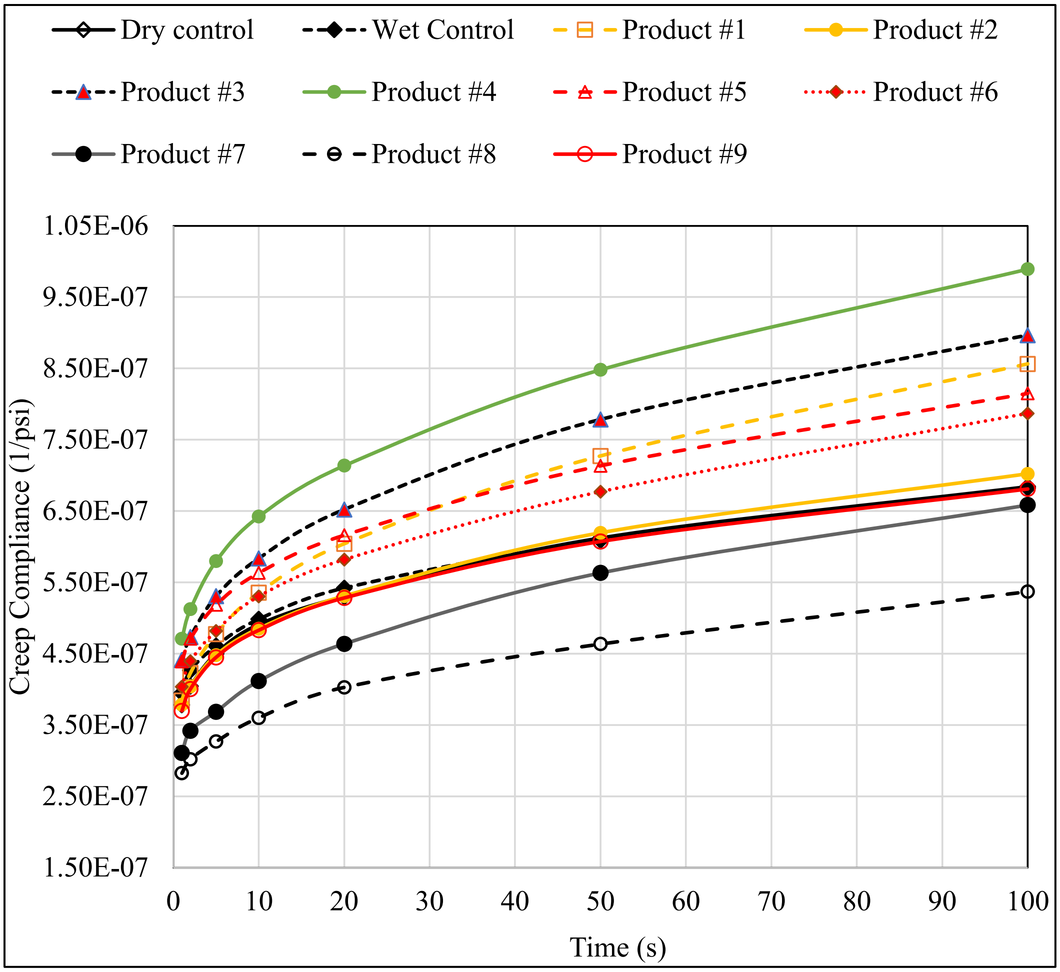
Figure 3.29 presents the IDT creep compliance results of asphalt mixture treated by different deicer solutions. Note that the "dry control" denotes the asphalt mixture sample was not treated by anything while the "wet control" denotes the asphalt mixture sample was treated by water instead of deicer solutions. The higher creep compliance value, the softer the mixture would be. As shown in Figure 3.29 (a), the water showed insignificant effects on the creep compliance (stiffness) of asphalt mixtures at -20°C, as the curves for the dry and wet control samples almost overlapped. It seemed that the deicer chemicals could softer the asphalt mixture at -20°C because the creep compliance of asphalt mixture increased after treated by the deicer chemicals. The product #3 ("Snow Slicer" treated rock salt) showed the most significant effect. The product #5 ("Clear Lane" product) slightly increased the creep compliance as compared to the control sample. However, mixed results were found at testing temperature of -10°C with some deicer chemicals increased the creep compliance while the others decreased that (Figure 3.29 (b)). The products #5 ("Clear Lane" product) and #9 ("Top Film" treated rock salt) slightly deceased the creep compliance values as compared to the dry control sample. The product #3 ("Snow Slicer" treated rock salt) also showed the most significant effect on the creep compliance at -10°C. At the testing temperature of 0°C, the products #2 (Rock salt – brine treated) and #9 ("Top Film" treated rock salt) had insignificant effect on the creep compliance of asphalt mixture.



(a)


Dry control
Wet Control
Product #1
Product #2
Product #3
Product #4
Product #5
Product #6
Product #7
Product #8
Product #9
Creep Compliance (1/psi)
6.00E-07
5.50E-07
5.00E-07
4.50E-07
4.00E-07
3.50E-07
3.00E-07
2.50E-07
2.00E-07
1.50E-07
0
10
20
30
40
50
60
70
80
90
100
Time (s)

(b)



(c)

***Figure 3.29 IDT creep compliance of asphalt mixtures treated by deicer solutions at various temperatures: (a) -20° C, (b) -10° C, and (c) 0° C***

Figure 3.30 presents the creep compliance of asphalt mixtures treated by various deicer solutions at a loading time of 50s to further illustrate the results. 50s is selected for the comparison because the tests reach a static status after this amount of loading time. As shown in this figure, at the testing temperature of -20°C, the deicer products seemed increase the creep compliance of asphalt mixture. At the testing temperatures of -10 and 0 °C (which are closer to the air temperature when deicer products applied in the field), products #2 and #9 showed similar creep compliance values to the wet control sample (treated with water only), implied that these two products had insignificant effects on the creep compliance of asphalt mixture. The products #7 (Calcium chloride (liquid) treated rock salt) and #8 (Beet juice treated rock salt) stiffened the asphalt mixture at 0°C. This may relate to good ice melting capacity of these two products at -4°C, which could result in less ice in the asphalt mixture.

The percentage changes of the creep compliance of asphalt mixtures (Eq. 3.4) treated by deicer solutions compared to the wet control are summarized in Table 3.15. Small change indicates mild effect on mixture properties from the deicers, which will be preferred by engineers.

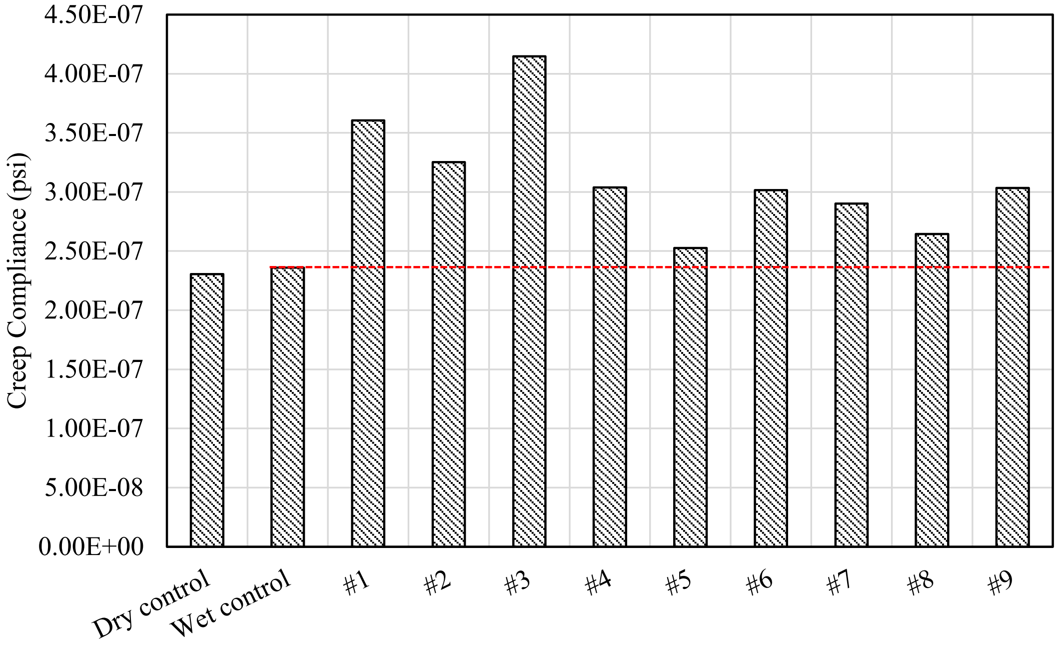
$$APC = \left|\frac{(A-B)}{B}\right| * 100 \quad (3.4)$$

where *APC* is the absolute percentage change of creep compliance (%), *A* is the creep compliance of asphalt mixture treated by deicer solution at 50s, and *B* is the creep compliance of the wet control sample (psi) at 50s (psi). As shown in this table, at -20°C, the absolute percentage change (*APC*) values for all the asphalt mixtures were higher than 10% except for #5. At 0 °C, products #2 and #9 showed *APC* values lower than 2%, implied that these two products had insignificant effects on the creep compliance of asphalt mixture.

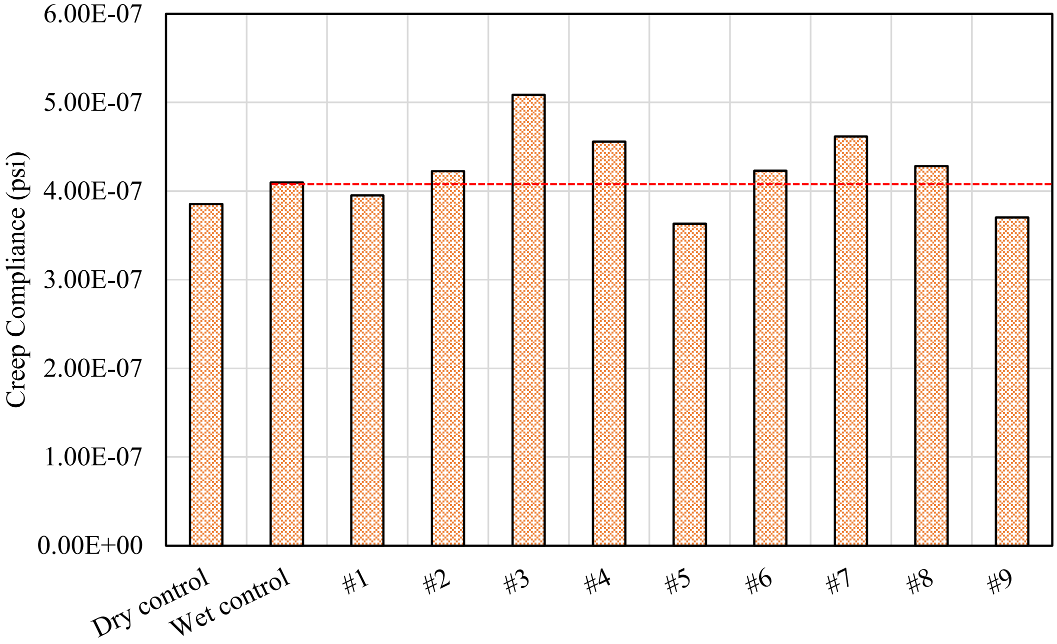
In sum, less/insignificant changes in creep compliance after deicer treatments would be ideal for deicer selections. In terms of the effects of deicer products on the creep compliance of asphalt mixture at low-temperatures, products #2 (Rock salt – brine treated) and #9 ("Top Film" treated rock salt) showed insignificant effects.

***Table 3.15 Absolute percentage change of creep compliance (APC) of asphalt mixtures treated by deicer solutions (%)***

| **Deicer Products** | **#1** | **#2** | **#3** | **#4** | **#5** | **#6** | **#7** | **#8** | **#9** |
|---|---|---|---|---|---|---|---|---|---|
| **-20 °C** | 52.7 | 37.8 | 75.8 | 28.8 | 7.1 | 27.8 | 22.9 | 12.1 | 28.6 |
| **-10 °C** | 3.5 | 3.1 | 24.2 | 11.3 | 11.3 | 3.3 | 12.7 | 4.5 | 9.6 |
| **0 °C** | 19.4 | 1.7 | 27.8 | 39.3 | 17.1 | 11.2 | 7.5 | 23.9 | 0.3 |



(a)



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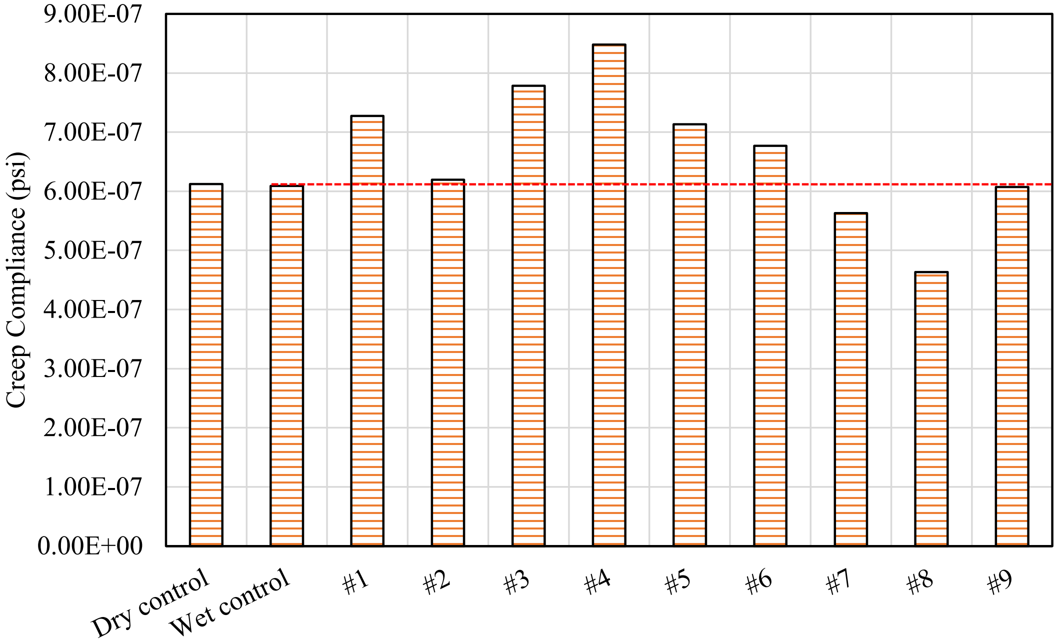


(c)

***Figure 3.30 IDT creep compliance of asphalt mixtures at time of 50s at various temperatures: (a) -20 ° C, (b) -10 ° C, and (c) 0 ° C***

*Indirect Tensile Strength*

Tensile strength was another important parameter for evaluating the low temperature cracking resistance of mixtures. Higher tensile strength at low temperatures indicated higher resistance to low temperature cracking. Unlike creep compliance test, the tensile strength test was destructive, i.e. the specimen was loaded until tensile failure occurs and could not be used again. The tests were conducted by applying a load to the specimens at a rate of 12.5 mm of vertical ram movement per minute and were conducted at the temperatures used for the creep test. The indirect tensile strength S was calculated using Equation 3.5.

$$S = \frac{2 \times P_{f,n}}{\pi \times b \times D} \tag{3.5}$$

where, $P_{f,n}$= failure (peak) load; b = specimen thickness; and D = specimen diameter.

Figure 3.31 illustrates the effects of deicer solutions on the IDT strength of asphalt mixture at -10°C. Generally, high IDT strength was desirable for asphalt mixture to resist low-temperature cracking. As shown in this figure, the wet control sample showed slightly lower IDT strength value than the dry control sample, indicating that the presence of water could degrade the low-temperature performance of asphalt mixture slightly. The products #1, #2, #4, and #6 degraded the IDT strength of asphalt mixture. The products #5, #7, #8, and #9 showed insignificant effects on the IDT strength of asphalt mixture. The product #3 ("Snow Slicer" treated rock salt) slightly increased the IDT strength as compared to the wet control sample.

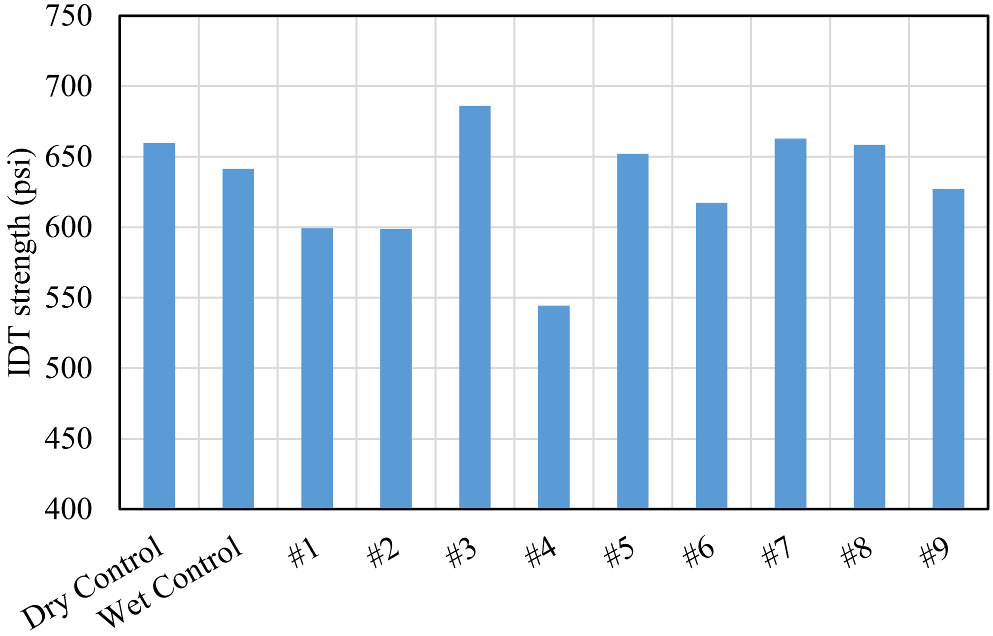


***Figure 3.31 DT strength of asphalt mixtures treated by deicer solutions at -10 ° C***

### 3.2.9 Freeze-Thaw Test of Concrete in the Presence of Deicer

#### ***Portland Cement Concrete (PCC)***

The freeze-thaw (F-T) test of PCC in the presence of deice solutions was conducted following ASTM C666. A mixture recommended by the MoDOT for rigid pavements was used (Sadati and Khayat 2016). This concrete was prepared with 323 kg/m$^3$ of cementitious materials that included 25% Class C fly ash, by mass, a water cement ratio (w/cm) of 0.40, and virgin aggregate. Crushed limestone with a maximum size of 25 mm was used for the virgin aggregate. Table 3.16 summarizes the mixture proportions and fresh properties of the concrete. The PCC beam samples were made in 3"x3"x16" (7.62 cm x 7.62 cm x 40.64 cm) molds for both control and samples with the presence of deicer solution. The samples were first cured for 14 days in a water bath and then subjected to F-T cycles either until 300 cycles occurred or until the relative dynamic modulus of elasticity reduced to 60% of the original modulus or lower. Instead of using thawing water as stated in ASTM C666, diluted deicer solution (9%, by weight) was used during the F-T cycles. Measurements before testing begun and then every 36 cycles thereafter were conducted including the mass of the sample and the frequency and velocity of an electrical pulse through the sample. The velocity was measured using a PROCEQ ultrasound with a frequency of 54 Hz (Figure 3.32(a)). Samples were kept in a temperature-controlled cabinet (Figure 3.32(b)) which exposed samples to freezing temperatures for four hours, followed by two hours of thawing. To calculate the relative dynamic modulus of elasticity (RDME), Equation 3.6 was used.

$$\mathrm{RDME}\ (\%) = \frac{\mathrm{v_n}^2}{\mathrm{v_0}^2} \tag{3.6}$$

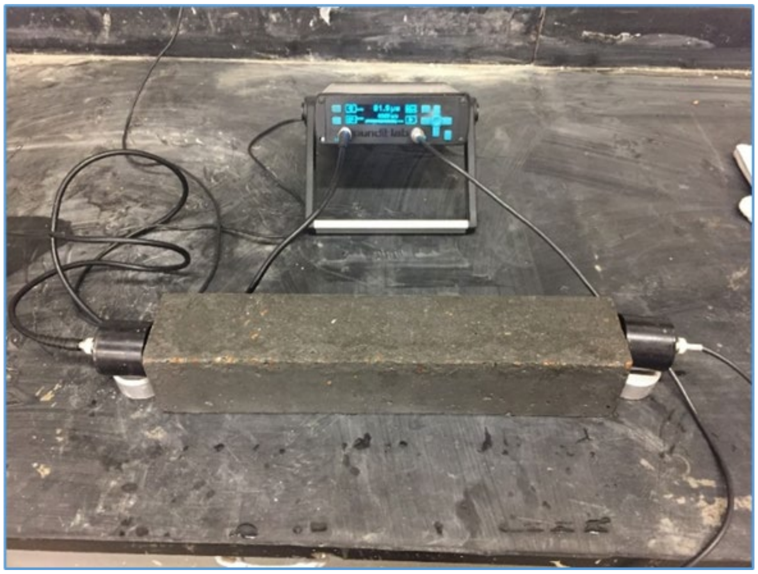
where, $v_0$ is the initial ultrasonic pulse velocity and $v_n$ is the ultrasonic pulse velocity at n cycles. The durability factor (DF) for each mixture was also determined using Equation 3.7.

$$\mathrm{DF} = \mathrm{RDME_f} \times \mathrm{n_f}/\mathrm{n_t} \tag{3.7}$$

where, $n_f$ is the cycles that the $RDME_f$ represents while $n_t$ is the cycles at which all testing was terminated, which in this case was 300 cycles. The $RDME_f$ represents either the RDME once it reaches 60% or lower, or the RDME after 300 cycles, whichever occurs sooner. The durability factor ranges from 0% to 100%. A higher durability factor suggests the sample has high resistance to F-T cycles. A lower durability factor indicates the sample’s durability is low and degraded quickly after many F-T cycles.

*Table 3.16 Mixture proportions and fresh properties of the PCC*

| Mixture proportions and properties | Value |
|---|---|
| Cementitious materials (kg/m$^3$) | 323 |
| Type I/II cement (kg/m$^3$) | 243 |
| Class C fly ash, by mass (%) | 25 |
| Class C fly ash (kg/m$^3$) | 81 |
| Water cementitious materials ratio (w/cm) | 0.4 |
| Water (kg/m$^3$) | 129 |
| Sand (kg/m$^3$) | 745 |
| Coarse virgin aggregate (kg/m$^3$) | 1121 |
| Air content (%) | 6±1% |
| Slump (mm) | 50 |



(a) Measuring frequency

(b) Freeze-thaw cabinet

*Figure 3.32 Freeze-thaw testing of PCC*

Table 3.17 presents the durability factor (DF) results of the PCCs with the presences of different dicer products. As shown in this table, the concrete beams treated with different deicer products showed similar DF values after 300 F-T cycles. All concrete beams had DF values higher than 90%, which indicated that the concrete beams (with the selected typical Missouri mix design) had good durability even with the presence of deicer products. No significant difference (on DF) could be found between the concrete beams with the presence of water and deicer products. The difference among the effects of different deicer products on DF values of concrete beams could not be identified since all concrete beams showed good durability. However, the surfaces of concrete beams were scaled after F-T cycles, as shown in Figure 3.33.

***Table 3.17 Durability factor results of the PCCs with the presences of different deicer products***

| Products | Durability Factor |
|---|---|
| Water | 96 ± 3 |
| Product #1 | 99 ± 3 |
| Product #2 | 98 ± 1 |
| Product #3 | 96 ± 4 |
| Product #4 | 98 ± 3 |
| Product #5 | 95 ± 6 |
| Product #6 | 97 ± 3 |
| Product #7 | 96 ± 5 |
| Product #8 | 97 ± 4 |
| Product #9 | 96 ± 3 |

*Figure 3.33 PCC beams after F-T cycles*

Although the concrete beams showed good DF results, the mass loss values of concrete beams with the presence of different deicer products varied (Figure 3.34), which indicated that the deicer products had different scaling effects on concrete beams. As shown in Figure 3.34, the concrete beams with the presence of the product #7 showed the lowest mass loss value than the other beams (even lower than those with the presence of water), indicating that the product #7 had little scaling effect on the concrete beams. The concrete beams with the presence of other deicer products (#2-#9) showed higher mass loss values than that of those with the presence of water. The concrete beams with the presence of product #2 showed the highest mass loss values.

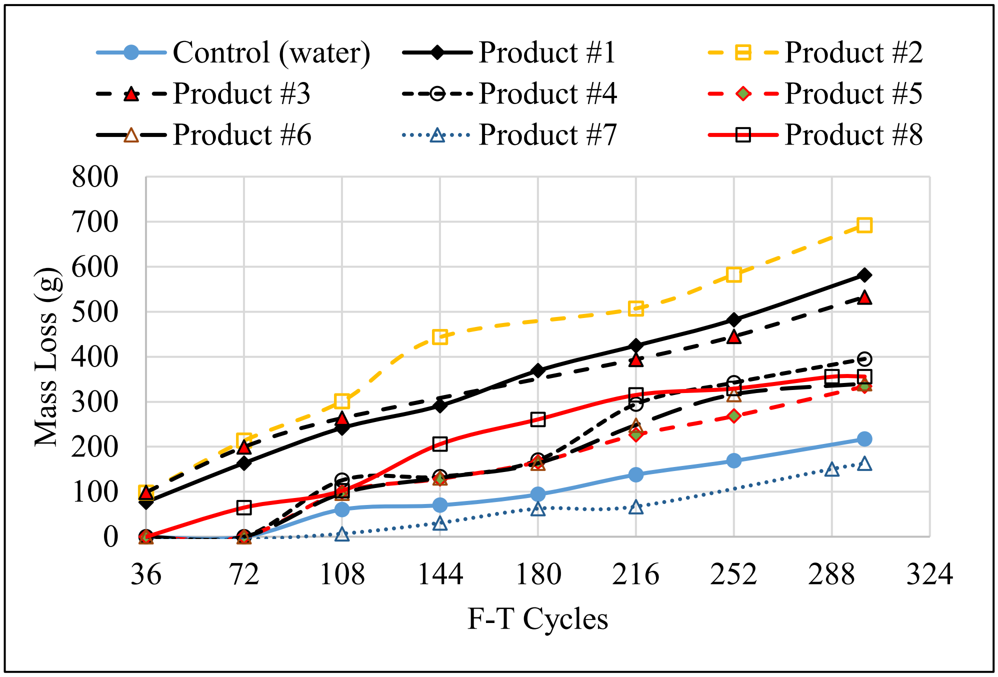


***Figure 3.34 Mass loss results of the PCCs with the presences of different deicer products***

***<u>Portland Cement Mortar (PCM)</u>***

For F-T tests of PCM, the SHRP H205.8 F-T cyclic test method with minor modifications was employed, and the mass loss (difference in mass before and after F-T cycles) was recorded. The PCM cylinder samples was made in 2” (diameter) × 4” (length) molds, using a mix design representative of MoDOT concrete mixes (Table 3.11). The prepared cylinders were cured for 24 hours in water before being placed in a temperature chamber with 100% relative humidity for 28 days. Then the dry weights of the samples were measured before being placed in plates, equipped with a sponge in their bottom, holding 560 mL of 9% deicer liquid (Figure 3.35). Plates with PCM cylinders were kept at -20.8 ± 0.2°C for about 2 h then at 23.2 ± 0.2°C for about another 2 h. Thirty F-T cycles were carried out. The scaled-off materials were removed from the samples, and they were air-dried overnight before recording the weight. Figure 3.36 presents the mass loss results of the PCM cylinders with the presence of different deicer solutions. As shown, the PCM cylinders showed little mass loss after subjecting to F-T cycles (less than 7 gram). These results indicated that the PCM cylinder with the typical Missouri mix design is resistant to F-T damages even with the presence of deicer solutions. Among all the cylinders, the PCM cylinders with the presence of product #9 showed the lowest mass loss value (similar to those with the presence of water), which implied that the product #9 had insignificant effect on the F-T resistance of PCM cylinders.

***Figure 3.35 F-T testing of PCM cylinders***

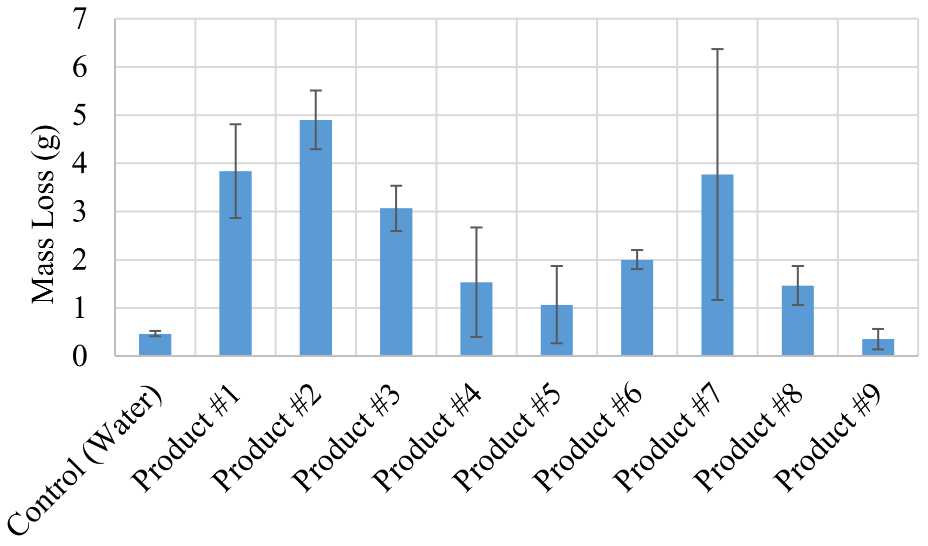


***Figure 3.36 Mass loss results of the PCM cylinders with the presences of different deicer products***

# CHAPTER 4 DEVELOPMENT OF EVALUATION MATRIX

In light of the findings from previous tasks, the team developed an evaluation matrix to assess the potential impacts (to the infrastructure, motor vehicles, and water bodies) under a holistic and multi-criteria framework. This evaluation matrix then was used to evaluate the tested deicer products (and designated combinations), taking into account the priorities of MoDOT stakeholders, and thus selected the “best” deicers to be deployed by MoDOT districts.

First, the following parameters was used as the quantifiable or measurable parameters for the deicer evaluation matrix: BOD, bond strength of asphalt pavement (bond strength (A)), bond strength of concrete pavement (bond strength (C)) friction coefficient after full ice removal (average of asphalt and concrete pavements), freezing point for 10 wt.% deicer, ice melting capacity (IMC) at 20 min, IMC at 60 min, corrosion rate, F/T mass loss (PCM), F/T mass loss (PCC), PCM splitting strength, asphalt stiffness, asphalt m-value, IDT strength of asphalt at -10°C, IDT creep compliance of asphalt average of -20°C, -10°C and 0°C. Subsequently, the multi-criteria decision support framework that developed in previous studies (Shi and Akin 2012; Shi et al. 2014; Jungwirth and Shi 2017) was adopted, which integrates the experimental data into a defensible decision-making process for selecting or formulating snow and ice control materials. The evaluation matrix was used to provide a comprehensive method to incorporate the multiple dimensions in comparing and selecting different deicer products.

Pairwise comparisons, shown in Table 4.1, were based on the fact that if the row parameter was considered more important than the column parameter, a number greater than 1 was assigned to the matrix based on the intensity of the importance. A higher number indicated greater importance. Conversely, if the parameter in the column was considered more important, the reciprocal of the non-zero value was determined in the matrix (Nazari and Shi 2019). The comparisons were used in a standardized matrix to determine the weights of importance of the decision criteria, as shown in Table 4.2. The standardized matrix was the result of the assigned value from Table 4.1 divided by the sum of the assigned values in the respective columns. For example, 1.00 from Row 2 Column 2 (BOD – BOD) in Table 4.1 divided by the sum of 7.24 in the last row and Column 2 of Table 4.1 were equal to 0.14 in Row 2 Column 2 of Table 4.2. A summary of the prioritization matrix is presented in Table 4.3, in which each column has been normalized, with 0 and 100 being the worst and best performer, respectively. Each decision weight in Table 4.3 was determined by calculating the average of the standardized rows in Table 4.2. For example, from Row 2 (BOD), the average of 0.14, 0.14, 0.14, 0.14, 0.14, 0.14, 0.13, 0.14, 0.14, 0.14, 0.14, 0.14, 0.14 and 0.14 was equal to 0.14. Based on the priorities set out in Table 4.3, the multi-criteria scoring matrix resulted in product #5 (“Clear Lane” product ) having the highest score with a score of 67.

## *Table 4.1 Pairwise comparisons based on multiple criteria.*

| Comparison | BOD | Bond strength (A) | Bond strength (C) | Friction coefficient | Freezing point | IMC at 20 min | IMC at 60 min | Corrosion rate | F/T mass loss (PCM) | F/T mass loss (PCC) | PCM splitting strength | Asphalt stiffness | Asphalt m-value | IDT strength of asphalt | IDT creep compliance of asphalt |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| BOD | 1.00 | 1.00 | 1.00 | 5.00 | 1.00 | 1.00 | 1.00 | 5.00 | 5.00 | 5.00 | 1.00 | 9.00 | 9.00 | 9.00 | 9.00 |
| Bond strength (A) | 1.00 | 1.00 | 1.00 | 5.00 | 1.00 | 1.00 | 1.00 | 5.00 | 5.00 | 5.00 | 1.00 | 9.00 | 9.00 | 9.00 | 9.00 |
| Bond strength (C) | 1.00 | 1.00 | 1.00 | 5.00 | 1.00 | 1.00 | 1.00 | 5.00 | 5.00 | 5.00 | 1.00 | 9.00 | 9.00 | 9.00 | 9.00 |
| Friction coefficient | 0.20 | 0.20 | 0.20 | 1.00 | 0.20 | 0.20 | 0.20 | 5.00 | 1.00 | 1.00 | 0.20 | 2.00 | 2.00 | 2.00 | 2.00 |
| Freezing point | 1.00 | 1.00 | 1.00 | 5.00 | 1.00 | 1.00 | 1.00 | 5.00 | 5.00 | 5.00 | 1.00 | 9.00 | 9.00 | 9.00 | 9.00 |
| IMC at 20 min | 1.00 | 1.00 | 1.00 | 5.00 | 1.00 | 1.00 | 1.00 | 5.00 | 5.00 | 5.00 | 1.00 | 9.00 | 9.00 | 9.00 | 9.00 |
| IMC at 60 min | 1.00 | 1.00 | 1.00 | 5.00 | 1.00 | 1.00 | 1.00 | 5.00 | 5.00 | 5.00 | 1.00 | 9.00 | 9.00 | 9.00 | 9.00 |
| Corrosion rate | 0.20 | 0.20 | 0.20 | 0.20 | 0.20 | 0.20 | 0.20 | 1.00 | 1.00 | 1.00 | 0.20 | 2.00 | 2.00 | 2.00 | 2.00 |
| F/T mass loss (PCM) | 0.20 | 0.20 | 0.20 | 1.00 | 0.20 | 0.20 | 0.20 | 1.00 | 1.00 | 1.00 | 0.20 | 2.00 | 2.00 | 2.00 | 2.00 |
| F/T mass loss (PCC) | 0.20 | 0.20 | 0.20 | 1.00 | 0.20 | 0.20 | 0.20 | 1.00 | 1.00 | 1.00 | 0.20 | 2.00 | 2.00 | 2.00 | 2.00 |
| PCM splitting strength | 1.00 | 1.00 | 1.00 | 5.00 | 1.00 | 1.00 | 1.00 | 5.00 | 5.00 | 5.00 | 1.00 | 9.00 | 9.00 | 9.00 | 9.00 |
| Asphalt stiffness | 0.11 | 0.11 | 0.11 | 0.50 | 0.11 | 0.11 | 0.11 | 0.50 | 0.50 | 0.50 | 0.11 | 1.00 | 1.00 | 1.00 | 1.00 |
| Asphalt m-value | 0.11 | 0.11 | 0.11 | 0.50 | 0.11 | 0.11 | 0.11 | 0.50 | 0.50 | 0.50 | 0.11 | 1.00 | 1.00 | 1.00 | 1.00 |
| IDT strength of asphalt | 0.11 | 0.11 | 0.11 | 0.50 | 0.11 | 0.11 | 0.11 | 0.50 | 0.50 | 0.50 | 0.11 | 1.00 | 1.00 | 1.00 | 1.00 |
| IDT creep compliance of asphalt | 0.11 | 0.11 | 0.11 | 0.50 | 0.11 | 0.11 | 0.11 | 0.50 | 0.50 | 0.50 | 0.11 | 1.00 | 1.00 | 1.00 | 1.00 |
| Sum | 8.24 | 8.24 | 8.24 | 40.20 | 8.24 | 8.24 | 8.24 | 45.00 | 41.00 | 41.00 | 8.24 | 75.00 | 75.00 | 75.00 | 75.00 |

### *Table 4.2 Standard matrix based on comparisons.*

| Comparison | BOD | Bond strength (A) | Bond strength (C) | Friction coefficient | Freezing point | IMC at 20 min | IMC at 60 min | Corrosion rate | F/T mass loss (PCM) | F/T mass loss (PCC) | PCM splitting strength | Asphalt stiffness | Asphalt m-value | IDT strength of asphalt | IDT creep compliance of asphalt | Weight |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| BOD | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 | 0.11 | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 |
| Bond strength (A) | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 | 0.11 | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 |
| Bond strength (C) | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 | 0.11 | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 |
| Friction coefficient | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.11 | 0.02 | 0.02 | 0.02 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 |
| Freezing point | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 | 0.11 | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 |
| IMC at 20 min | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 | 0.11 | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 |
| IMC at 60 min | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 | 0.11 | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 |
| Corrosion rate | 0.02 | 0.02 | 0.02 | 0.00 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.03 | 0.03 | 0.03 | 0.03 | 0.02 |
| F/T mass loss (PCM) | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.03 | 0.03 | 0.03 | 0.03 | 0.02 |
| F/T mass loss (PCC) | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.03 | 0.03 | 0.03 | 0.03 | 0.02 |
| PCM splitting strength | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 | 0.11 | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 |
| Asphalt stiffness | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 |
| Asphalt m-value | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 |
| IDT strength of asphalt | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 |
| IDT creep compliance of asphalt | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 |
| Sum | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |

*Table 4.3 Summary of the prioritization by weight factors*

| Evaluation Factors | BOD | Bond strength (A) | Bond strength (C) | Friction coefficient | Freezing point | IMC at 20 min | IMC at 60 min | Corrosion rate | F/T mass loss (PCM) | F/T mass loss (PCC) | PCM splitting strength | Asphalt stiffness | Asphalt m-value | IDT strength of asphalt | IDT creep compliance of asphalt | Score |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Weight Factor | 0.12 | 0.12 | 0.12 | 0.03 | 0.12 | 0.12 | 0.12 | 0.02 | 0.02 | 0.02 | 0.12 | 0.01 | 0.01 | 0.01 | 0.01 | NA[*] |
| Deicer #1 | 100.00 | 81.25 | 79.25 | 68.00 | 100.00 | 14.76 | 0.00 | 56.96 | 23.44 | 17.64 | 0.00 | 67.60 | 52.75 | 38.67 | 60.91 | 53 |
| Deicer #2 | 96.24 | 42.75 | 42.60 | 100.00 | 35.35 | 23.81 | 26.74 | 0.00 | 0.00 | 0.00 | 69.47 | 41.22 | 25.27 | 38.31 | 38.50 | 46 |
| Deicer #3 | 83.62 | 87.25 | 100.00 | 48.00 | 100.00 | 22.86 | 8.16 | 34.33 | 40.29 | 25.43 | 70.53 | 8.88 | 36.86 | 100.00 | 100.00 | 64 |
| Deicer #4 | 99.88 | 45.75 | 50.62 | 32.00 | 64.65 | 100.00 | 16.62 | 100.00 | 73.99 | 47.34 | 17.64 | 66.21 | 46.81 | 0.00 | 87.91 | 57 |
| Deicer #5 | 94.99 | 50.13 | 74.97 | 96.00 | 61.62 | 89.05 | 21.90 | 72.07 | 84.25 | 57.03 | 72.82 | 52.24 | 40.40 | 76.02 | 30.16 | 67 |
| Deicer #6 | 98.13 | 77.75 | 38.59 | 56.00 | 68.69 | 0.00 | 5.29 | 60.83 | 63.74 | 56.05 | 74.31 | 0.00 | 0.00 | 51.42 | 45.87 | 51 |
| Deicer #7 | 97.08 | 91.75 | 0.00 | 28.00 | 44.44 | 59.52 | 100.00 | 58.48 | 24.91 | 84.22 | 78.52 | 100.00 | 100.00 | 83.65 | 23.36 | 66 |
| Deicer #8 | 49.86 | 0.00 | 71.51 | 0.00 | 0.00 | 42.86 | 85.05 | 34.84 | 75.46 | 53.55 | 100.00 | 19.71 | 14.50 | 80.42 | 0.00 | 48 |
| Deicer #9 | 0.00 | 100.00 | 37.48 | 60.00 | 46.46 | 55.24 | 75.83 | 83.52 | 100.00 | 100.00 | 78.66 | 79.46 | 23.89 | 58.37 | 25.13 | 59 |

*NA = not applicable

# CHAPTER 5 CONCLUSIONS AND RECOMMENDATIONS

This study conducted a comprehensive and quantitative evaluation of snow and ice control chemicals currently used by various MoDOT districts for highway maintenance operations based on laboratory tests. The infrastructure impacts of products on pavement structures, and performance characteristics were assessed. Based on the testing results and analysis, the following conclusions can be drawn:

- The deicer products (solution, 9% by weight) evaluated are not too basic or too acidic with pH values ranged from 7.84 to 8.54.
- The products #7, #8, #9 (which are calcium chloride (liquid) treated rock salt, beet juice treated rock salt, and “Top Film” treated rock salt, respectively) showed better ice melting capacities than the other evaluated products. The product #6 which is the calcium chloride (flake/pellet) treated rock salt showed the lowest ice melting capacity. The product #7 (calcium chloride (liquid) treated rock salt) showed the best ice melting capacity among all the studied products.
- The asphalt binder BBR test results indicated that some of the deicer products (#6 and #8) showed degrading effects on the low-temperature performance of asphalt binder, indicating by the increased stiffness and lowered m-value. However, the asphalt binder treated by the product #7 (calcium chloride (liquid) treated rock salt) showed improved low-temperature performance with low stiffness and high m-value. Although the asphalt binder treated by the product #3 (“Snow Slicer” treated rock salt) had higher stiffness than the controlled binder, it had higher m-value. Therefore, the effects of the product #3 on low-temperature performance of asphalt binder could not be identified by this test.
- An acceptable deicer product should have little effects on the IDT creep compliance and strength of asphalt mixture. According to the results, products #2 (Rock salt – brine treated) and #9 (“Top Film” treated rock salt) had insignificant effects on the creep compliance of asphalt mixture, regardless of testing temperatures.
- Higher IDT strength of asphalt mixtures indicates higher low-temperature cracking resistance. The products #1, #2, #4, and #6 degraded the IDT strength of asphalt mixture at -10°C. The products #5, #7, #8, and #9 showed insignificant effects on the IDT strength of asphalt mixture. The product #3 (“Snow Slicer” treated rock salt) slightly increased the IDT strength as compared to the wet control sample.
- All concrete beams had DF values higher than 90%, which indicated that the concrete beams (with the selected typical Missouri mix design) had excellent durability even with the presence of deicer products. No significant difference (on DF) could be found between the concrete beams with the presence of water and deicer products.
- The deicer products had different scaling effects on concrete beams. The product #7 had little scaling effect on the concrete beams. The concrete beams with the presence of other deicer products (#2-#9) showed higher mass loss values (more significant scaling effect) than that of those with the presence of water. The concrete beams with the presence of product #2 showed the highest mass loss values.

- The PCM cylinder with the typical Missouri mix design was resistant to F-T damages, even with the presence of deicer solutions. The deicer products (especially product #9) had insignificant effect on the F-T resistance of PCM cylinders.
- When commercial deicer “Ice Ban” was added to rock salt, the lowest “characteristic temperature” could be achieved for this type of deicer, which would ultimately help the most in preventing black ice formation on roads. The treatment of rock salt with Ice Ban also helped the most in anti-icing, among all the other types on treated salts.
- The products #1 and #4 had the lowest BOD with values below 1 mg/L and product #9 had the highest BOD 49.53 mg/L.
- The lowest freezing point was related to Snow Slicer Treated Rock Salt (product #3) at 3 wt.% (-2.03 °C), 10 wt.% (-7.25 °C) and 23 wt.% (-23.14 °C). However, rock salt (Deicer #1) had the lowest freezing point at 5 wt.% (-3.44 °C), 10 wt.% (-7.25 °C) and 15 wt.% (-11.91 °C). On the other hand, Ice Ban Treated Rock Salt (Deicer #4) had the lowest freezing point at 20 wt.% (-17.88 °C). It should be noted that in all concentrations studied, deicers other than control (NaCl reagent) had the lowest freezing point temperature.
- There were statistically significant differences between the ice bond strength onto the surface of pavements A and C. The differences between the ice/pavement bond strengths on the deiced pavements were notably higher than those between the control groups A and C.
- The single factor ANOVA revealed that there were statistically significant differences across the ice/pavement bond strengths of different ND and deicer groups (#ND to #9), given that the p-value of 7.52E-05 was considerably lower than 0.05.
- The single factor ANOVA revealed that there was no statistically significant difference across the friction coefficients of different Deicer groups (#1 to #9).
- The product #4 showed least corrosive behavior towards the carbon steel. Brine treated rock salt (product #2) turned out to be the most corrosive deicer, relative to other chloride salt-based deicers.
- The single factor ANOVA revealed that there were statistically significant differences between the corrosion rates of steel in the different types of diluted deicer solutions, given that the p-value of 2.3E-06 was considerably lower than 0.05. In other words, a p-value of 0.05 or lower corresponds to a statistically significant difference between the two groups of data (with confidence level of 95% or higher).
- An evaluation matrix to assess the potential impacts (to the infrastructure, motor vehicles, and water bodies) under a holistic and multi-criteria framework was developed. The results indicated that products #5 (“Clear Lane” Produce), #7 (Calcium Chloride (liquid) Treated Rock Salt) and #3 (“Snow Slicer” Treated Rock Salt) scored above 60 out of 100.
- We recommend to MoDOT that products #5, #7 and #3 perform better for winter maintenance operations and have less impact on the environment, infrastructure and motor vehicles compared to other deicers tested in this research.
- Among the three recommended deicers, deicer #5 with a score of 67 is the first priority, then deicer #7 with a score of 66 is the second priority, and finally deicer #3 with a score of 64 is the third priority.

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# APPENDIX A

## Survey Questionnaire

**Q1**. Please provide your Name, Title, Agency, Phone number, and Email Address:

**Q2**. Does your agency have experience in the use of deicer products for anti-icing, deicing, or pre-wetting operations? If so, please describe any success stories and lessons learned and summarize any significant changes in materials, equipment or practices during the last decade or so.

**Q3**. What type of deicer products has your agency used for snow/ice control on roadways? Please check all that apply.

- Untreated rock salt;
- Slat brine treated rock salt;
- Magnesium chloride flake/pellet treated rock salt
- Magnesium chloride liquid treated rock slat
- Calcium chloride flake/pellet treated rock salt
- Calcium chloride liquid treated rock slat
- Beet juice treated rock salt
- Slat brine
- Magnesium chloride liquid
- Calcium chloride liquid
- Potassium acetate
- Liquid brine blends
- Other

**Q4**. Please provide more details (e.g., brand name) of the deicer products checked above and explain whether they have been used for anti-icing, deicing or pre-wetting.

**Q5**. Please elaborate on your agency's experience in implementing the aforementioned deicer products, in terms of their advantages and disadvantages respectively.

The advantages may include 1) low cost per lane mile, 2) low effective temperature, 3) high ice melting capacity, 4) fast action in facilitating snow/ice removal, 5) longevity on pavement, 6) ease of application, 7) overall safety benefits for winter roads, etc.

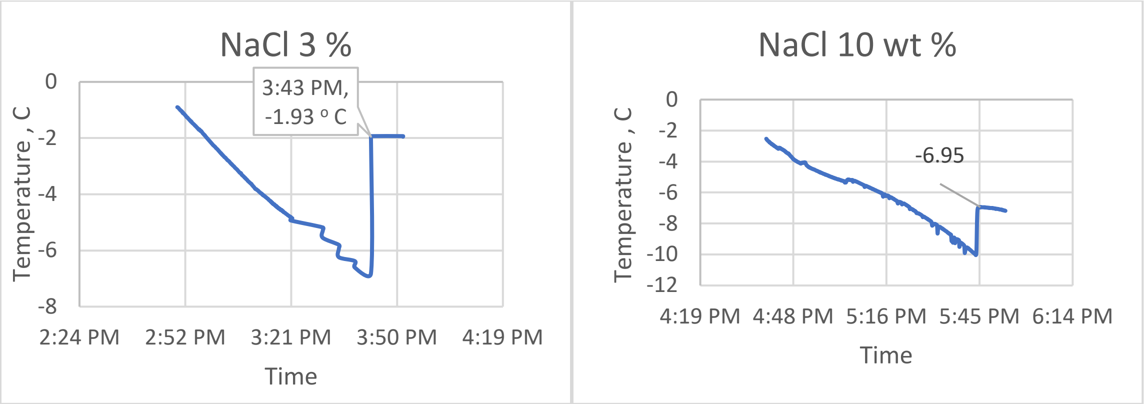
The disadvantages may include 1) corrosion to metals, 2) impact on concrete pavement, 3) impact on asphalt pavement, 4) impact on water quality, 5) impact on soil and vegetation, 6) impact on wildlife and human health, 7) overall effects to equipment or infrastructure, 8) overall effects to the natural environment, etc.

**Q6**. If your agency has systematically tested or evaluated different deicer products to inform better decision-making, please explain the type of tests and evaluation criteria used and the challenges you see; or provide the reports to Dr. Shi at xianming.shi@wsu.edu.

**Q7**. What do you see as the promising alternative deicer in the near future and why? Please share other information, comments or suggestions you would like to provide on the use of deicer products.

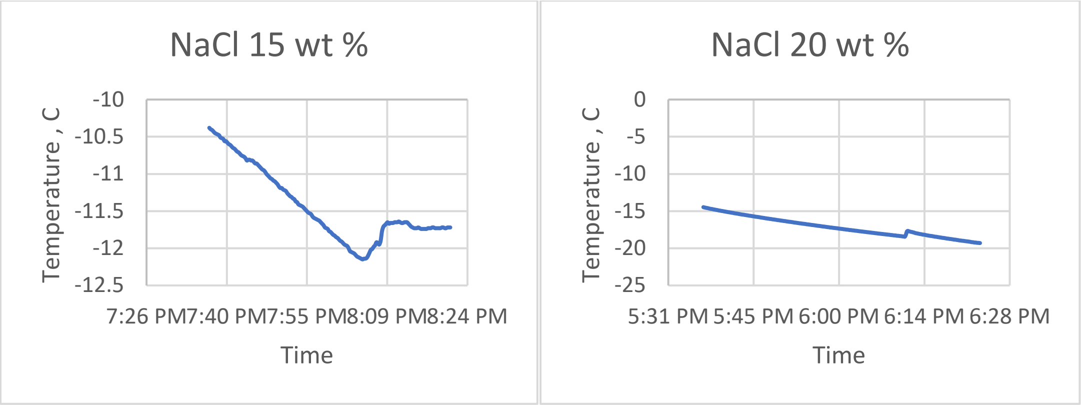
# APPENDIX B

## Raw experimental data: freezing point temperature of various deicers



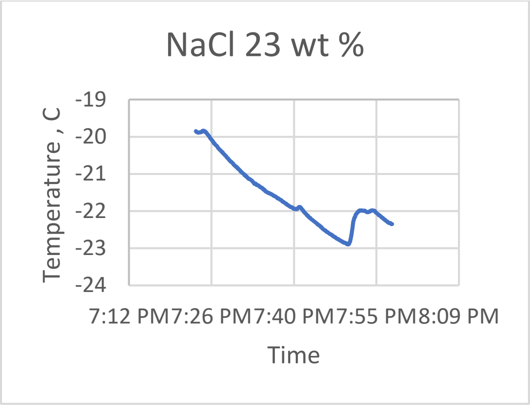
(a) NaCl 3%

(b) NaCl 10%



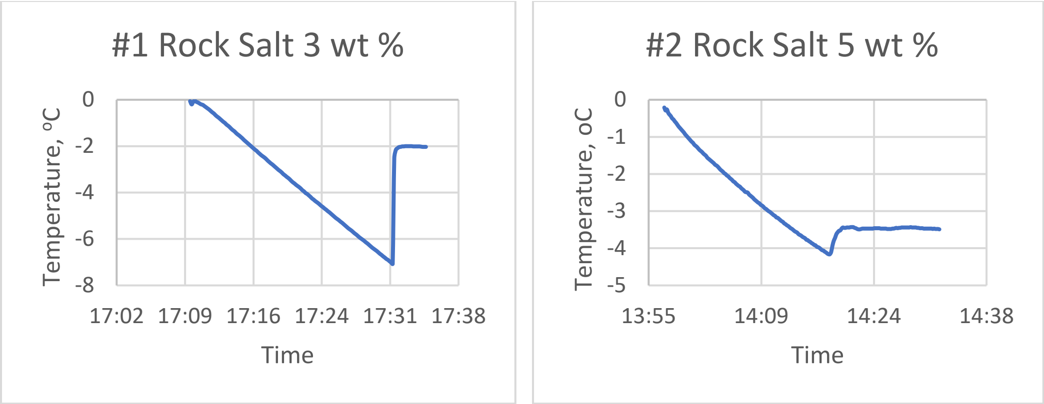
(c) NaCl 15%

(d) NaCl 20%



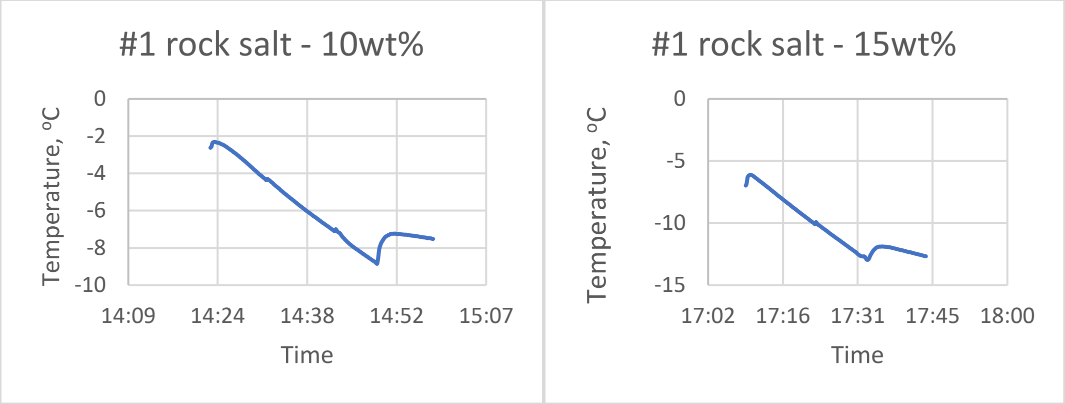
(e) NaCl 23%

**Fig. B-0:** Freezing point curves for NaCl samples.



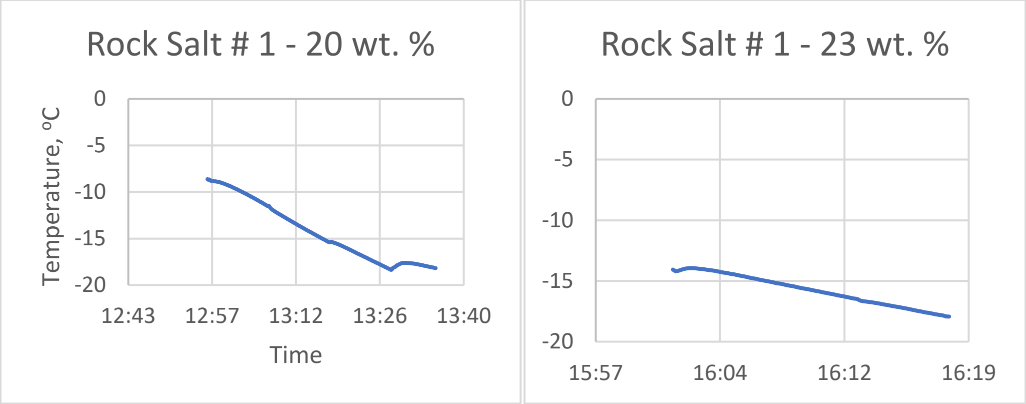
(a) #1 Rock Salt 3%

(b) #1 Rock Salt 5%



(c) #1 Rock Salt 10%

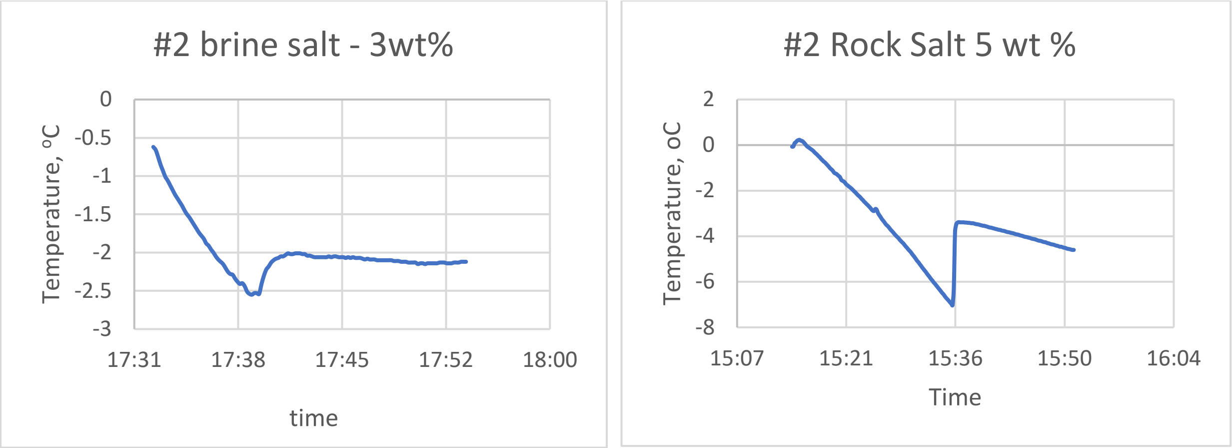
(d) #1 Rock Salt 15%



(e) #1 Rock Salt 20%

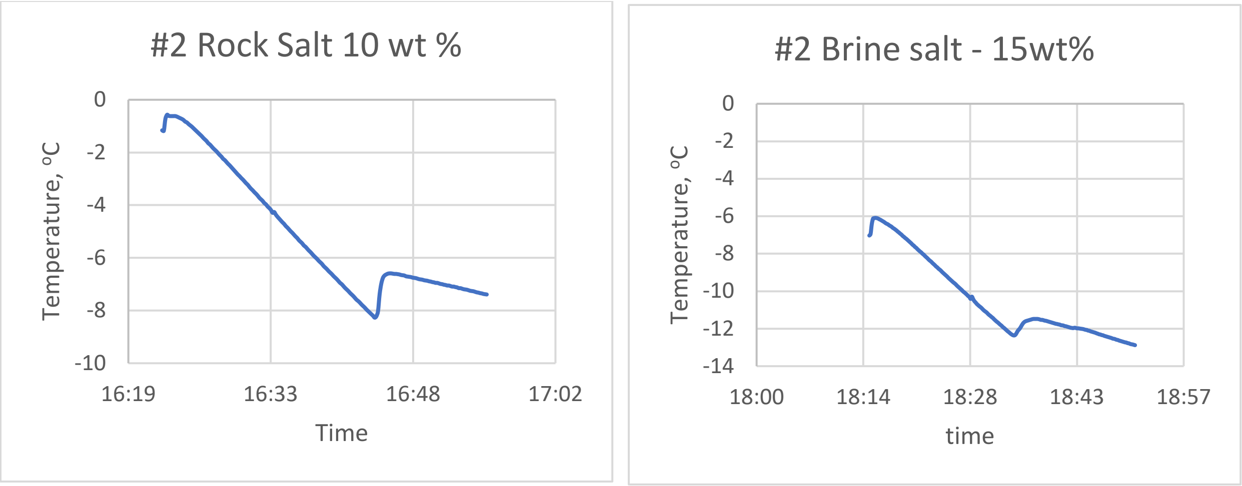
(f) #1 Rock Salt 23%

**Fig. B-1:** Freezing point curves for Rock Salt (#1) – untreated [baseline].



(a) #2 Rock Salt 3%

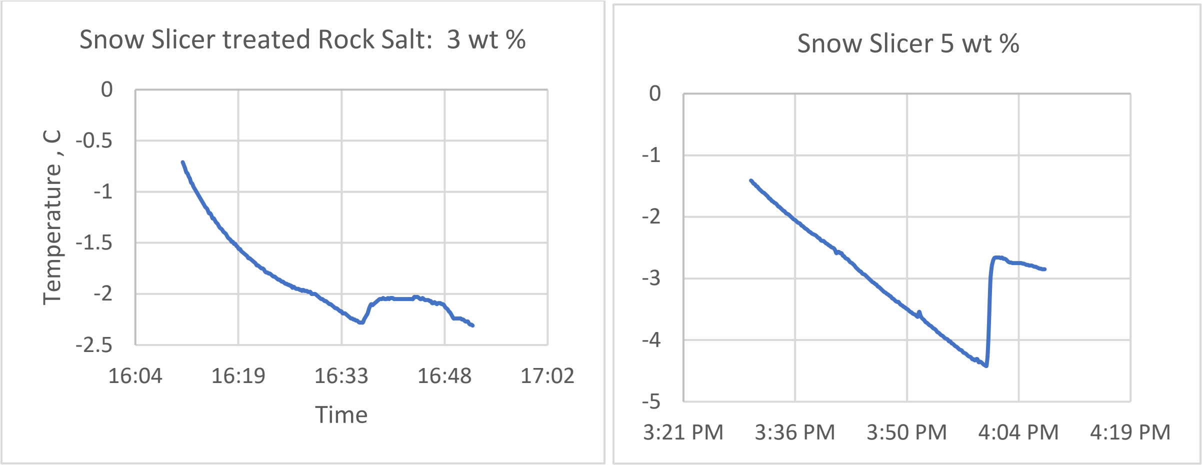
(b) #2 Rock Salt 5%



(c) #2 Rock Salt 10%

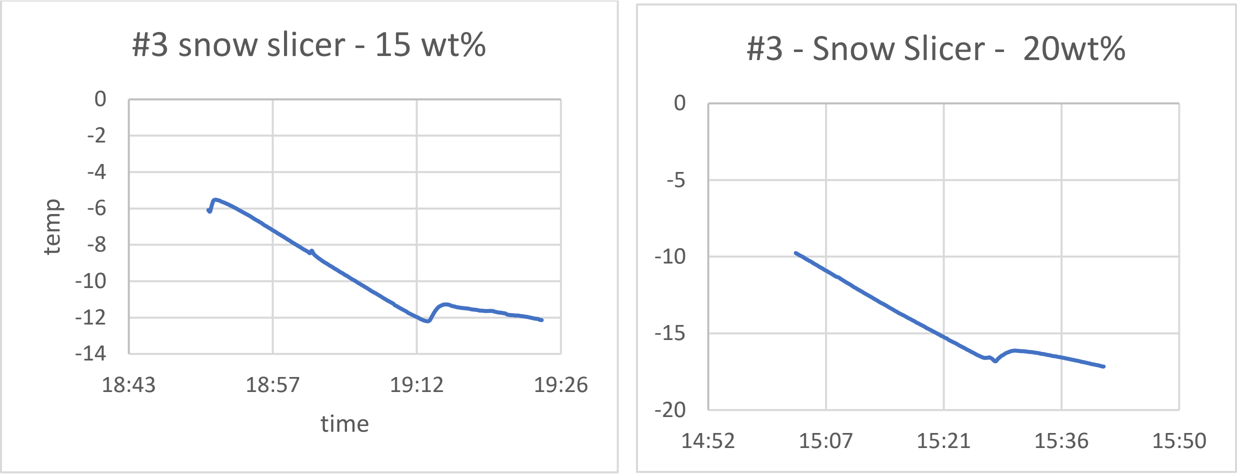
(d) #2 Rock Salt 15%

**Fig. B-2:** Freezing point curves for Rock Salt (#2) – brine treated.



(a) #3 Snow Slicer 3%

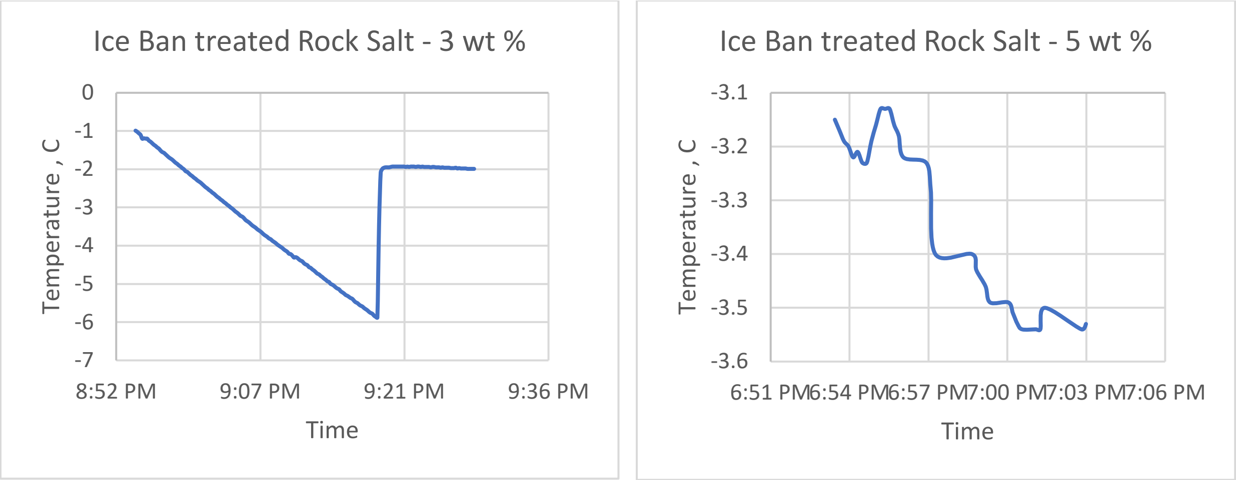
(b) #3 Snow Slicer 5%



(c) #3 Snow Slicer 15%

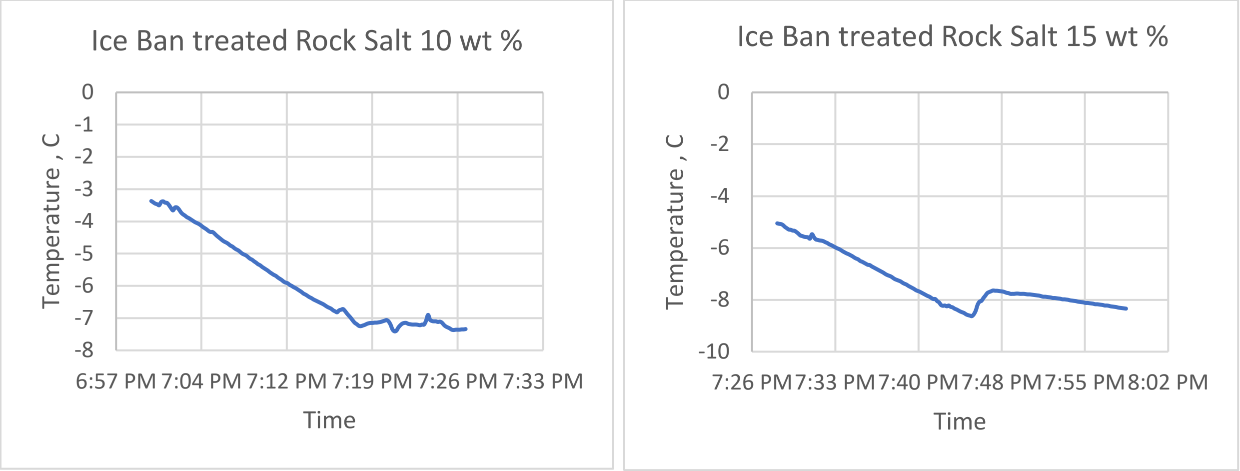
(d) #3 Snow Slicer 20%

**Fig. B-3:** Freezing point curves for Snow Slicer Treated Rock Salt (#3).



(a) #4 Ice Ban 3%

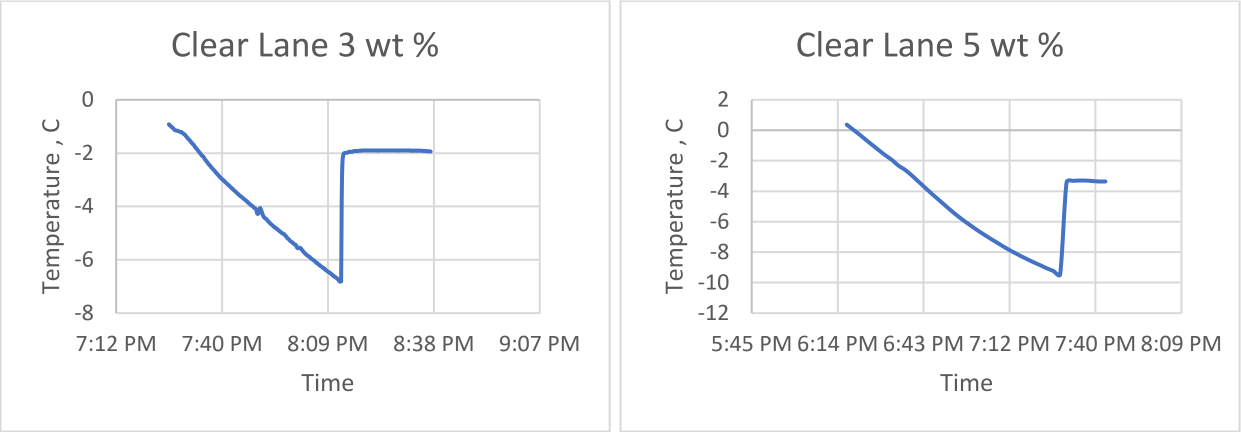
(b) #4 Ice Ban 5%



(c) #4 Ice Ban 10%

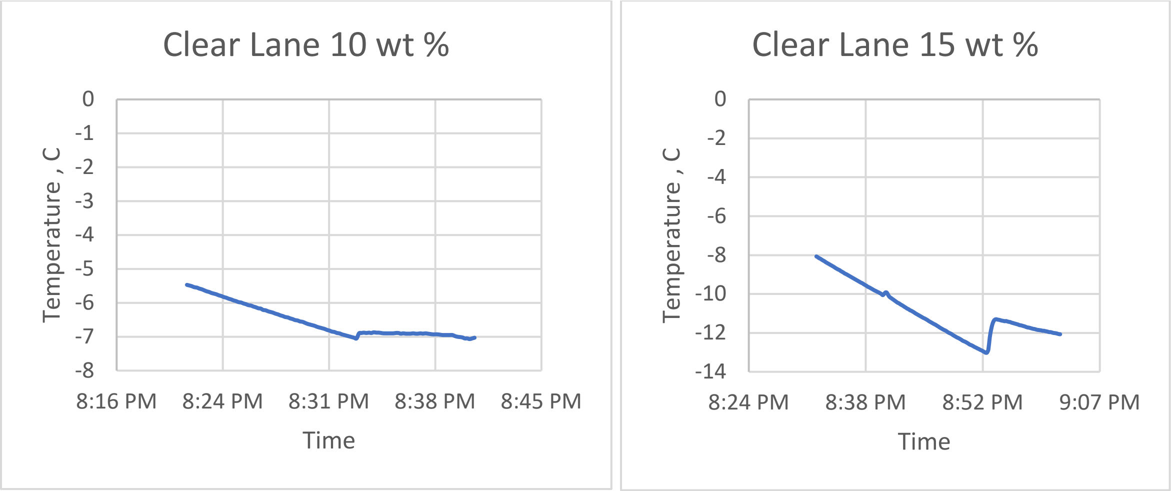
(d) #4 Ice Ban 15%

**Fig. B-4:** Freezing point curves for Ice Ban Treated Rock Salt (#4).



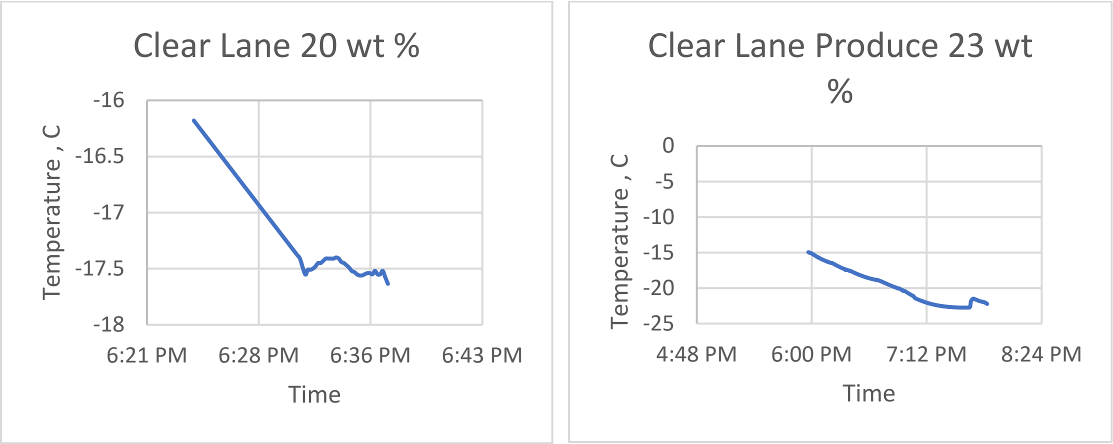
(a) #5 Clear Lane 3%

(b) #5 Clear Lane 5%



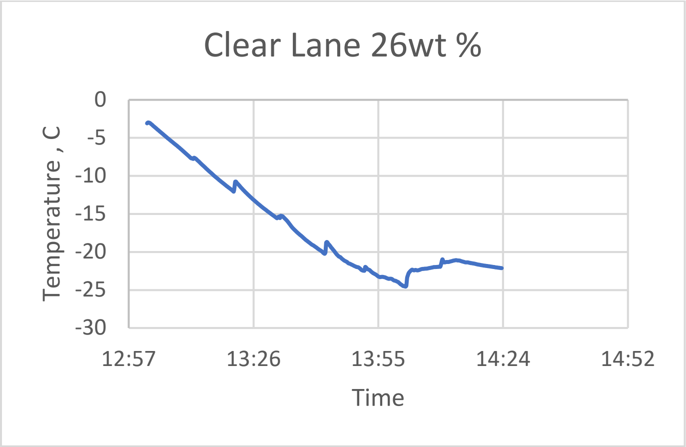
(c) #5 Clear Lane 10%

(d) #5 Clear Lane 15%



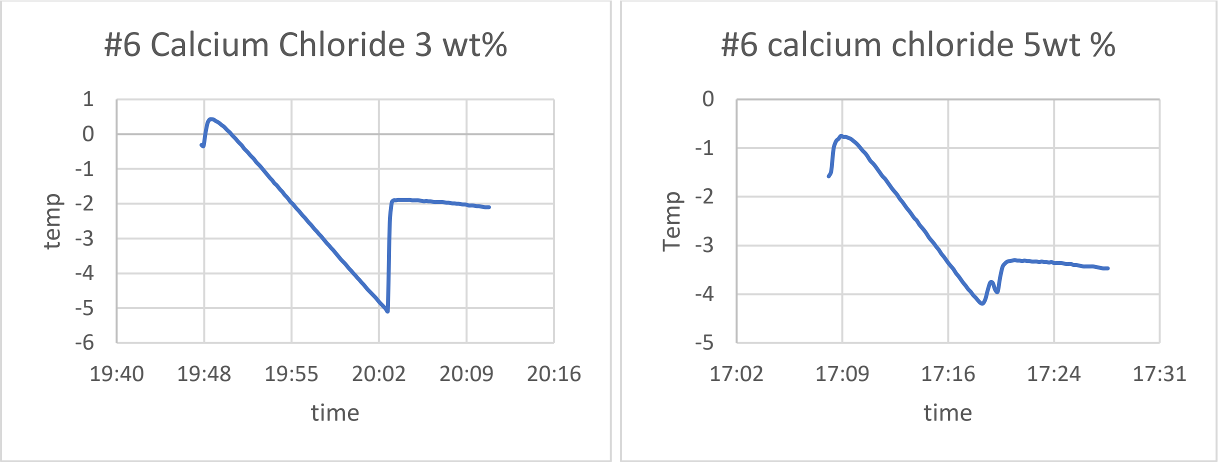
(e) #5 Clear Lane 20%

(f) #5 Clear Lane 23%



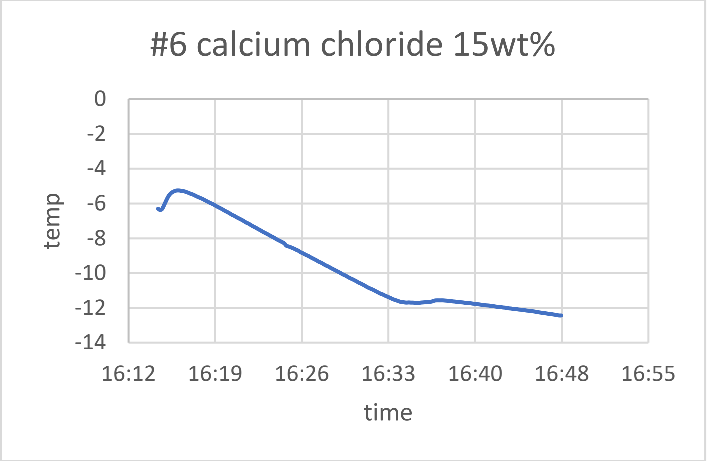
(g) #5 Clear Lane 26%

**Fig. B-5:** Freezing point curves for Clear Lane Produce (#5).

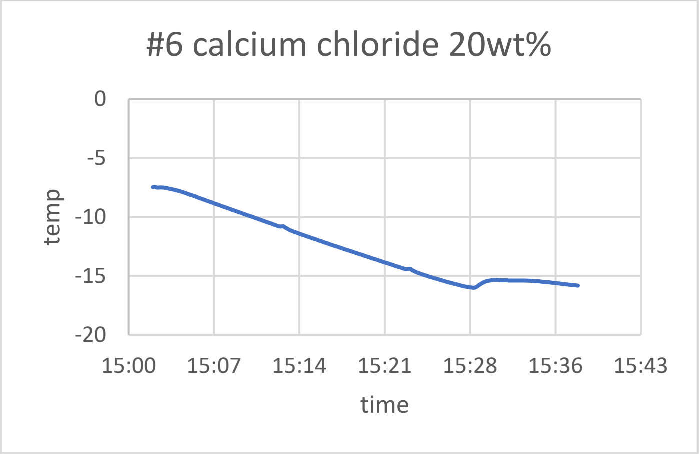


(a) #6 Calcium Chloride 3%

(b) #6 Calcium Chloride 5%

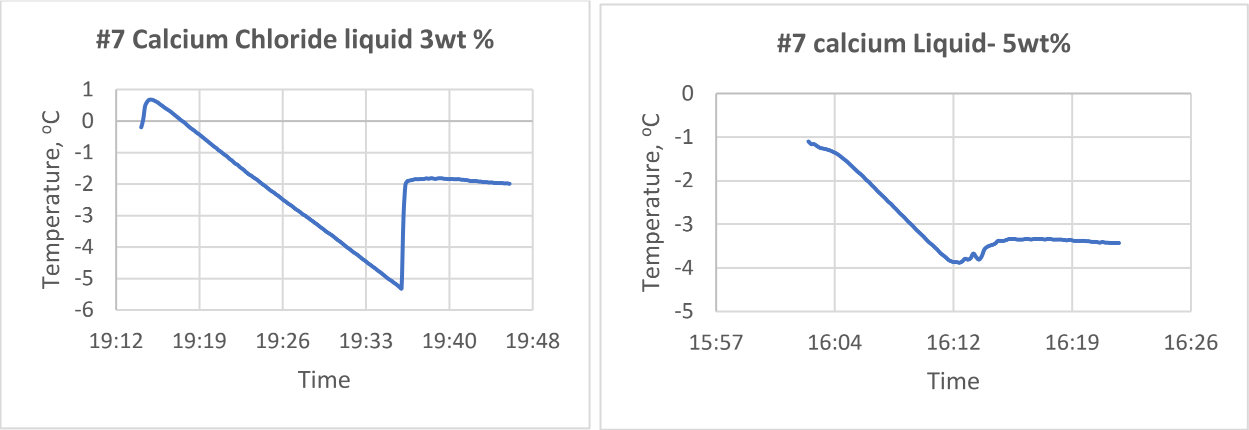


(c) #6 Calcium Chloride 15%



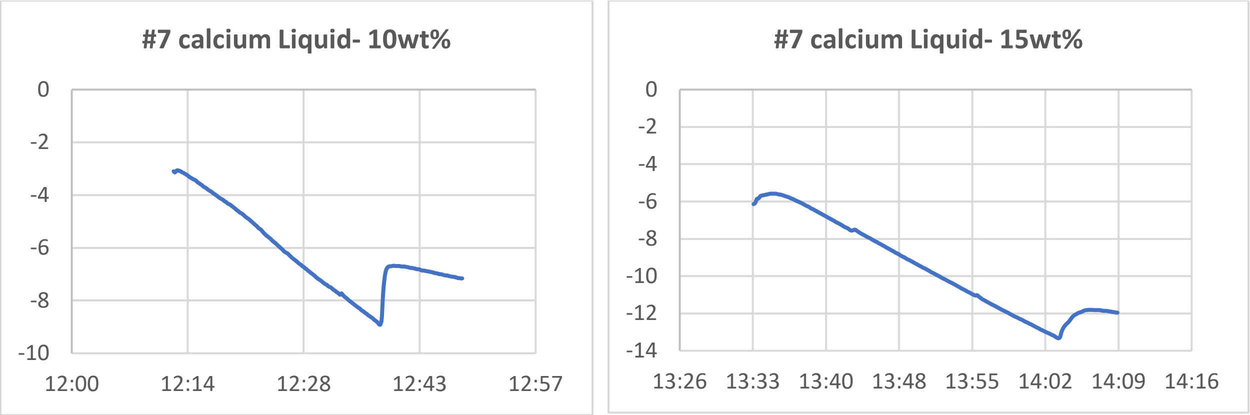
(d) #6 Calcium Chloride 20%

**Fig. B-6:** Freezing point curves for Calcium Chloride pellets Treated Rock Salt (# 6).



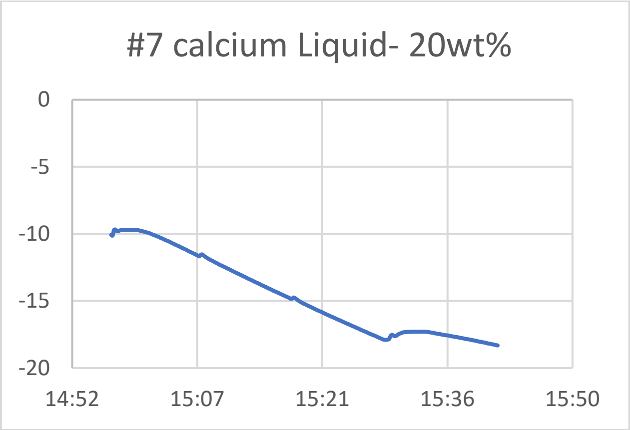
(a) #7 Calcium Chloride 3%

(b) #7 Calcium Chloride 5%



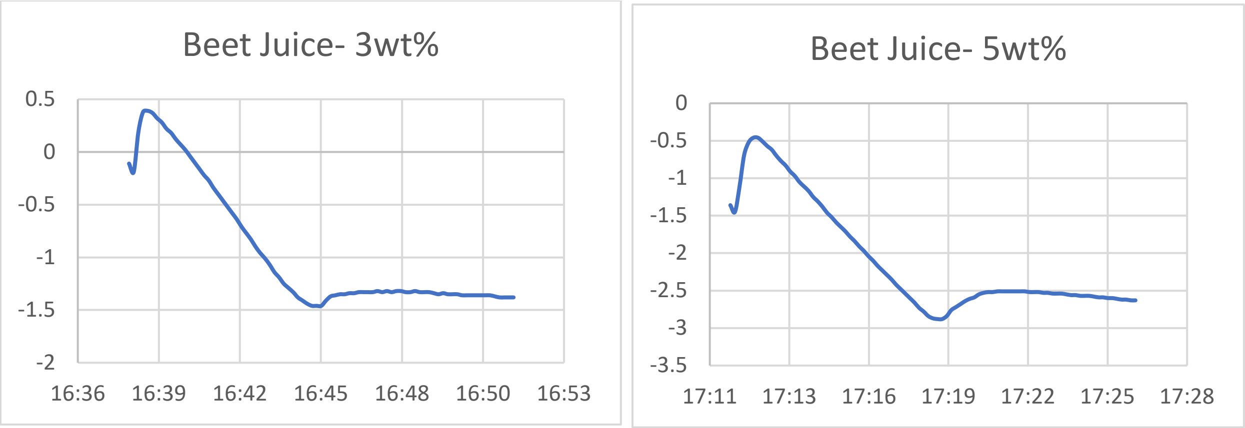
(c) #7 Calcium Chloride 10%

(d) #7 Calcium Chloride 15%



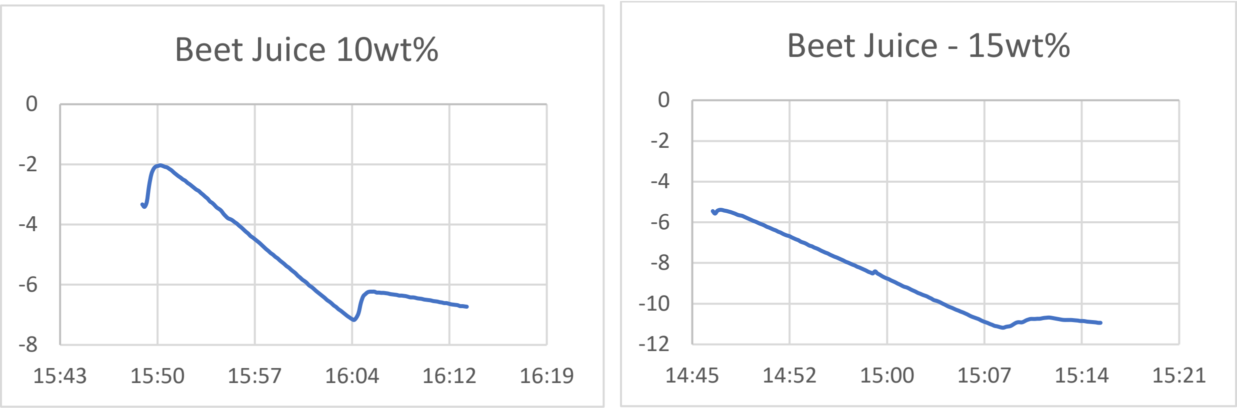
(e) #7 Calcium Chloride 20%

**Fig. B-7:** Freezing point curves for Calcium Chloride liquid Rock Salt (#7).



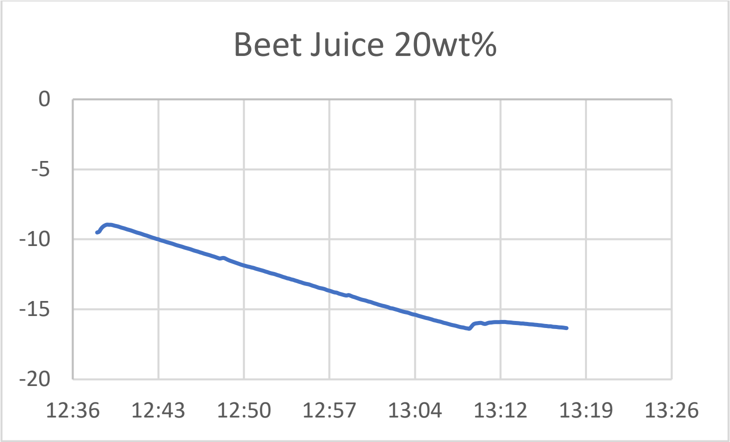
(a) #8 Beet Juice 3%

(b) #8 Beet Juice 5%



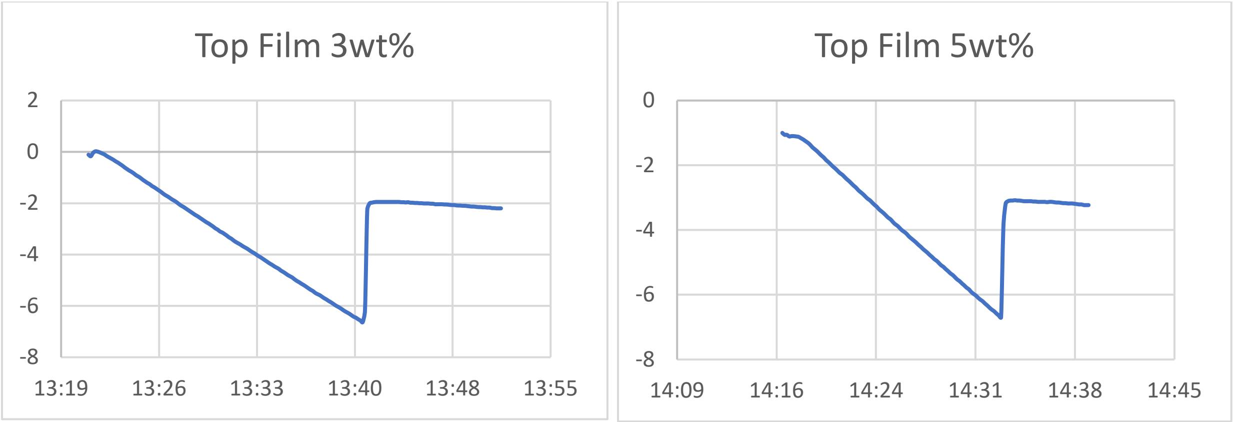
(c) #8 Beet Juice 10%

(d) #8 Beet Juice 15%



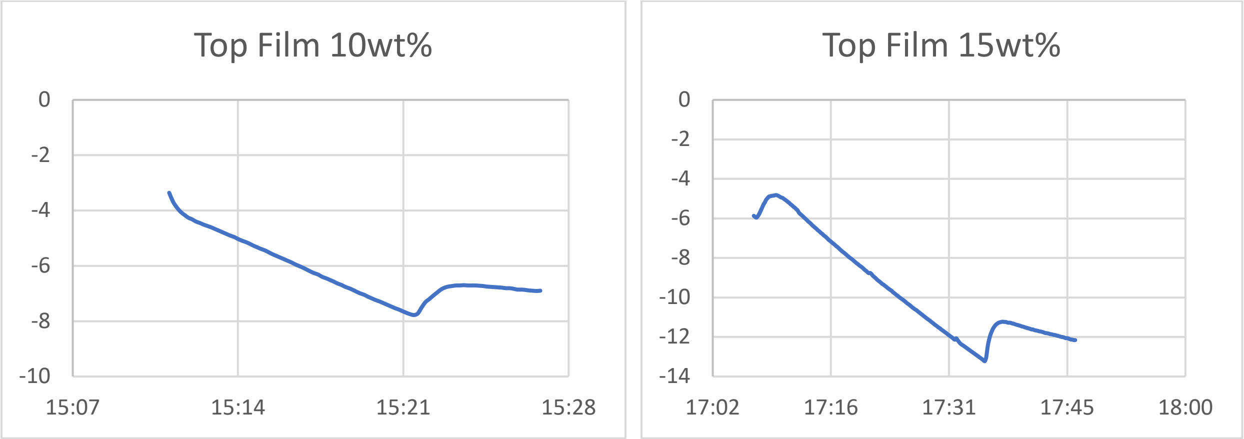
(d) #8 Beet Juice 20%

**Fig. B-8:** Freezing point curves for Beet Juice Treated Rock Salt (#8).



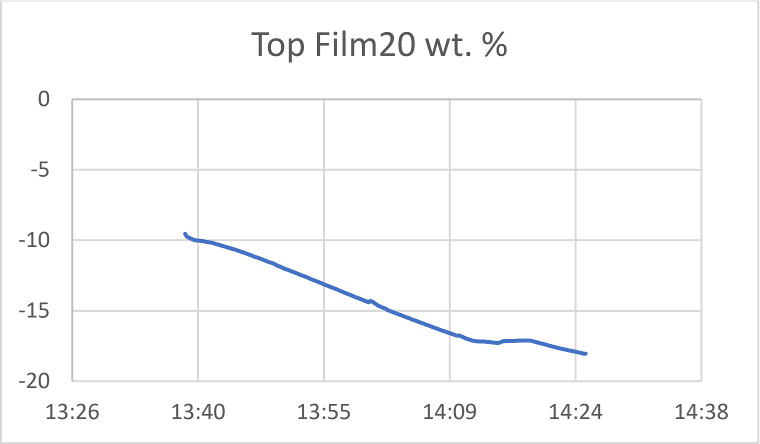
(a) #9 Top Film 3%

(b) #9 Top Film 5%



(c) #9 Top Film 10%

(d) #9 Top Film 15%



(e) #9 Top Film 20%

**Fig. B-9:** Freezing point curves for Top Film with Calcium Chloride Treated Rock Salt (#9).