Investigating Longevity of Corrosion Inhibitors and Performance of Deicer Products Under Storage or After Pavement Application

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INVESTIGATING LONGEVITY OF CORROSION INHIBITORS AND PERFORMANCE OF DEICER PRODUCTS UNDER STORAGE OR AFTER PAVEMENT APPLICATION

Final Report

for the
Washington State Department of Transportation and
the Transportation Pooled Fund led by
the Pacific Northwest Snowfighters Association

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16. ABSTRACT

This study evaluated the longevity of corrosion inhibitors and the performance of inhibited deicer products under storage or after pavement application. No significant degradation of corrosion inhibitor or loss of chlorides was seen during the months of field storage. The fate and transport of the inhibitors differed from those of the chlorides, in which dilution by precipitation and likely wicking of the deicer into the pavement and the top snow layer contributed to the loss of inhibitor and chlorides. The accelerated UV-degradation lab study found little degradation of GLT and FreezGard inhibitors but significant degradation of CCB inhibitor. While these inhibitors demonstrated their effectiveness in corrosion inhibition, they showed no side benefits in deicer performance. No significant difference in anti-icing performance was observed between the three liquid deicers during the two storm events. All three liquid deicers worked effectively for anti-icing applications under the investigated conditions. It is unnecessary to implement any mixing for the liquid deicer tanks, other than immediately prior to the use of the liquid deicers to ensure uniform composition and minimize stratification. Without dilution by precipitation (the black ice event), the percent of chloride recovered from the pavement by day 4 was approximately 30%, 20%, and 50% for NaCl+GLT, CCB, and FreezGard respectively. Up to 80% of the CCB inhibitor was recovered from the pavement 4 days after the deicer application. While such residuals could be washed away by precipitation, their presence on the pavement could potentially be measured and considered when re-applying chemicals for snow and ice control. This project revealed that the relative corrosivity of deicer solutions on the field pavement differed from that in the lab.

17. KEY WORDS

Winter maintenance, snow and ice control, corrosion inhibitor, deicer performance, longevity, laboratory testing, field investigation, deicing chemicals, sodium chloride, magnesium chloride, calcium chloride, DSC, UV-vis

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Abbreviations and Acronyms

AASHTO	American Association of State Highway and Transportation Officials
AgCl	silver chloride
ANN	artificial neural network
ASTM	American Society of Testing and Materials
BP	back-propagation
°C	degrees Celsius
$CaCl_2$	calcium chloride
CCB	Calcium Chloride with Boost
CMA	calcium magnesium acetate
CoV	coefficient of variance
D_{app}	apparent diffusion coefficient
D_{eff}	effective diffusion coefficient
DI	de-ionized water
DOTs	Departments of Transportation
DSC	differential scanning calorimetry
E_{corr}	corrosion potential
EIS	electrochemical impedance spectroscopy
°F	degrees Fahrenheit
FHWA	Federal Highway Administration
FOTs	field operational tests
H	heat flow (from DSC thermogram)
i_{corr}	corrosion current density
KAc	potassium acetate
KCl	potassium chloride
KFm	potassium formate
LOS	level of service
LP	linear polarization
$MgCl_2$	magnesium chloride
MPY	milli-inches per year
NaAc	sodium acetate
NACE	National Association of Corrosion Engineers
NaCl	sodium chloride
NCHRP	National Center for Highway Research Program
OCP	open circuit potential
OH^-	hydroxyl
P	phosphorus
PCR	percent corrosion rate

PNS	Pacific Northwest Snowfighters
PVC	polyvinylchloride
SAE	Society of Automotive Engineers
SCC	self-compacting concrete
SCE	saturated calomel electrode
SHRP	Strategic Highway Research Program
SMSE	sum of mean square error
T_c	characteristic temperature (from DSC thermogram)
UV-vis	ultraviolet-visible spectroscopy or spectrophotometry
WTI	Western Transportation Institute

EXECUTIVE SUMMARY

Prior to this research, little was known about how long the corrosion inhibitors and the deicer products remain effective during storage and on the pavement once applied during the winter storm. The direct cost of inhibited chemicals can be much higher than that of the non-inhibited chemicals. As such, this study aimed to evaluate the longevity of corrosion inhibitors and the performance of corrosion-inhibited deicer products under various storage conditions or after pavement application.

Multiple established analytical methods were used to monitor the temporal evolution of the identified deicer properties under field storage, by randomly sampling the solid or liquid deicers periodically and analyzing them in the laboratory. For deicer characterization, the differential scanning calorimetry (DSC) thermogram can provide information on the characteristic temperature (T_c) and the heat flow (H) during the liquid/solid phase transition of a given deicer, which also shed light on a more realistic working temperature range than a deicer's eutectic temperature. Specifically, the first peak temperature at the high temperature end of the warming cycle is defined as the T_c of the deicer, which corresponds to the temperature below which ice crystals start to form in the aqueous phase. The H for a deicer solution indicates the amount of thermal energy needed for the liquid/solid phase transition. Conceptually, the stronger a deicer, the lower the T_c and the smaller the H associated with the T_c peak. A strong correlation between the DSC data (T_c and H) and the Modified SHRP Ice Melting test data has been developed. This provides another opportunity to utilize the DSC test results, that is, to predict the ice melting capacity (*IMC*) of a chloride-based deicer. The key findings of field monitoring are presented as follows.

Deicer Product	Salt Concentration (by vendor)	Corrosion Inhibitor Concentration (by vendor)	Salt Concentration (by WTI)	Corrosion Inhibitor Concentration (by WTI)	Inhibitor to Chloride Ratio
NaCl+GLT	specified 23%	5%	19.3%	4.3%	1:4.5
CCB	31+%	12%	42.4%*	11.1%	1:3.8
FreezGard	29-31%	1.7%	36.1%*	2.4%	1:15.0
IceSlicer	NA	1.5%	NA	0.2%*	NA

- Three liquid deicers ($MgCl_2$-based FreezGard, Calcium Chloride with Boost - CCB, and NaCl+GLT) and one solid deicer (NaCl-based IceSlicer) were selected for the field storage monitoring (see Table above) and the key properties tested include the chloride and inhibitor concentrations, corrosion parameters (E_{corr} and *PCR*), pH, electrical conductivity, and performance parameters (T_c and $IMC_{30^{\circ}F,\ 60min}$). None of liquid deicers lost their quality over the 14 months of field storage, regardless of the storage condition (mixed or non-mixed). The NaCl-based solid deicer did not lose its quality over the 12 months of field storage, regardless of the storage condition (covered or uncovered). For all four deicers, the observed fluctuations in their properties seem to be non-seasonal but more likely attributable to the sampling and measuring variabilities. <u>No significant degradation of corrosion inhibitor or loss of chlorides was seen during the months of field storage. During the 14-month field monitoring, NaCl+GLT was the only liquid deicer to have non-passing corrosion scores, suggesting potential shelf-life issues.</u>

- From an accelerated UV-degradation study conducted in the laboratory, the effect of exposure conditions (temperature, UV intensity, and time) on the resulting inhibitor concentration was generally insignificant for the NaCl+GLT and FreezGard deicers but significant for the CCB deicer. For the CCB deicer, the blocking of UV light by the storage tanks was likely beneficial in preventing its inhibitor degradation over the 14-month field storage monitoring period.

- The GLT inhibitor used alone or as additive to the NaCl-based deicer showed no benefit in suppressing effective temperature or in providing ice melting capacity. The inhibitor packages used in the CCB and FreezGard deicers slightly increased the effective temperature of their respective brine and showed little effect on the ice melting capacity (based on the *DSC* data). However, different from GLT, these inhibitor packages showed some limited ice melting capacity when used alone. In a word, while these inhibitors demonstrated their effectiveness in corrosion inhibition, they showed no side benefits in deicer performance.

- With few exceptions, the IceSlicer samples from the covered pile generally featured slightly higher chloride concentrations and significantly lower inhibitor concentrations, relative to those from the uncovered pile. While the chloride concentration in both covered and uncovered piles remained relatively consistent over the 12 months of field storage, the inhibitor concentration in both piles tended to increase over time. The deicer corrosivity to steel (*PCR*) fluctuated between 60 and 100, regardless of the storage condition or the sieving of the deicer sample, indicating unacceptable corrosivity levels under the specific storage conditions investigated. The inhibitor-to-chloride concentration ratio in the cistern attached to the uncovered pile remained fairly consistent in the first eight months of monitoring. Yet the low inhibitor concentrations in the cistern during last four months may be correlated with the high inhibitor concentrations in the uncovered pile, both suggesting that the leaching rate of chloride from the uncovered pile exceeded that of the corrosion inhibitor.

- ANN has demonstrated great potential in finding meaningful, logical results from the noisy data associated with the metallic corrosion experiments. One ANN model was established to correlate the corrosion data from the electrochemical test method with those from the PNS/NACE test method (featuring a R-square of 0.84). Two additional ANN models were established to achieve better understanding of the complex correlation between the deicer composition (deicer type, chloride and inhibitor concentrations, pH, and electrical conductivity) and the deicer corrosivity (in *PCR*) and performance (in T_c) respectively. According to the ANN modeling, there are strong correlations inherent in the deicer samples (indicated by the R-square values of 0.91 and 0.98 for *PCR* and T_c respectively), whereas the trends differ as a function of the deicer type.

- High E_{corr} values generally corresponded with low corrosivity (*PCR*) values. The E_{corr} value higher than -562 mV (vs. SCE) generally corresponded to *PCR* values lower than 30, which is desirable per the guidelines by the Pacific Northwest Snowfighters Association. It should be noted, however, that an E_{corr} value lower than -562 mV_{SCE} does not necessarily indicate a *PCR* value higher than 30. As such, the electrochemical test could be used as a quality assurance tool for rapid assessment of deicer corrosivity to mild steel.

Deicer Product	Salt Concentration (by vendor)	Corrosion Inhibitor Concentration (by vendor)	Salt Concentration (by WTI)	Corrosion Inhibitor Concentration (by WTI)	Inhibitor to Chloride Ratio
NaCl+GLT	23%	5%	18.8%	4.7%	1:4.0
CCB	31+%	12%	30.3%	16.2%	1:1.9
FreezGard	29-31%	1.7%	36.2%	1.2%	1:30.2

This study also investigated the longevity of corrosion inhibitors and the performance of three corrosion-inhibited deicer products (see Table above), by daily sampling of deicer residuals on the pavement for seven days after deicer application for a black ice event, a man-made snow event, and a natural snow event respectively. To simulate realistic climatic and logistical situations, the field operational tests were conducted at the TRANSEND facility at Lewistown, MT (the target and actual conditions for the three events are shown in the Table below). Subsequently, the analytical methods established previously were used to analyze the properties of pavement-collected samples in the laboratory. The key findings are presented as follows.

	Black Ice Event	**Man Made Snow Event**	**Natural Snow Event**
Target Precipitation	No precipitation	Minimum 1 inch of snow	1-4 inches in the first 24 hours
Actual Precipitation	Total of 0.75″ of precipitation (mostly snow/ice) during day 4 to day 7.	1″ of man-made snow; a total of 0.26″ of natural snow during day 3 and day 4.	3.5-4″ in the first 24 hours; about 0.75″ of blowing snow on day 2.
Target Air Temperature	25-32 °F	15-25 °F	25-32 °F
Target Pavement Temperature	Less than 32 °F	Less than 25 °F	25-32 °F
Moisture Content in Snow (Average Density)	Not applicable	30-40% (24 lb/ft^3)	20-40% (19 lb/ft^3)
Target Deicer Application Rate	30 gallons/lane-mile	60 gallons/lane-mile	60 gallons/lane-mile
Actual Application Rate	33±5 gallons/l-m	53±4 gallons/l-m *	55±6 gallons/l-m *
Target Wind Speed	Not specified	Less than 6 mph	Not specified
Average Wind Speed	6 mph	9 mph	9 mph
Average Wind Direction	SSW to NNE (coming from 200°)	SW to NE (coming from 228°)	SSE to NNW (coming from 173°)

* These high application rates were for improved product recovery and subsequent analysis, and they are not representative of what should be applied.

- <u>In general, no significant difference in anti-icing performance was observed between the three liquid deicers, based on the periodical visual observations made during the two (man-made and natural snow) storm events. All three liquid deicers worked effectively for anti-icing applications under the investigated conditions, even though the field operational tests did not incorporate real or simulated traffic.</u>

- The samples collected from the control test lanes (with no deicer applied) seemed to contain contaminants that affect their UV-vis spectrum, pH, and corrosion data, yet their low chloride concentration and low conductivity suggested the absence of salt. The E_{corr} data of steel in control samples suggest that the natural snow event and the black ice event collected the least and the most amount of contaminants from pavement respectively, while the man-made snow event fell in between.

- Out of the seven test days for the three events, NaCl+GLT had the greatest number of passing *PCR* values (14/21), followed by CCB (13/21) and FreezGard (11/21).

- A number of mechanisms may have accounted for the much lower chloride recovery from the pavement during the natural snow event, relative to the man-made snow event, including warmer pavement temperature, more precipitation, loss of deicer to the leveling-off step, and more time waited before day-one sampling.

- The longevity of the corrosion inhibitor and chlorides of liquid deicers after pavement application depended on the deicer type, storm type, and likely other field factors. In general, the fate and transport of the corrosion inhibitors differed from those of the chlorides, in which dilution by precipitation and likely wicking of the deicer into the pavement and the top snow layer contributed to the loss of inhibitor and chlorides. UV-degradation, if any, might have played a minor role.

- The black ice event featured a total of 0.75″ of precipitation (mostly snow/ice) during day 4 to day 7. The percent of chloride recovered from the pavement by day 4 was approximately 30%, 20%, and 50% for NaCl+GLT, CCB, and FreezGard respectively. Starting on day 5, the chloride recovery for all three deicers significantly dropped, attributable to the rain precipitation on day 3 and the snow precipitation on day 3 (trace amount), day 4 (>1/2″), and day 5 (1/2″). Up to 80% of the CCB inhibitor was recovered from the pavement four days after the deicer application. The *PCR* of residuals recovered from the pavement by day 4 was approximately 40, 15 and 35 for NaCl+GLT, CCB, and FreezGard respectively. Note that the relative corrosivity of deicer solutions on the field pavement differed from that of them tested in the laboratory, where the *PCR* was 32, 21, and 16 for NaCl+GLT, CCB, and FreezGard respectively.

- The man-made snow event featured 1″ of artificial snow and a total of 0.26″ of natural snow during day 3 and day 4. The percent of chloride recovered from the pavement by day 7 was approximately 20%, 16%, and 8% for NaCl+GLT, CCB, and FreezGard respectively. Up to 38% and 26% of the inhibitors were recovered from the pavement seven days after the application of NaCl+GLT and CCB respectively. The *PCR* of residuals recovered from the pavement by day 7 was approximately 51, 72 and 31 for NaCl+GLT, CCB, and FreezGard respectively. The un-diluted samples collected from the deicer test lanes during the man-made snow event featured the greatest number of non-passing *PCR* values. This could be partly attributed to the generally low inhibitor concentrations that remained on the pavement, coupled with the relatively high chloride concentrations that remained on the pavement. The *PCR* values showed no clear relationship with storm type, deicer type or sampling time.

- The natural snow event featured 3.5-4″ of natural snow in the first 24 hours and about 0.75″ of blowing snow on day 2. The percent of chloride recovered from the pavement was less than 0.7% by day 6 and less than 0.5% by day 7, for all three deicers. Up to 21% and 4% of the GLT inhibitor was recovered from the pavement one day and five days after the deicer application respectively. Up to 83% of the FreezGard inhibitor was recovered from the pavement seven days after the deicer application. Such unusually high inhibitor recovery efficiencies for the natural snow event present a significant contrast to the extremely low chloride recovery. The *PCR* of residuals recovered from the pavement by day 1 was approximately 7, 10 and 18 for NaCl+GLT, CCB, and FreezGard respectively. The undiluted samples collected from the deicer test lanes during the natural snow event featured the lowest *PCR* values, all of which remained below the PNS-specified 30%. This could be attributed to the extremely low chloride concentrations that remained on the pavement. The *PCR* values showed no clear relationship with storm type or deicer type.

In summary, the five objectives of this research were achieved to various degrees by this work as follows.

- The longevity of the corrosion inhibitors and the duration in which they persist with the deicer (both under storage and after pavement application): - *achieved.* No significant degradation of corrosion inhibitor or loss of chlorides was seen during the months of field storage. During the 14-month field monitoring, NaCl+GLT was the only liquid deicer to have non-passing corrosion scores, suggesting potential shelf-life issues. The longevity of the corrosion inhibitor and chlorides of liquid deicers after pavement application depended on the deicer type, storm type, and likely other field factors. In general, the fate and transport of the corrosion inhibitors differed from those of the chlorides, in which dilution by precipitation and likely wicking of the deicer into the pavement and the top snow layer contributed to the loss of inhibitor and chlorides. UV-degradation, if any, might have played a minor role.
- The possible effects of temperature, UV intensity, exposure, and dilution on inhibitors in common chloride deicers and deicer performance: - *mostly achieved.* From an accelerated UV-degradation study conducted in the laboratory, the effect of exposure conditions (temperature, UV intensity, and time) on the resulting inhibitor concentration was generally insignificant for the NaCl+GLT and FreezGard deicers but significant for the CCB deicer.
- The cost-effectiveness of including inhibitors in deicers: - *partially achieved.* This research suggests that the inhibitors did not provide side benefits in deicer performance, which should be considered during the collaborative decision-making for materials selection.
- Any inhibitor effect on freezing point suppression or deicer effectiveness: - *achieved.* While these inhibitors demonstrated their effectiveness in corrosion inhibition, they showed no side benefits in deicer performance.
- The most effective deicer for different winter weather scenarios: - *achieved.* In general, no significant difference in anti-icing performance was observed between the three liquid deicers, based on the periodical visual observations made during the two (man-made and natural snow) storm events. All three liquid deicers worked effectively for anti-icing

applications under the investigated conditions, even though the field operational tests did not incorporate real or simulated traffic.

Implementation Recommendations

- The three liquid deicers ($MgCl_2$-based FreezGard, $CaCl_2$-based CCB, and NaCl+GLT) investigated did not lose their quality over the 14 months of field storage, regardless of the storage condition (mixed or non-mixed). As such, it is unnecessary to implement any mixing for the liquid deicer tanks during storage. However, it is important to do so immediately prior to the use of the liquid deicers, to ensure uniform composition and minimize stratification.

- It would be best to cover solid deicers during field storage to minimize leaching of active ingredients (especially corrosion inhibitor), but the solid deicer after 12 months storage under uncovered conditions can still be an effective deicer despite its reduced corrosion inhibition.

- When determining whether the inclusion of corrosion inhibitor in deicers is economical, be aware that the investigated inhibitor packages did not show any side benefits in deicer performance and they served merely as corrosion inhibitors for the deicer products. The fate and transport of inhibitors differed from those of chlorides, once applied on the pavement.

- Without dilution by rain or snow precipitation (e.g., the early days of black ice event), the percent of chloride recovered from the pavement by day 4 was approximately 30%, 20%, and 50% for NaCl+GLT, CCB, and FreezGard respectively. Up to 80% of the CCB inhibitor was recovered from the pavement four days after the deicer application. While such residuals could be washed away by precipitation, their presence on the pavement could potentially be measured and taken into consideration when re-applying chemicals for snow and ice control.

- This project revealed that the relative corrosivity of deicer solutions on the field pavement differed from that of them tested in the laboratory. It merits further investigation to develop laboratory tests that can correlate better with the actual field corrosion of metals caused by deicer exposure, taking the fate and transport of corrosion inhibitors (vs. chlorides), relative humidity, temperature cycles, etc. in the service environment into account.

CHAPTER 1 INTRODUCTION

1.1. Problem Statement

In cold-climate regions such as the northern U.S. and Canada, snow and ice control operations are essential to maintaining the roadway safety, mobility and productivity as they provide safe driving surfaces in the winter weather. These maintenance activities offer direct benefits to the public such as fewer accidents, improved mobility and reduced travel costs, while providing indirect benefits such as sustained economic productivity, reduction in accident claims and continued emergency services. Each winter season, large amounts of solid and liquid chemicals (known as deicers[1]) as well as abrasives are applied onto highways to keep them clear of ice and snow. Deicers (mainly sodium chloride [NaCl], magnesium chloride [$MgCl_2$], and calcium chloride [$CaCl_2$]) can be found in a wide variety of snow and ice control products used on winter highways to either prevent the bonding of ice to the roadway (anti-icing) or break the bond between ice and the roadway (de-icing). Prior to application onto roadways, liquid salts are also added to abrasives or solid salts to make them easier to manage, distribute, and stay on roadways (pre-wetting). Transportation agencies are under increasing pressure to maintain high levels of safety and mobility even during the winter months, while working with limited financial and staffing resources and recognizing the environmental challenges related to chemical and material usage [1-4].

With professionals from the transportation agencies in the States of Washington, Oregon, Montana, Idaho, Colorado and British Columbia, the Pacific Northwest Snowfighters (PNS) Association has become a recognized pioneer in establishing and standardizing chemical products for snow and ice control. A central feature of the PNS guidelines for new product qualification for deicers is the presence of corrosion inhibitor(s) in deicers, and the qualification and evaluation of all deicers by a modified National Association of Corrosion Engineers (NACE) corrosion test. It is a popular practice to add corrosion inhibitors and other additives to deicer products, aimed to reduce their corrosive effects on the transportation infrastructure and the motor vehicles. Laboratory tests indicate corrosive effects can be reduced by at least 70 percent with the addition of inhibitors. The inhibitors are often organic, made from phosphates or carbohydrates, which are biodegradable and/or photo-degradable.

Prior to this research, little was known about how long the corrosion inhibitors and the deicer products remain effective during storage and on the pavement once applied during the winter storm. The direct cost of inhibited chemicals can be much higher than that of the non-inhibited chemicals. The U.S. spends \$2.3 billion annually to keep roads clear of snow and ice [5]; in Canada, more than \$1 billion is spent annually on winter maintenance [6]. As the transportation agencies spend millions of dollars each year on the deicers, there were growing concerns over the longevity of corrosion inhibitors in such chemicals and whether the inhibitors will work effectively in the field environment subsequent to shed storage, sunlight exposure, and dilution. These uncertainties need to

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[1] For simplicity, we use the term *deicer* to refer to all chemicals for anti-icing, de-icing, and pre-wetting operations.

be addressed before economical decisions can be made regarding the use of corrosion-inhibited deicers. In this context, this research was initiated to shed light on the fate and transport of chlorides and corrosion inhibitors under storage or after pavement application during winter storms and to address such knowledge gaps that have significant implications for winter road maintenance practitioners.

1.2. Background

1.2.1. Snow and Ice Control: Current Practices and Performance Measures

Over the last two decades, maintenance departments in North America have gradually made two transitions in their snow and ice control strategies. First is the transition from the use of abrasives to the use of more chemicals [7]. Currently, the U.S. applies approximately 20 million tons of salts each year for winter road maintenance according to the year 2008 data provided by the Salt Institute. This is partially owing to the negative impact of abrasives to water quality and aquatic species, air quality, vegetation, and soil and the hidden cost of sanding. It has been recognized that the detrimental environmental impacts of abrasives are generally greater than those of chemicals. Depending on its particle size, sand may contribute greatly to air pollution, can potentially cause serious lung disease, and is listed as a carcinogen [8]. Sand also poses significant risk for water quality and may threaten the survivability of aquatic species especially during spring runoff [7]. Sand is a relatively inexpensive material but costs of damage caused by repeated applications, along with substantial removal/clean-up costs can make it less cost-effective [9]. Even after cleanup, 50 to 90 percent of the sand may remain somewhere in the environment [10]. It would take a significantly higher amount of abrasives to maintain a reasonable level of service (LOS), relative to the amount of chemicals that would require.

In more recent years there is the transition from mostly deicing to anti-icing wherever possible [11], considering the multiple benefits of the latter (e.g., improved LOS, reduced need for chemicals, and associated cost savings and safety/mobility benefits). Anti-icing is the application of chemical freezing-point depressants to the roadway in advance of deteriorating weather conditions, aimed to prevent black ice formation and to prevent or weaken the bond between ice and the road surface. Reliable weather forecasts are crucial to a successful anti-icing program, as the pavement surface temperature dictates the timing for anti-icing applications and the appropriate application rate. When conducted properly, anti-icing can reduce the amount of plowing and chemicals required [12] or eliminate the need for abrasives [13]. Anti-icing also led to success stories in many states, including Colorado, Idaho, Minnesota, Montana, Oregon, Washington, etc. [11]. Nonetheless, most agencies currently take a toolbox approach customized to their local snow and ice control needs and funding/staffing/equipment constraints. Depending on the road weather scenarios, resources available and local rules of practice, maintenance agencies use a combination of tools for winter road maintenance and engage in activities ranging from anti-icing, deicing, sanding, to mechanical removal (e.g., snowplowing), and snow fencing.

There are growing concerns over the impact of deicers on the transportation infrastructure, motor vehicles and the environment [1-4, 14-17]. Over five billion dollars are spent each year by state and local agencies to repair infrastructure damage caused by snow and ice control operations. When using road salts for snow and ice control, the average costs due to corrosion and environmental effects are estimated at least three times as high as the nominal cost [18]. However, such hidden costs are often ignored in formulating highway winter maintenance strategies. Chemical deicers, especially those based on chlorides, may cause corrosion damage to the motor vehicles and transportation infrastructure such as reinforced or pre-stressed concrete structures and steel bridges [15]. One study has estimated that road salt imposes infrastructure corrosion costs of at least \$615 per ton, vehicular corrosion costs of at least \$113 per ton, and aesthetic costs of \$75 per ton if applied near environmentally sensitive areas, plus uncertain human health costs [19]. Each year, the cost of deicer corrosion on motor vehicles was estimated to be \$32 per vehicle [20], totaling at more than \$2 billion [18]. The cost of installing corrosion protection measures in new bridges and repairing old bridges in the Snowbelt states was estimated to be between \$250 million and \$650 million annually [21]. Parking garages, pavements, roadside hardware, and non-highway objects near winter maintenance activities are also exposed to the corrosive effects of deicers. Furthermore, repairs to the infrastructure translate to costs for the user in terms of construction costs, traffic delays and lost productivity, i.e., indirect costs of corrosion maintenance, repair and rehabilitation. The relative corrosivity of deicers is dependent on many details related to the metal/deicer system. Therefore, no general conclusions should be made when ranking corrosion risks of different deicer products. Instead, it is important to note the test protocol employed, the metal coupons tested, the deicer concentrations, the test environment, etc. It is also extremely difficult to relate laboratory test results of corrosion resistance to the actual field performance of metals [15].

In this context, roadway maintenance agencies strive to keep winter maintenance activities cost-effective and environmentally responsible, while ensuring winter roadway safety and mobility. These agencies need unbiased knowledge regarding a number of key issues in snow and ice control operations, such as: under various road and weather conditions, what amount of chemicals and/or abrasives really need to be applied for achieving a safe driving surface condition, how long the chemicals/abrasives applied onto the roadway would be effective, etc. In light of previous research, direct surface measurements (visual, pavement temperature, friction, etc.) may serve as a tool to address the aforementioned issues and thus improve roadway winter maintenance operations. Even though currently such measurements may not be a viable operational tool to be used in winter maintenance, they can be used as a great research tool. NCHRP Project 6-14 (completed in 2002) suggested two scenarios that appear to be promising for operational trial by state departments of transportation (DOTs). First, qualitative surface measurements or indices can be used to provide information to support winter maintenance decision-making. Second, surface measurements or indices and locations can be transmitted in near-real-time from the winter maintenance patrol or snowplow/spreader vehicles to a central office where the information is processed and transmitted to various users [22].

Measures and standards for deicers range from physical, chemical and environmental attributes to time-dependent performance and measures of corrosiveness. Levelton Consultants summarized some of the standard test methods of PNS, the Strategic Highway Research Program (SHRP), American Society for Testing and Materials (ASTM), and American Association of State Highway and Transportation Officials (AASHTO) [4]. For instance, the PNS test protocols include a large number of tests for physical, chemical and environmental attributes of deicers. For continuity, these are listed in entirety as available in the 2010 Pacific Northwest Snowfighters Snow and Ice Control Chemical Products Specifications and Test Protocols [23]:

- *Percent Concentration of Active Ingredient in the Liquid*
- Weight per Gallon
- *Corrosion Control Inhibitor Presence and Concentration*
- *pH*
- *Corrosion Rate*
- Percent Total Settleable Solids and Percent Solids Passing a 10 Sieve
- *Total Phosphorus*
- Total Cyanide
- Total Arsenic, Barium, Cadmium, Chromium, Copper, Lead, Selenium and Zinc
- Total Mercury
- Milliequivalents or "meq"
- Moisture Content of Solid Chemical Products.
- Gradation
- Visual Inspection and Field Observations.
- Toxicity Test
- Ammonia - Nitrogen
- Total Kjeldalh Nitrogen
- Nitrate and Nitrite as Nitrogen
- Biological Oxygen Demand
- Chemical Oxygen Demand
- Frictional Analysis
- Insoluble Material

The SHRP physiochemical characteristics have two major categories of tests to: 1) determine material properties and 2) define deicing potential. The first category of tests consists of

- “Principal chemical species identification and quantification.
- Minor chemical species identification and quantification. These potentially include additives and impurities.
- Moisture content including, if appropriate, water of hydration.
- Percent water insolubles.
- Identification of hazardous or toxic constituents.
- pH of aqueous solution. [24]”

The second category of SHRP physiochemical characterization tests consists of

- “Freezing points and associated deicer concentrations in water.

- Eutectic temperatures and eutectic compositions.
- Solubility, chiefly at temperatures between 0°C and the eutectic temperature.
- Heats of solution in water.
- Viscosities of aqueous deicer solutions. [24]"

Measures of deicer performance have been determined by SHRP and primarily include the Ice Melting Test (SHPR H-205.1 and H-205.2), Ice Penetration Test (SHRP H-205.3 and H-205.4), and Ice Undercutting Test (SHRP H-205.5 and H-205.6). Drawbacks of the SHRP ice melting, penetration, undercutting tests include the differences between actual and theoretical performance and, more importantly, the difficulty "to predict or design for the optimum combination of deicer and associated practices [24]".

Both SHRP and PNS have test protocols for laboratory analyses of the corrosivity of deicers. The SHRP materials compatibility tests generally take advantage of ASTM test methods in quantifying the deicer effect (or compatibility with) metals, nonmetals, concrete and pavement. The PNS test protocol for corrosivity is a modified version of the National Association of Corrosion Engineers (NACE) Standard TM1069-95. Levelton Consultants note many disadvantages to this test method, including a constant inhibitor concentration, lack of temperature and humidity control, and no direct correlation to field conditions [4].

Notably, Levelton Consultants mention the trend towards "performance-based methodologies" in determining procedures and how this can accommodate technical advances in measurement science [4], such as using differential scanning calorimetry versus eutectic curves.

When selecting chemicals for winter road maintenance, agencies tend to consider their performance characteristics (e.g., effective temperature and ice melting capacity) along with their cost, application rates required for various road weather scenarios, and environmental risks (including those to metals and concrete). For deicers, one widely used tool to aid such decisions is its eutectic curve, which presents the eutectic temperature as a function of deicer concentration on the weight basis. Eutectic temperature is the minimum temperature that a deicer solution remains in liquid form. During the process of melting snow or ice, additional water is produced and the concentration of the deicer is reduced, which may cause the solution to re-freeze. Thus, the eutectic temperature can be significantly different from the effective temperature for a deicer. In current practice, the effective temperature of deicers is generally determined by a consensus of field experience instead of a laboratory test. Factors that contribute to "effective temperature" include dilution and relative temperatures of pavement versus snow. The minimum effective temperature is the lowest temperature a deicer should probably be used, for practical purposes; because the amount of deicer needed at colder temperatures may be unreasonably high in order to achieve sufficient level of service.

1.2.2. Chemicals for Winter Road Maintenance

Deicers applied onto highways often contain chlorides as freezing-point depressants because of their cost-effectiveness, including mainly NaCl, $MgCl_2$, and $CaCl_2$, sometimes blended with proprietary corrosion inhibitors. A recent survey of highway maintenance agencies conducted by the Western Transportation Institute (WTI) indicated that NaCl was the most frequently used deicer, followed by abrasives, then $MgCl_2$, agro-based products, $CaCl_2$, and others. Less than 25% of the survey respondents used alternative deicers such as potassium acetate (KAc), sodium acetate (NaAc), calcium magnesium acetate (CMA), and potassium formate (KFm) [14].

NaCl is the most widely used chemical due to its abundance and low cost; however, its effectiveness is minimal below pavement temperatures of 10°F (-12°C) [2]. $MgCl_2$ brines feature better performance at lower temperatures [14, 25]. Field studies have shown $CaCl_2$ to be more effective than NaCl, owing to its ability to attract moisture and stay on the roads [26]. The use of $MgCl_2$ or $CaCl_2$ for anti-icing may cause damage to concrete [16] and lead to potentially slippery conditions under certain circumstances [27, 28]. In addition to chlorides, acetates such as KAc and CMA are used for anti-icing or deicing respectively. For anti-icing applications, KAc is an attractive alternative to chlorides since it is less corrosive and has low effective temperature and benign impacts on surrounding soils and ecosystems. Its disadvantages, however, include the cost of applications, high corrosivity to galvanized steel[3], and deleterious impact on concrete (e.g., aggravated ASR - alkali silica reaction) and asphalt pavements [14]. The negative impacts of acetates and formates are greater than perceived by winter maintenance practitioners, especially with respect to damage to pavements, structures and water quality.

Also available are a variety of agro-based chemicals used either alone or as additives for other winter maintenance chemicals [29]. They have emerged since the late 1990s, often produced through the fermentation and processing of beet juice, molasses, corn, and other agricultural products [30, 31]. Recently glucose/fructose and unrefined sugar have been mixed in sand to prevent freezing and added in salt brine for anti-icing [32]. Agro-based additives increase cost but may provide enhanced ice-melting capacity, reduce the deicer corrosivity, and/or last longer than standard chemicals when applied on roads [8, 33]. Such products can be very expensive if used alone; however, they are frequently mixed with other common deicers to lower their freezing point and inhibit their corrosiveness [29]. The deployment of commercial agro-based products has been hindered by concerns over their toxicity to the aquatic ecosystems adjacent to highways (due to high phosphate, nitrate, or total organic content), high cost, and quality control issues [8]. Phosphorus (P) spurs the growth of algae, reducing oxygen for other aquatic biota [8]. The common agro-based products are proprietary and generally contain chloride salts and low molecular-weight carbohydrates derived from sugar beet, molasses, or corn; and there are user

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[2] At 5°F, NaCl still works but it would take much more applied salt to be effective.

[3] KAc has been found to be highly corrosive to galvanized steel, but relatively non-corrosive to mild steel.

concerns over their possible attraction to wildlife or high P content (per the discussions on the Snow-Ice List Serve). Recently, Taylor *et al.* [34] evaluated the brines made of glycerol, NaCl, $MgCl_2$, and commercial deicers individually or in combination and concluded that the blend of 80% glycerol with 20% NaCl showed the greatest promise in good performance and low negative impacts. This blend however has very high viscosity and its dilution allows anti-icing application but reduces effectiveness. Furthermore, this specific study did not examine the environmental impact of glycerol-based blends to aquatic species. The use of glycerol may pose potential risk to water quality, which has to be mitigated by limiting its dosage in the formulation and controlling the contaminants in it. It merits more research to explore the synergism of glycerol and other additives in optimizing the anti-icing formulations.

1.3. Study Objective

The objective of this study was to evaluate the longevity of corrosion inhibitors and the performance of corrosion-inhibited deicer products under storage or after pavement application. Specifically, this study aims to answer or at least shed light on the following fundamental questions relevant to winter maintenance practitioners, using the combination of laboratory and field investigations:

- the longevity of the corrosion inhibitors and the duration in which they persist with the deicer (both under storage and after pavement application);
- the possible effects of temperature, UV intensity, exposure, and dilution on inhibitors in common chloride deicers and deicer performance;
- the cost-effectiveness of including inhibitors in deicers;
- any inhibitor effect on freezing point suppression or deicer effectiveness; and
- the most effective deicer for different winter weather scenarios.

1.4. How This Report Is Organized

The following chapter will discuss the inhibitor longevity and deicer performance under storage conditions, whereas Chapter 3 will discuss the inhibitor longevity and deicer performance after pavement application during three types of winter storms. Finally, Chapter 4 summarizes the key findings from this project, followed by suggestions and recommendations for implementation by the winter maintenance practitioners. Appendices conclude this report, which include the standard operating procedures for both laboratory and field investigations as well as the details of deicer performance during field operational tests.

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CHAPTER 2 INHIBITOR LONGEVITY AND DEICER PERFORMANCE UNDER STORAGE

This chapter presents the methodology, results and discussion pertinent to the investigation of the longevity of corrosion inhibitors and the performance of corrosion-inhibited deicer products under various storage conditions. The work started by developing or establishing the appropriate methods of rapidly and reliably quantifying the chloride and inhibitor concentrations, solution pH and conductivity, deicer performance and corrosion characteristics. Subsequently, the established analytical methods were used to monitor the temporal evolution of the identified deicer properties under field storage, by randomly sampling the solid or liquid deicers periodically and analyzing them in the laboratory.

2.1. Experimental

2.1.1. Deicers of Interest

This study involved three liquid deicers and one solid deicer of interest to the project sponsors. These include the inhibited NaCl liquid deicer, the inhibited $CaCl_2$ liquid deicer (Calcium Chloride with Boost, or CCB^{TM}), the inhibited $MgCl_2$ liquid deicer (FreezGard CI Plus^{TM}), and the inhibited NaCl-based solid deicer (IceSlicer Elite^{TM}). They represent deicer products under selected PNS categories, with individual chloride and inhibitor concentrations provided in Table 1 and Table 2 respectively. The inhibited NaCl liquid deicer was prepared by WTI by adding a given amount of Shield GLT^{TM} inhibitor (by Paradigm Chemical LLC, Lakewood, CO) into the mixture of well water and solid "rock salt" from Compass Minerals (Overland Park, KS) with salt/water weight ratio of 20/80 and stirring to blend (as specified by the GLT vendor), whereas the CCB, FreezGard, and IceSlicer were purchased from America West (Pasco, WA), Compass Minerals (Overland Park, KS), and Redmond Minerals (Redmond, UT) respectively.

TABLE 1 Chloride and inhibitor concentrations of the deicer products for the field monitoring study, as stated by the vendor or measured independently.

Deicer Product	Salt Concentration (by vendor)	Corrosion Inhibitor Concentration (by vendor)	Salt Concentration (by WTI)	Corrosion Inhibitor Concentration (by WTI)	Inhibitor to Chloride Ratio
NaCl+GLT	specified 23%	5%	19.3%	4.3%	1:4.5
CCB	31+%	12%	42.4%*	11.1%	1:3.8
FreezGard	29-31%	1.7%	36.1%*	2.4%	1:15.0
IceSlicer	NA	1.5%	NA	0.2%*	NA

* These reported concentrations are likely higher than the actual concentrations, for unknown reasons. Note that the salt concentrations reported by WTI were calculated based on the elemental concentrations of cations (Na, Ca, or Mg) measured using the inductively-coupled plasma (ICP), whereas the vast majority of the salt concentrations reported in this project were calculated based on ion-selective sensor measurements of chloride concentration. There could be cations that are associated with the corrosion inhibitor or other additives, instead of the Cl^- anions.

TABLE 2 Salt concentrations and percent corrosion rate (*PCR*) of the deicer products, as tested by the Analytical Laboratories Inc., Idaho.

Product	%$CaCl_2$ (Ca)	%$MgCl_2$ (Mg)	%KCl (K)	%NaCl (Na)	%Chloride	%NaCl (Cl)	%$CaCl_2$ (Cl)	%$MgCl_2$ (Cl)	PCR
2008 NaCl+GLT	NA	NA	0.06	20.49	11.2	18.46			30.7
2010 NaCl+5%GLT	0.03	NA	0.04	23.64	14.1	23.24			32.5
2008 CCB	31.57	0.12	1.39	0.69	21.0		32.87		20.8
2008 Freezegard	0.36	31.42	0.17	0.28	24.1			32.36	16.1

* Note that the 2008 products were for the field monitoring study (detailed in Chapter 2) whereas the 2010 product was for the field operational tests (detailed in Chapter 3). The salt concentrations were calculated in two ways, one by the cation and one by the anion.

The inhibitor concentration in the solid deicer - IceSlicer Elite (Table 1) was measured by WTI using the total phosphorus method, whereas the inhibitor concentrations in the other three liquid deicers were measured by WTI using the UV-vis method. The WTI-measured inhibitor concentration for IceSlicer Elite was much lower than that provided by the vendor, mostly because of the limited solubility of the inhibitor in the salt brine. The vendor thus no longer markets this specific product formulation and all the data provided in this report are purely for research purposes.

2.1.2. Laboratory Testing

All the deicer samples from field storage were stored in the refrigerator. Prior to laboratory testing, they were removed from cold storage and allowed to reach room temperature (21 to 23°C). For each deicer property, at least three duplicate samples were tested or at least three readings were taken (e.g., pH and electrical conductivity).

MEASURING CHLORIDE CONCENTRATION IN DEICER SAMPLES

First of all, every liquid deicer received from the vendor was diluted 100 times before being tested to determine its chloride ion (Cl^-) concentration by chemical titration. The titration followed the Mohr's method [1], as detailed in Appendix A3. Additionally, elemental analysis of as-received deicers was conducted using ICP to estimate the salt concentration in each deicer, which indirectly validated the chloride concentration. For each deicer, once the as-received chloride concentration was measured, a less time-consuming alternative method was used to determine Cl^- concentration in deicer solutions with unknown properties (e.g., deicers solutions sampled from storage tanks).

We used custom-made chloride ion-selective sensors to quickly measure the chloride concentration in deicer samples, as detailed in Appendix A3. This is a proven technology, i.e., the Cl^- concentration is obtained by measuring the electrochemical potential (*E*) of a calibrated silver/silver chloride (Ag/AgCl) electrode (relative to a reference electrode). The chloride sensor functions as a redox electrode and the reaction is between the silver metal (Ag) and its salt — silver chloride (AgCl):

$$Ag^0(s) + Cl^- \rightarrow AgCl(s) + e^-$$

The silver sensor was fabricated by electroplating AgCl on the surface of clean silver wire, which entails the use of a Princeton Applied Research Potentiostat/Galvanostat Model 263A to apply a series of galvanostatic steps to the wire immersed in a 1.0 M potassium chloride (KCl) solution. Once cleaned with de-ionized water, the fabricated sensor was stored in 1.0 M KCl solution. Before using it for measurements, the sensor was calibrated by sequentially immersing it in at least five standard solutions with known Cl^- concentration. Different chloride sensors were fabricated, calibrated, and used for each type of deicer (NaCl, $CaCl_2$, and $MgCl_2$). On each testing day, a chloride concentration standard curve was established for the sensor for each deicer type. There generally was a very strong linear correlation between the *E* of the sensor and logarithm of molar concentration of Cl^-. If R-square of the linear regression was lower than 0.9, the calibration process was repeated. If the problem continued, then the chloride sensor was re-fabricated. We used a saturated calomel electrode (SCE) as the reference electrode and each *E* reading was taken in the solution of interest after allowing it to stabilize for a few minutes. Subsequently, the sensor's response (*E*) to any field storage deicer sample was compared against the standard curve to derive its Cl^- concentration.

MEASURING INHIBITOR CONCENTRATION IN DEICER SAMPLES

Ultraviolet-visible spectroscopy or spectrophotometry (UV-Vis) has been routinely used in the quantitative determination of solutions of transition metal ions and highly conjugated organic compounds. Organic compounds, especially those with a high degree of conjugation, also absorb light in the UV or visible regions of the electromagnetic spectrum. As detailed in Appendix A4, we first identified the *characteristic* UV-absorption peak (in a certain wavelength range) for each of the corrosion inhibitors in the three liquid deicers, using a Molecular Devices® Spectromax 384 Plus UV-vis spectrophotometer to collect the full spectrum (190 to 750 nm) data of each inhibited deicer. The inhibited NaCl liquid deicer (with Shield GLT™), the inhibited $CaCl_2$ liquid deicer (CCB™) and the inhibited $MgCl_2$ liquid deicer (FreezGard CI Plus™) each showed a characteristic UV-absorption peak near 275 nm, 264 nm and 260 nm respectively.

Then, we used UV-vis to rapidly detect the presence and concentration of corrosion inhibitor in deicer samples. On each testing day, an inhibitor concentration standard curve was established for each deicer type, using at least five standard solutions with known inhibitor concentration. There generally was a very strong linear correlation between the absorbance intensity at the characteristic peak wavelength and the inhibitor concentration. If R-square of the linear regression was lower than 0.9, the calibration process was repeated. To avoid background noise and interference, the UV spectrum of deicer samples without corrosion inhibitor were tested as control. Subsequently, the UV-vis signal of any field storage deicer sample was compared against the standard curve to derive its inhibitor concentration.

Standard curves were established both using the pure corrosion inhibitors provided by the vendors and using as-received corrosion-inhibited deicers. Due to the initial color of the inhibitors, each inhibitor required a unique dilution rate in order to establish standard curves with very strong correlation as indicated by R-square. The FreezGard standard curves were established using diluted inhibitor solutions between 0.1% and 1.0%, whereas the Shield GLT and CCB inhibitor-only standard curves used diluted inhibitor solutions between 0.0375% and 0.1%. For best results, all the NaCl+GLT, CCB, and FreezGard deicer samples were diluted to 1.0%, 0.1% and 10% respectively, before the UV-vis analysis.

As for the solid deicer IceSlicer Elite^{TM}, we tested the use of UV-vis to quantify its inhibitor concentration once it was prepared into 23 wt% solution but failed to obtain a strong correlation for standard curves. This may be attributable to the dark color of the deicer, the relatively high content of suspended solids in the liquid solution, and the poor solubility of its inhibitor (as mentioned earlier). As such, we followed the suggestions by the vendor and used the total phosphorus measurement to quantify the inhibitor concentration, as detailed in Appendix A9. IceSlicer contained a corrosion inhibitor with phosphates that were present in a condensed inorganic form, which had to be converted to a reactive orthophosphate using acid and heat prior to the analysis of total P in the sample. A Hach DRB 200 reactor was used in conjunction with a Hach DR/890 Colorimeter, following the Hach Method 10127 "Molybdovanadate Method with Acid Persulfate Digestion, Test 'N Tube™ Procedure" to determine total P concentration in all Iceslicer samples.

MEASURING pH AND CONDUCTIVITY OF DEICER SAMPLES

The pH of deicer sample solutions was determined following the ASTM D 1293 test method, using a Fisher Scientific® Accumet Basic AB15 pH meter. The pH meter was calibrated following the manufacturer's instructions, using a range of pH buffer solutions of 4, 7, and 10. The pH meter was placed into a continuously stirred deicer sample and allowed to stabilize for a few minutes before taking the reading. The pH meter calibration was conducted periodically to reduce any potential shift in readings. In most cases, the pH of as-received or as-sampled deicers was measured and reported. In some cases, the deicer samples were diluted 5 times (1 part deicer to 4 parts de-ionized water), in order to examine the effect of such dilution (as followed by the PNS Association) on the pH reading.

The conductivity of deicer sample solutions was measured using a Eutech Instruments® CON510 Bench Meter. The conductivity meter was calibrated following the manufacturer's instructions, using vendor-provided standard solutions. The standard solutions were made of reagent-grade salt solutions with known conductivity. The conductivity meter was placed into a continuously stirred deicer sample and allowed to equilibrate for a few minutes before taking the reading (in units of mS/cm).

CONDUCTING DSC ANALYSIS OF DEICER SAMPLES

The use of a differential scanning calorimetry (DSC) thermogram to rapidly and consistently quantify deicer performance was initially proposed by Shi et al. [2], based on work by Han and Bischof [3] who investigated freezing and thawing of salt brine in biological systems. DSC is an experimental technique that measures the energy necessary to maintain a near-zero temperature difference between the test substance and an inert reference material, with the two subjected to an identical temperature program. By measuring the heat flow, DSC can detect phase transitions and quantify energy change, and measure kinetics of the transitions.

For deicer characterization, the DSC thermogram can provide information on the characteristic temperature (T_c) and the heat flow (H) during the liquid/solid phase transition of a given deicer, which also shed light on a more realistic working temperature range than a deicer's eutectic temperature. Specifically, the first peak temperature at the high temperature end of the warming cycle is defined as the T_c of the deicer, which corresponds to the temperature below which ice crystals start to form in the aqueous phase. The T_c for a deicer solution can be compared to that of NaCl brine and thus indicates its effective temperature range relative to NaCl brine. The H for a deicer solution indicates the amount of thermal energy needed for the liquid/solid phase transition. Conceptually, the stronger a deicer, the lower the T_c and the smaller the H associated with the T_c peak. A strong correlation between the DSC data (T_c and H) and the Modified SHRP Ice Melting test data has been developed. This provides another opportunity to utilize the DSC test results, that is, to predict the ice melting capacity (*IMC*) of a chloride-based deicer.

In this study, we conducted the DSC analysis of deicer samples following the method developed by Akin and Shi [4], as detailed in Appendix A7. We used a TA Instruments® DSCQ200 unit and Thermal Analysis software to quantify the thermal properties of deicers. All samples were run as liquids. The solid IceSlicer samples were first made into 23 wt.% solutions with de-ionized water. Then all liquid samples were run at 3:1 dilution. Ten µL of each sample were pipetted into an aluminum capsule and hermetically sealed, and then weighed. All samples were run in triplicate against an empty-pan reference. The test program was set to run from 77 to -76°F (first stabilized at 25°C, then cooled to -60°C, stabilized, and finally warmed to 25°C) with cooling/heating rates of 3.6°F (2°C) per minute. Initial results showed that DSC was a reliable quality control tool for deicer performance.

For data analysis, the warming cycle thermogram was used and when more than one peak was present (e.g., NaCl), the temperature and heat flow associated with the warmer peak were reported. The average values of characteristic temperature (T_c, in °F) and integrated heat flow (H, in J/g) were reported for each deicer sample. In general, if the coefficient of variance (CoV) for the H was greater than 10 percent or the standard deviation for the T_c was greater than 0.5°F, then additional tests were performed. We also used the T_c and H results to predict the performance of chloride-based deicers in the Modified SHRP Ice Melting Test, using the following equation developed by Akin and Shi [4]:

$$IMC_{30^\circ \mathrm{F}}(\text{mL brine}) = -0.02265T_c + 1.965\log(\Delta H) + 0.03285t - 2.1761 \quad (\mathrm{R}^2 = 0.94)$$

where *IMC* = expected volume of brine that will be collected in Modified SHRP Ice Melting Test after *t* minutes (mL)

ΔH = 345 J/g minus heat flow (H in J/g) of warmer peak from DSC, in which

345 J/g was the heat flow obtained using pure water
T_c = characteristic temperature on warming cycle from DSC (°F)
t = time between 10 and 60 (minutes)

TESTING CORROSION OF DEICER SAMPLES TO METAL

The corrosion of deicer samples to metal was tested using two different methods, one of which was a gravimetric method and the other was an electrochemical method. As detailed in Appendix A6, the gravimetric method followed the National Association of Corrosion Engineers (NACE) Standard TM0169-95 as modified by the PNS Association, but used de-ionized water in place of distilled water. The PNS had modified the NACE method so that it used 30 ml of a 3% aqueous solution of the as-received deicer per square inch of coupon surface area for the corrosion test. The test entailed cyclic immersion (10 minutes in the solution followed by 50 minutes exposed to air) of multiple parallel coupons for 72 hours on a custom design machine by AD-Tek®. Three 1.38″ x 0.56″ x 0.11″ ASTM F 436, Type 1 TSI® steel washers with a Rockwell Hardness of C 38-45 were used in each deicer solution and in the de-ionized water and NaCl control solutions for testing. The weight loss result in MPY (milli-inch per year) was translated into a percentage, or percent corrosion rate (PCR), in terms of the 72-hour average corrosivity of the deicer solution relative to the solid salt (NaCl).

The electrochemical method was established to allow rapid determination of corrosion rate of metals and to reveal information pertinent to the corrosion and inhibition mechanisms, as detailed in Appendix A5. Corrosion to mild steel (ASTM A 36) coupons was measured using a Gamry Instruments® Potentiostat with an 8-channel Electrochemical Multiplexer ECMB. Deicer solutions were diluted to 3% by volume. After the metal samples were cleaned with acetone and deionized water and dried, they were placed in a continuously mixed deicer solution for 24 hours to monitor the open circuit potential (OCP) of metals. A three-electrode system was used, with the steel coupon being the working electrode, a platinum wire being the counter electrode and a SCE being the reference electrode. At 24 hours of immersion, the weak polarization curve of each metal sample was taken to measure the corrosivity of deicers. Each deicer sample was tested using four repetitions of steel coupons. We used a weak potentiodynamic polarization technique, i.e., measuring the current-potential plot of the steel in deicer solution when an external potential signal (DC perturbation) was applied within ± 30 mV range of its OCP at a sweeping rate of 1 mV/s. By measuring the weak polarization curve, we obtained the corrosion potential (E_{corr}) of the steel in the deicer solution and its instantaneous corrosion rate in terms of corrosion current density (i_{corr}). The weak polarization curves were able to provide “signature” information pertinent to the corrosion behavior of steel in each deicer and could be used for deicer products. We also tried another type of electrochemical test protocol, by incorporating wet-dry cycles (i.e., 1-hr wet, 4-hr dry, 1-hr wet, 16-hr dry followed by 2-hr wet) into the 24-hour duration. Such cyclic 24-hr immersion prior to the electrochemical test, however, failed to provide a better correlation between the PNS/NACE and the electrochemical test results than the continuous 24-hr immersion and was thus not used for the testing of deicer samples.

2.1.3. Field Sampling

MIXING AND SAMPLING PROTOCOL

The liquid deicers were contained in six 3000-gallon Norwesco® above-ground tanks stored outside, located in a containment basin at the TRANSEND® cold regions test-bed at Lewistown, MT, as shown in Figure 1. They were stored throughout the observation and sampling period, from April 2008 to May 2009. The tanks were made of a UV-stabilized high-density polyethylene resin (ExxonMobil HDPE HD 8660 Rotational Molding Resin) that provides outstanding environmental stress crack resistance.

FIGURE 1 The six 3000-gallon tanks full of liquid deicers at TRANSEND. Along the center line are the three pumps used to mix one tank of each deicer.

Each of the three deicers had a designated mixed and non-mixed tank. The three "mixed" tanks were mixed once a week for one hour for the first month and twice monthly for one hour thereafter. The tanks were mixed using an on-site pump system where the input of the pump was connected to the bottom of the tank and the output of the pump was connected to a top valve on the top of the tank creating a vortex to ensure uniform mixing, following the design specifications by the South Dakota DOT. One-liter brine samples were collected from each tank once a week for the first month and once monthly thereafter for 13 months. The sample collection method required the pour valve at the bottom of the tank to be opened and allowed flow for about 3 minutes to flush the system, at which point the liquid deicer was collected into a sterilized plastic bottle and sealed. Tank sampling occurred immediately following the second tank mixing of the month. Stratified samples of the mixed and non-mixed tanks were collected once every six months or so to determine if the deicer solutions remained homogenous over time. Stratified samples were collected at three levels; top, middle, and bottom within the tanks, using a Van Dorn Bottle®.

For the solid NaCl-based deicer (IceSlicer), both covered and uncovered storage facilities (identical to those shown in Figure 2) were built on site and the deicer was stored using two methods: in a pile outside with full exposure to the elements; and in a pile stored within an enclosure. The deicer was stored throughout the observation and sampling period, from December 2008 to December 2009. The enclosure consisted of three walls and a roof (Coverall and Versatube Building Systems, 24′x20′x12′, White) with a wind and rain screen on the open side (String Reinforced Polyethylene Sheeting from US Netting, 12′x25′ on steel cable and grommets). The floor of the building was lined with pond liner (30 mm polyvinylchloride or PVC). The pile of solid deicer stored outside sat on pond liner with the soil beneath burmed on all sides and sloping at a 3 to 5% angle to a water collection cistern buried in the ground.


(a) (b)

FIGURE 2 Photograph of (a) uncovered IceSlicer on the outdoor slope pad and (b) a 10% salt-sand mixture inside the storage facility at TRANSEND.

The sampling method for the solid NaCl deicer collected from both the storage enclosure and the pile left outside followed the ASTM D 632 method, which required at least three sub-samples to be selected at random from the top, middle and bottom profiles of each storage pile. This was to ensure a representative cross-section of the material being collected. A sub-sample was obtained from a randomly chosen area within the top third, at the midpoint, and at the bottom third of the total volume of material. Following the specifications provided by the Washington State DOT, we used a sampling tube for sub-sample collection to ensure a cross sectional representation of the materials. A sample tube is typically constructed of thick-walled PVC pipe 1 ½″ in diameter and no less than 48″ long with a tapered 45-degree edge on one end to obtain desired sample depths and quantities. Each sub-sample was collected by scraping aside the top layer of material to a depth of at least one inch then driving the sampling tube into the material to a depth of no less than six inches to collect a total target sample weight of at least five pounds. The collected sub-samples of the solid deicer were thoroughly mixed in a 5-gallon bucket to make up one composite sample representative of the storage pile. In some cases, the sample was then pulverized so that it passed through a 300-µm (No. 50) sieve.

METEOROLOGICAL DATA COLLECTION

For this study, we monitored the air temperature and relative humidity (Campbell Scientific® CD215), wind speed and direction (Young® wind monitor 05103), barometric pressure (Setra® 278), and solar radiation (Apogee® PYR-P Pyranometer CS300) at the storage site at Lewistown, MT. Pavement temperature was monitored using Omega® Type T thermocouples embedded at the asphalt pavement surface located 20 ft from the pavement edge as well at 15 inches below the asphalt pavement surface located 10 ft from the edge of the asphalt pavement. A Campbell Scientific® CR1000-XT data logger was used to capture and record readings from all the meteorological sensors.

LABORATORY STUDY OF INHIBITOR LONGEVITY

To better understand the results from the field investigation where many parameters fluctuate over the time of investigation, experiments were conducted in the MSU Civil Engineering Department Sub-zero Science and Engineering Facility to investigate how UV intensity, temperature, and exposure time affect the longevity of corrosion inhibitors in deicer products. As illustrated in Figure 3, there are many factors in the field environment that could potentially affect the longevity and performance of inhibitors. In this study, we focused on the factors highlighted in light blue in the diagram.

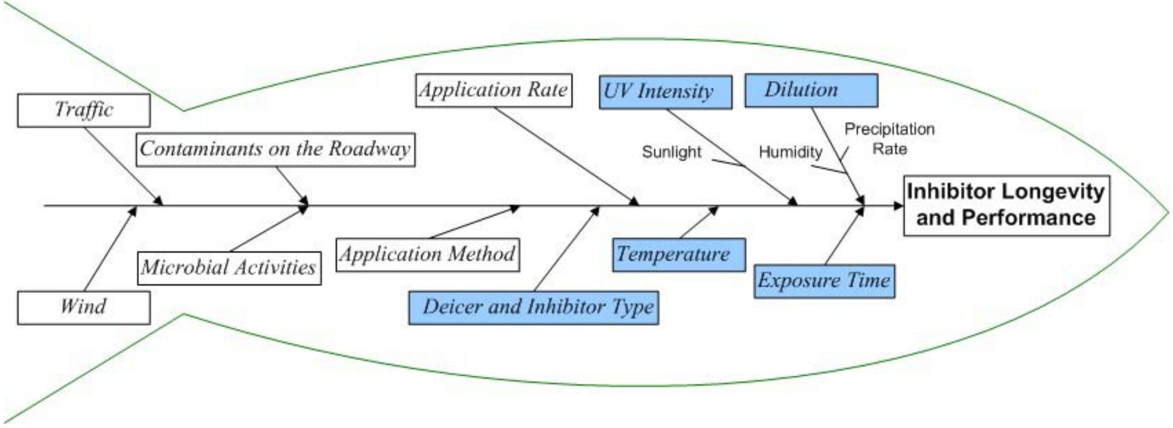

FIGURE 3 Fish diagram illustrating the influential factors in inhibitor longevity and performance.

In the laboratory, we preliminarily explored the dilution effect on inhibitor concentration. The preliminary laboratory testing was conducted by applying liquid deicers on asphalt pucks (8″ in diameter and 2″ in thickness) in the environmental chamber. The asphalt pucks were fabricated at the MSU, following the Montana DOT specifications that were used for the asphalt pavement at the TRANSEND field test-bed. Experiments were conducted to determine how to apply a stream of liquid deicer on such simulated pavement surface at the appropriate application rate. To determine the percent recovery of deicers from the asphalt puck, a known volume of deicer at a known concentration was applied. The generated brine was then collected from the asphalt puck using a pipette. Unfortunately, for all three liquid deicers, the percent of recovery was well below 10%, subsequent to a simulated black ice event, due to the loss to evaporation and to pavement pore structure and edges. Thereafter, we decided to leave the investigation of dilution effect on inhibitor concentration to the field operational tests.

TABLE 3 Design scheme of experiments to investigate the factors affecting the inhibitor longevity under the laboratory conditions

Products	Temperature	Time	UV Exposure
CCB	28	72	UVb
CCB	28	48	UVa
CCB	18	96	UVa+UVb
CCB	18	48	UVa
CCB	-9.4	72	None
CCB	-9.4	24	UVb
CCB	40	96	UVa
CCB	40	48	UVa+UVb
CCB	40	24	none
FreezGard CI Plus	28	96	None
FreezGard CI Plus	28	24	UVa+UVb
FreezGard CI Plus	18	72	UVb
FreezGard CI Plus	18	48	None
FreezGard CI Plus	18	24	UVa
FreezGard CI Plus	-9.4	96	UVb
FreezGard CI Plus	-9.4	48	UVa+UVb
FreezGard CI Plus	40	72	UVa+UVb
FreezGard CI Plus	40	72	UVa
NaCl + GLT	28	72	UVa
NaCl + GLT	28	24	UVb
NaCl + GLT	18	96	Uva
NaCl + GLT	18	48	UVb
NaCl + GLT	-9.4	72	UVa+UVb
NaCl + GLT	-9.4	24	None
NaCl + GLT	40	96	UVb
NaCl + GLT	40	72	None
NaCl + GLT	40	48	UVa+UVb
IceSlicer Elite	28	96	UVa+UVb
IceSlicer Elite	28	48	UVb
IceSlicer Elite	28	48	None
IceSlicer Elite	18	24	UVa+UVb
IceSlicer Elite	18	72	None
IceSlicer Elite	-9.4	96	UVb
IceSlicer Elite	-9.4	96	None
IceSlicer Elite	-9.4	24	UVa
IceSlicer Elite	40	24	UVa

As such, we focused on the effect of inhibitor (deicer) type, temperature (in ºC), UV intensity, and time (in hours) on the inhibitor degradation and the experimental design is presented in Table 3. For each set of experimental parameters shown in Table 2, five duplicate samples were tested. Following the conclusion of the experiment, the corrosion inhibitor concentration for each deicer was measured using the UV-vis (for the three liquid deicers) or total phosphorus (for IceSlicer) method.

2.2. Results and Discussion

2.2.1. Meteorological Conditions at the Storage Site

This section presents the temporal evolution of meteorological conditions at the storage site for the three liquid deicers and the one solid deicer, at the TRANSEND facility at

Lewistown, MT. Such information may help to explain the temporal evolution of deicer properties under storage, as detailed later. Figure 4 presents the change of average weekly air temperature and relative humidity over the time period of deicer storage. It shows that the average weekly air temperature fluctuated greatly with the season (mostly between 0ºF and 70ºF) whereas the fluctuation of relative humidity did not show a seasonal trend (mostly between 35% and 70%).

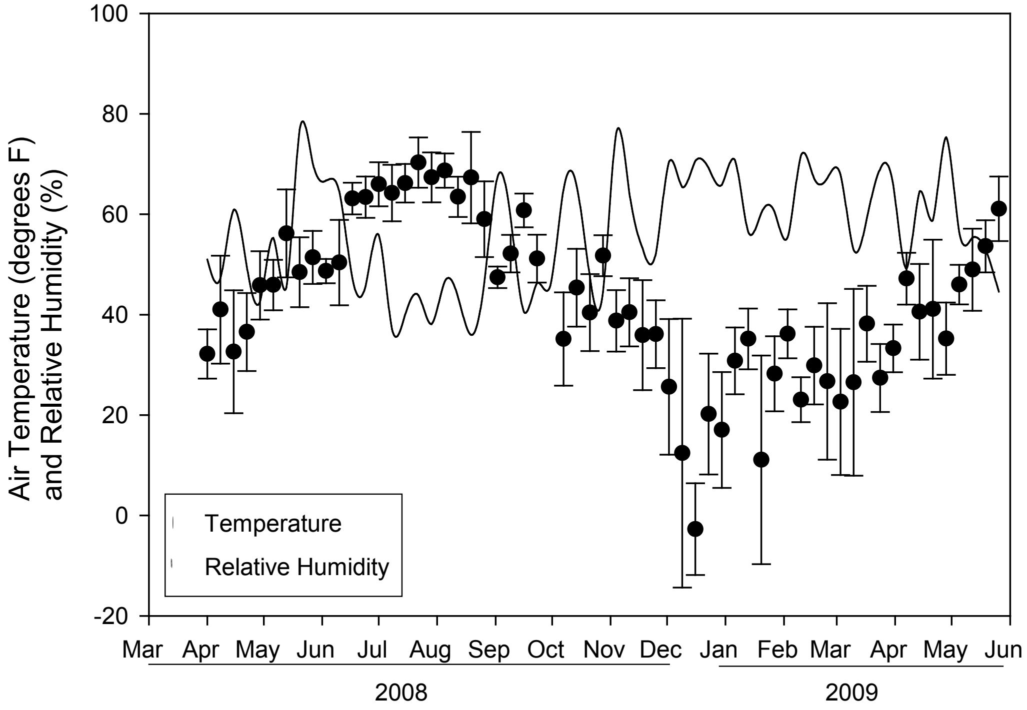

FIGURE 4 Temporal evolution of average weekly air temperature and relative humidity at the storage site.

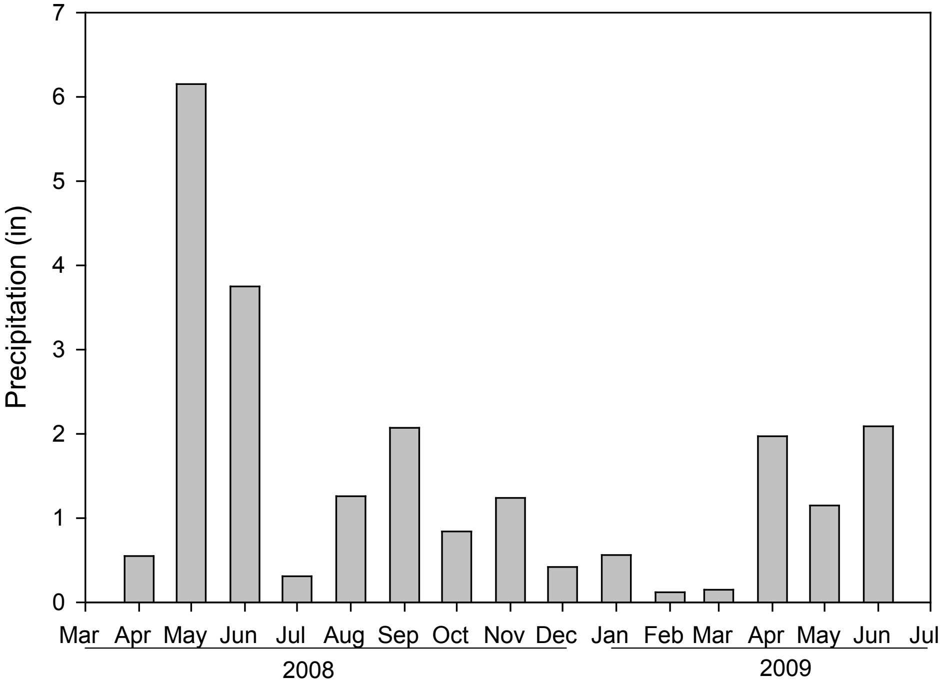

FIGURE 5 Temporal evolution of average monthly precipitation at the storage site.

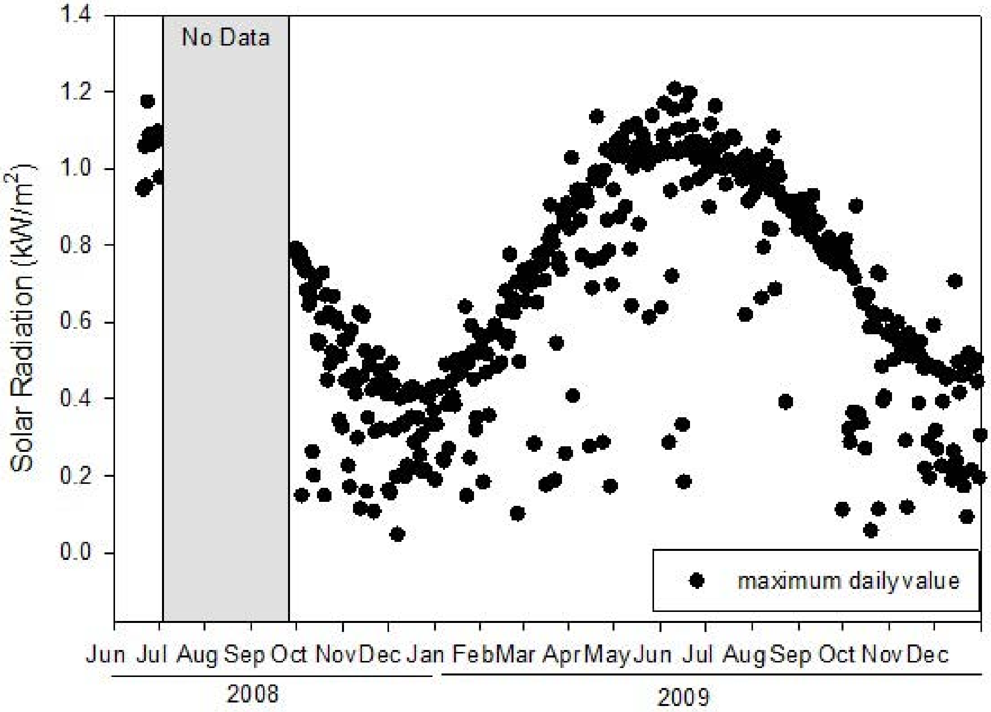

FIGURE 6 Temporal evolution of maximum daily solar radiation at the storage site.

Figure 5 presents the change of average monthly precipitation over the time period of deicer storage. Note that the reported precipitation includes both rain and snow. During the months of December, January, February, and March, the reported precipitation was mostly from snowmelt water. Since precipitation is generally measured in inches of liquid water and not in snowfall amounts, snow is usually converted into inches of water by dividing by 10. Figure 6 presents the change of maximum daily solar radiation at the storage site, which shows a trend of seasonal fluctuations mostly between 0.1 and 1.2 kW/m^2. In general, the maximum daily solar radiation at the storage site was low during winter weather and high during summer weather.

2.2.2. Longevity of $MgCl_2$-based FreezGard under Storage

This section presents the temporal evolution of properties of the $MgCl_2$-based FreezGard deicer over the months of field storage monitoring, including the chloride and inhibitor concentrations, corrosion parameters (E_{corr} and PCR), pH, electrical conductivity, and performance parameters (T_c and $IMC_{30°F}$). The data are often presented in the form of average value ± standard deviation, especially when the data variability over time was limited. There was no significant difference in deicer properties between mixed and non-mixed samples collected from the FreezGard CI Plus tanks, therefore the mixed and non-mixed sample data were combined for analysis.

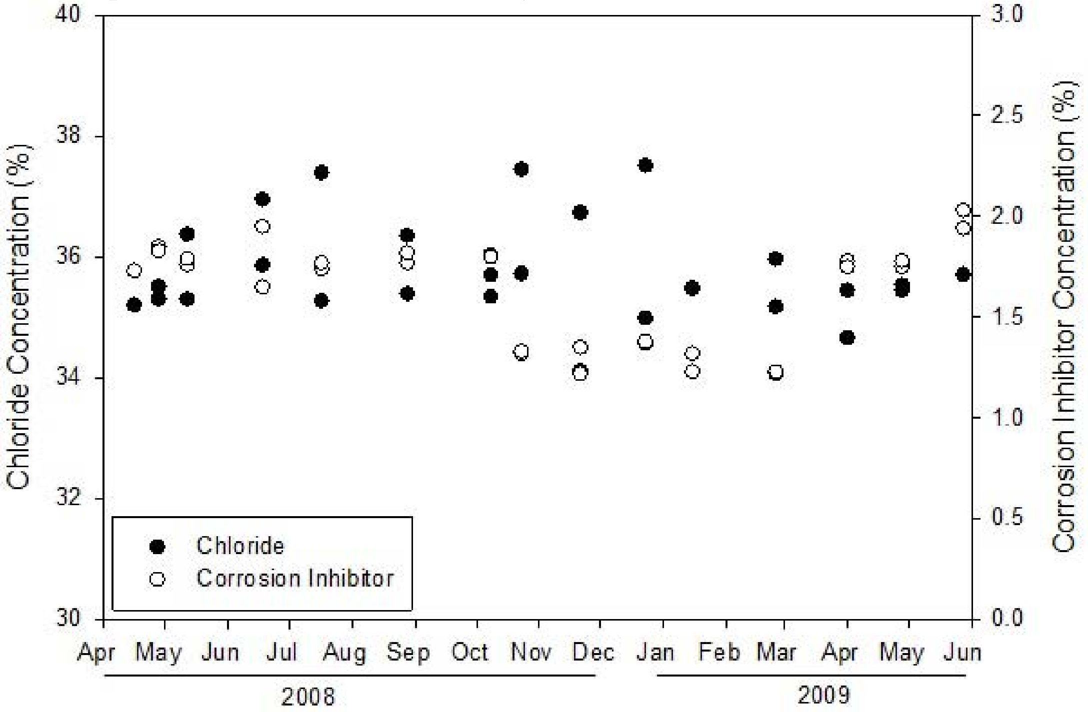

FIGURE 7 Temporal evolution of chloride and inhibitor concentrations in the FreezGard deicer tanks.

Figure 7 presents the change of chloride and inhibitor concentrations over the time period of the FreezGard deicer storage. It shows that during the field storage months the average chloride and inhibitor concentrations in the FreezGard deicer generally remained within

35.6±0.8% and 1.7±0.3% respectively. The observed fluctuations seem to be non-seasonal but more likely attributable to the sampling and measuring variabilities. No significant degradation of corrosion inhibitor was seen during the 14 months of field storage. The inhibitor-to-chloride concentration ratio in the mixed and non-mixed FreezGard tanks was highly consistent over the months of field storage and both averaged at 1:21.

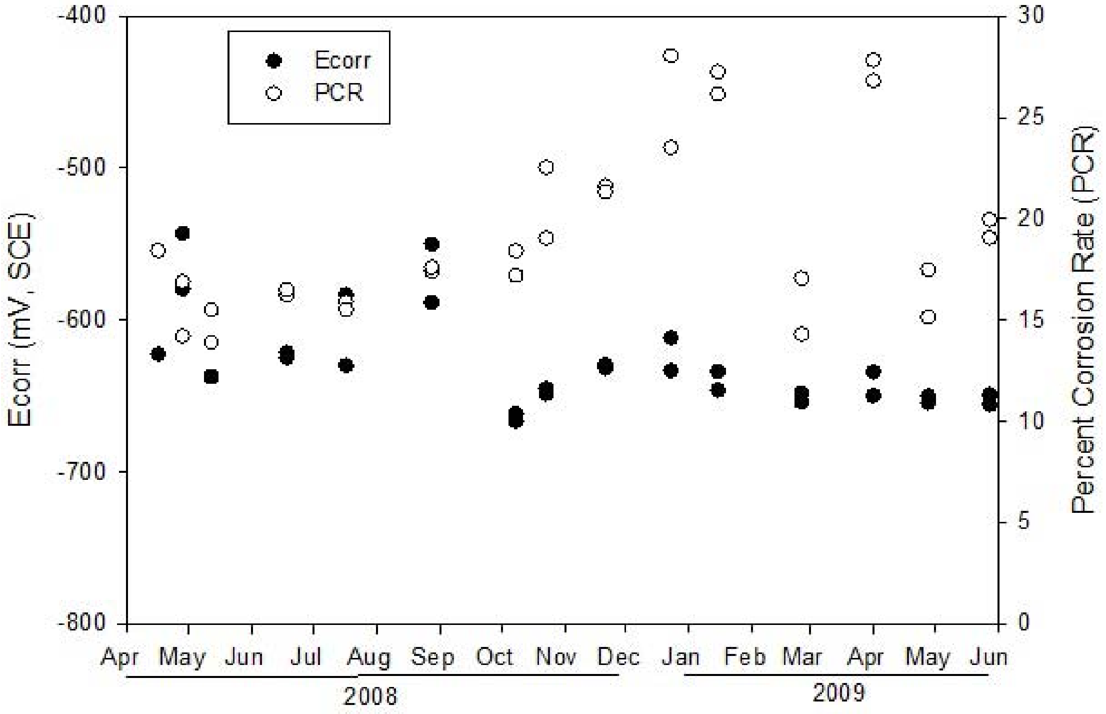

FIGURE 8 Temporal evolution of deicer corrosivity to steel (indicated by E_{corr} and *PCR*) in the FreezGard deicer tanks.

Figure 8 presents the change of deicer corrosivity over the time period of the FreezGard deicer storage. It shows that during the field storage months the corrosion potential of mild steel (E_{corr}) remained fairly consistent within -630±27 mV (SCE) whereas the deicer corrosivity to steel (*PCR*) generally remained within 19.7±3.9%. During the 14 months of field sampling and monitoring, the PCR of the FreezGard deicer remained below 30%, indicating PNS-acceptable corrosivity levels under the specific storage conditions investigated. The observed fluctuations seem to be non-seasonal but more likely attributable to the sampling and measuring variabilities. There were larger fluctuations seen in the PCR data than in the E_{corr} data for unknown reasons and the correlations between chloride and inhibitor concentrations with the *PCR* and between the E_{corr} and *PCR* will be discussed in a later section of this chapter.

Finally, during the field storage months the pH and electrical conductivity of the FreezGard deicer samples remained very consistent within 6.3±0.2 and 99.4±1.1 mS/cm respectively. The DSC-derived characteristic temperature (T_c) and ice melting capacity ($IMC_{30°\mathrm{F},\ 60\mathrm{min}}$) of the FreezGard deicer samples remained very consistent within 10.2±1.2

°F and 3.7±1.1 mL/mL (snowmelt/deicer) respectively[4]. These data further validate the fact that the FreezGard deicer product did not lose its quality over the 14 months of field storage, regardless of the mixing action in the liquid tanks.

2.2.3. Longevity of $CaCl_2$-based CCB under Storage

This section presents the temporal evolution of properties of the $CaCl_2$-based CCB deicer over the months of field storage monitoring, including the chloride and inhibitor concentrations, corrosion parameters (E_{corr} and PCR), pH, electrical conductivity, and performance parameters (T_c and $IMC_{30°F}$). Figure 9 presents the change of chloride and inhibitor concentrations over the time period of CCB deicer storage. There was no significant difference in chloride concentration between mixed and non-mixed samples collected from the CCB tanks, therefore the mixed and non-mixed sample data were combined for analysis. During the field storage months the average chloride concentration in the CCB deicer fluctuated more than that in the FreezGard deicer, but remained within 37.0±3.0%.

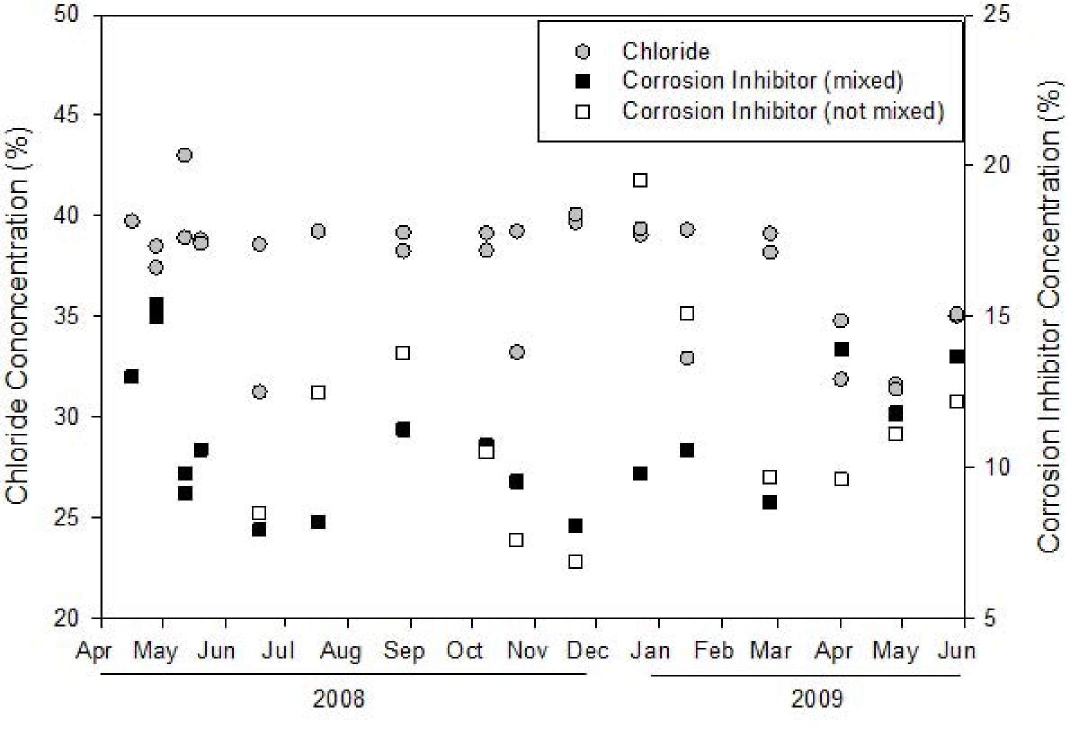

FIGURE 9 Temporal evolution of chloride and inhibitor concentrations in the CCB deicer tanks.

There was a significant difference in corrosion inhibitor concentration between mixed and non-mixed tanks (0.01 for $p>0.05$), therefore inhibitor concentration data were not combined for analysis. The average inhibitor concentration in mixed and non-mixed tanks generally remained within 9.3±1.7% and 11.2±3.3% respectively, with the mixed

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[4] For the 30% $MgCl_2$ brine made from reagent-grade magnesium chloride solid, the T_c (by DSC) and $IMC_{30°F,\ 60min}$ (by SHRP Ice Melting Test) was 8.5±0.4 °F and 4.4 mL/mL respectively.

tanks showing lower readings[5] and less data variability. The observed fluctuations seem to be non-seasonal but more likely attributable to the sampling and measuring variabilities. No significant degradation of corrosion inhibitor was seen during the 14 months of field storage. The inhibitor-to-chloride concentration ratio in the mixed and non-mixed CCB tanks was highly variable over the months of field storage and averaged at 1:4.0 and 1:3.3 respectively.

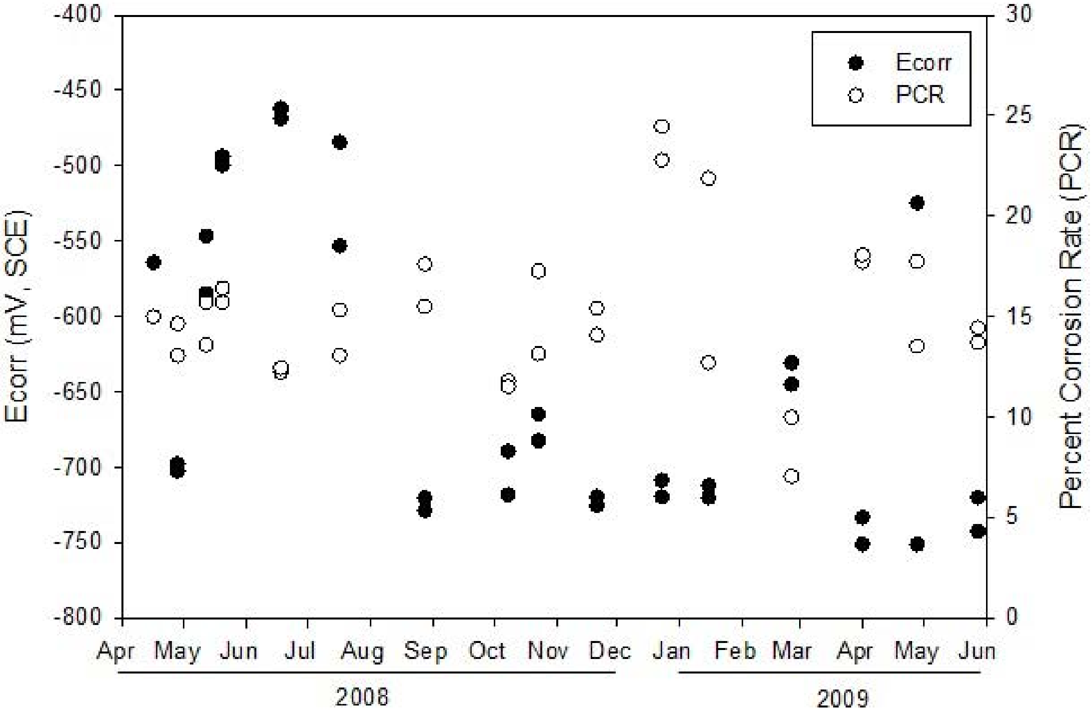

FIGURE 10 Temporal evolution of deicer corrosivity to steel (indicated by E_{corr} and *PCR*) in the CCB deicer tanks.

There was no significant difference in corrosion data between mixed and non-mixed samples collected from the CCB tanks, therefore the mixed and non-mixed sample data were combined for analysis. Figure 10 presents the change of deicer corrosivity over the time period of the CCB deicer storage. It shows that during the field storage months the corrosion potential of mild steel (E_{corr}) remained within -663±91 mV (SCE) whereas the deicer corrosivity to steel (*PCR*) generally remained within 15.0±3.3%. During the 14 months of field sampling and monitoring, the *PCR* of the CCB deicer remained below 30%, indicating PNS-acceptable corrosivity levels under the specific storage conditions investigated. The observed fluctuations seem to be non-seasonal but more likely attributable to the sampling and measuring variabilities. The correlations between chloride and inhibitor concentrations with the *PCR* and between the E_{corr} and *PCR* will be discussed in a later section of this chapter.

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[5] While this seems to be counter-intuitive, the mixing of liquid CCB deicer in the tank might have slightly facilitated the inhibitor degradation by enhancing the dissolved oxygen concentration.

Finally, during the field storage months the pH of the CCB deicer samples remained very consistent within 5.0±0.2. The electrical conductivity of the mixed and non-mixed CCB deicer samples generally remained within 132.2±0.9 and 130.6±4.2mS/cm respectively. The DSC-derived characteristic temperature (T_c) and ice melting capacity ($IMC_{30°F,\ 60min}$) of the CCB deicer samples remained very consistent within 11.2±1.2 ºF and 3.8±0.1 mL/mL (snowmelt/deicer) respectively[6], suggesting similar performance characteristics to FreezGard. These data further validate the fact that the CCB deicer product did not lose its quality over the 14 months of field storage, regardless of the mixing action in the liquid tanks.

2.2.4. Longevity of NaCl+GLT under Storage

This section presents the temporal evolution of properties of the NaCl+GLT deicer over the months of field storage monitoring, including the chloride and inhibitor concentrations, corrosion parameters (E_{corr} and PCR), pH, electrical conductivity, and performance parameters (T_c and $IMC_{30°F}$). Figure 11 presents the change of chloride and inhibitor concentrations over the time period of CCB deicer storage. There was no significant difference in chloride concentration between mixed and non-mixed samples collected from the NaCl+GLT tanks, therefore the mixed and non-mixed sample data were combined for analysis. During the field storage months the average chloride concentration in the NaCl+GLT deicer fluctuated more than the other two liquid deicers, but remained within 14.8±5.0%. This is partially attributable to the poor solubility of rock salt observed during the field storage. A solid salt layer was periodically observed at the bottom of the tanks[7], which helps to explain why the measured chloride concentrations were lower than the target concentration (20% by weight)[8].

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[6] For the 32% $CaCl_2$ brine made from reagent-grade calcium chloride solid, the T_c (by DSC) and $IMC_{30°F,\ 60min}$ (by SHRP Ice Melting Test) was 16.2±0.4 ºF and 4.0 mL/mL respectively.

[7] Since it was not a saturated NaCl solution, this anomaly may be explained by the lack of agitation and possible effect of GLT and other impurities on the salt solubility. In fact, agitation was able to put part of this salt layer back into solution.

[8] The target concentration was 20% by weight instead of 23% by weight, due to a miscalculation occurred during the initial preparation of the NaCl+GLT solution.

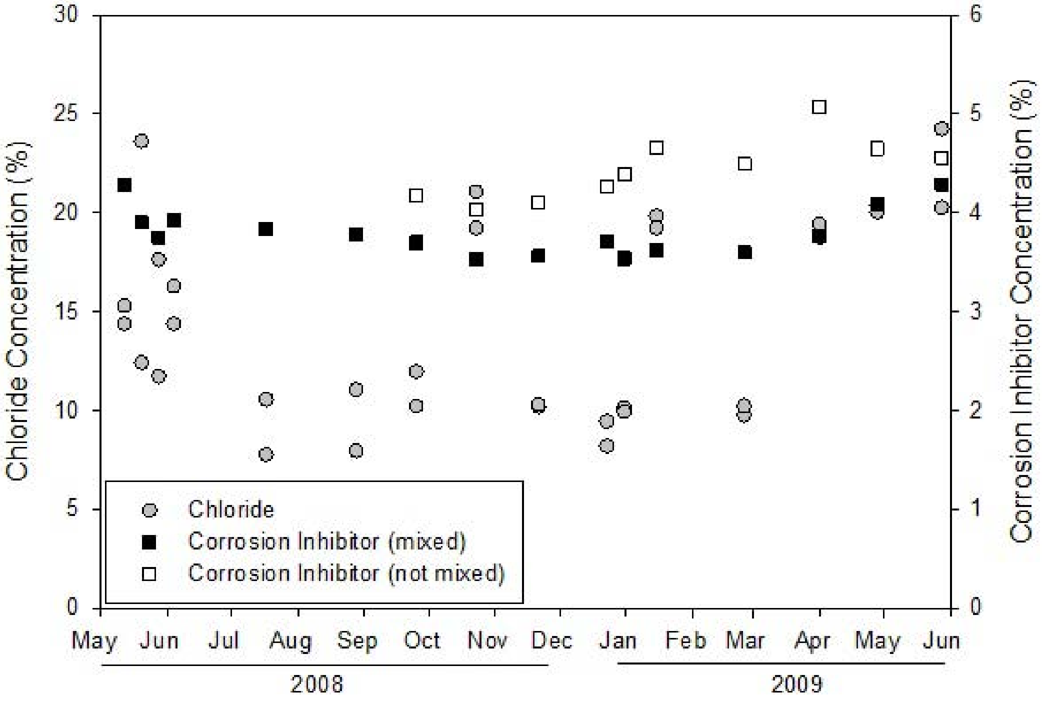

FIGURE 11 Temporal evolution of chloride and inhibitor concentrations in the NaCl+GLT deicer tanks.

There was a significant difference in corrosion inhibitor concentration between mixed and non-mixed tanks (0.025 for p>0.05), therefore inhibitor concentration data were not combined for analysis. The average inhibitor concentration in mixed and non-mixed tanks generally remained within 3.8±0.2% and 4.3±0.4% respectively, again with the mixed tank showing lower readings[9] and less data variability. The observed fluctuations seem to be non-seasonal but more likely attributable to the sampling and measuring variabilities. The data fluctuations can be quantified by coefficients of variance, which were 34%, 5%, and 9% over the field storage months for the combined chloride concentration, the mixed-tank inhibitor concentration, the non-mixed-tank inhibitor concentration respectively. No significant degradation of corrosion inhibitor was seen during the 14 months of field storage. The inhibitor-to-chloride concentration ratio in the mixed and non-mixed NaCl+GLT tanks was highly variable over the months of field storage and averaged at 1:4.0 and 1:3.4 respectively.

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[9] Similar to the case of CCB, the mixing of liquid NaCl+GLT deicer in the tank might have facilitated the inhibitor degradation by enhancing the dissolved oxygen concentration.

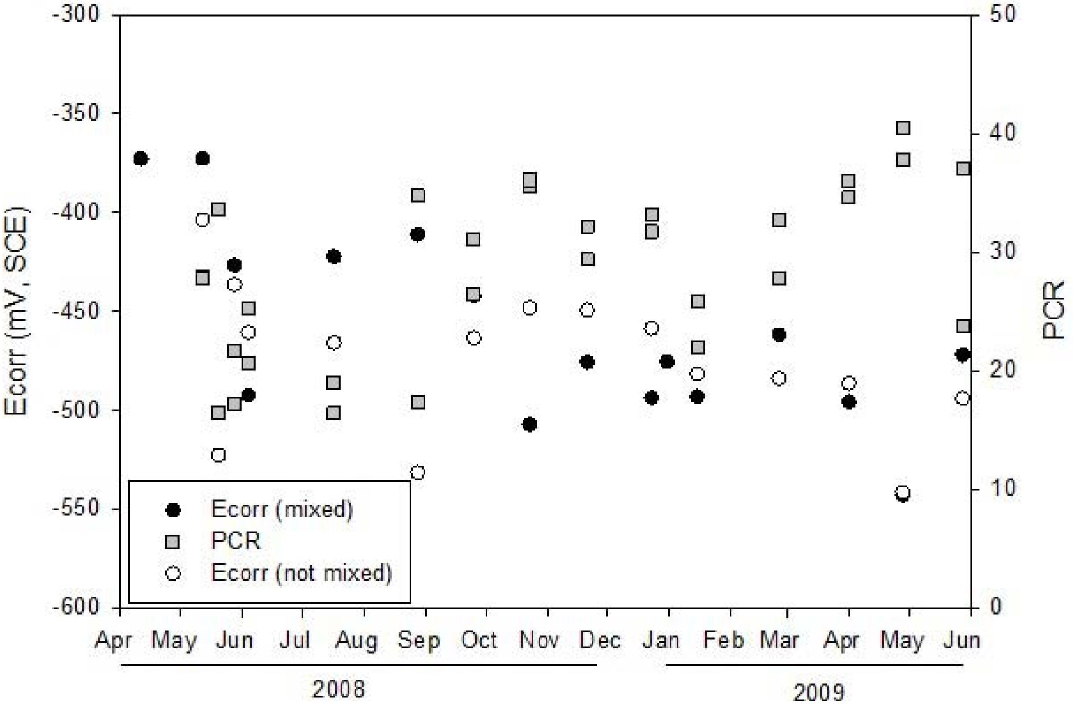

FIGURE 12 Temporal evolution of deicer corrosivity to steel (indicated by E_{corr} and *PCR*) in the NaCl+GLT deicer tanks.

Figure 12 presents the change of deicer corrosivity over the time period of the NaCl+GLT deicer storage. It shows that during the field storage months the corrosion potential of mild steel (E_{corr}) remained within -487.1±94.1 mV (SCE) and -480.5±42.7 (SCE) for mixed and non-mixed NaCl+GLT respectively whereas the deicer corrosivity to steel (*PCR*) generally remained within 29.4±7.9. The data fluctuations can be quantified by coefficients of variance, which were 27%, 19%, and 9% over the field storage months for the combined *PCR*, the mixed-tank E_{corr}, the non-mixed-tank E_{corr} respectively. It is interesting to note that the higher variability in the corrosion potential data for mild steel immersed in deicer samples from the mixed tank, relative to those from the non-mixed tank. This may be related to the dissolved oxygen concentration affected by the mixing and the solubility issue of the rock salt in the aqueous solution with GLT. During the 14 months of field sampling and monitoring, the *PCR* of the NaCl+GLT deicer occasionally exceeded 30%, indicating unacceptable corrosivity levels under the specific storage conditions investigated. The observed fluctuations seem to be non-seasonal but more likely attributable to the sampling and measuring variabilities. The correlations between chloride and inhibitor concentrations with the *PCR* and between the E_{corr} and *PCR* will be discussed in a later section of this chapter.

Finally, during the field storage months the pH and electrical conductivity of the NaCl+GLT deicer samples remained within 7.6±0.6 and 189.5±19.9 mS/cm respectively. The DSC-derived characteristic temperature (T_c) and ice melting capacity ($IMC_{30°F,\,60min}$) of the NaCl+GLT deicer samples remained very consistent within 23.5±1.9 ºF and

3.8±0.2 mL/mL (snowmelt/deicer) respectively[10], suggesting higher T_c and similar $IMC_{30°F}$ relative to the $MgCl_2$- or $CaCl_2$-based liquid deicers. These data further validate the fact that the NaCl+GLT deicer product did not lose its quality over the 14 months of field storage, regardless of the mixing action in the liquid tanks. The data also suggest GLT to be a less stable inhibitor package than the inhibitors in the FreezGard or CCB deicers and GLT may interfere with the solubility of rock salt in aqueous solution. As such, extra caution should be exercised in the process of making such GLT-inhibited salt brine products.

2.2.5. Stratified Sampling of Liquid Deicer Tanks

This section presents the properties of stratified samples obtained from the top, middle and bottom of the mixed and non-mixed deicer tanks, including the chloride and inhibitor concentrations, pH, and corrosion parameters (E_{corr} and PCR). Such samples were obtained every six months or so in order to shed light on the effect of mixing on the homogeneity of liquid deicers in the storage tanks. For each of the three liquid deicers, no significant difference was observed in the electrical conductivity of the stratified samples, regardless of the mixing action, sampling date, or sampling depth. This implies that electrical conductivity of the solution is not a sensitive indicator for quality assurance of the deicers.

Figures 13(a) and 13(b) show that after the first seven months of storage the non-mixed FreezGard deicer tank featured the lowest chloride concentration and the highest inhibitor concentration at the bottom of the tank, whereas the mixed FreezGard deicer tank featured the opposite tendency for unknown reasons. After 13 months of field storage, the chloride and inhibitor concentrations in both mixed and non-mixed tanks became more uniform along the tank depth. Figure 13(c) shows that after the first seven months of storage both the mixed and non-mixed tanks featured the lowest pH at the bottom of the tank. Figures 13(d) and 13(e) suggest that there was little difference in the corrosivity of FreezGard deicer samples to mild steel regardless of the mixing action. The mild steel coupons in the 13-months-old deicer samples from both FreezGard deicer tanks featured lower corrosion potentials, relative to those in the 7-months-old deicer samples. In the case of the middle samples, such decrease in the E_{corr} of mild steel was accompanied by a slight increase in the PCR, particularly for the non-mixed FreezGard deicer tank.

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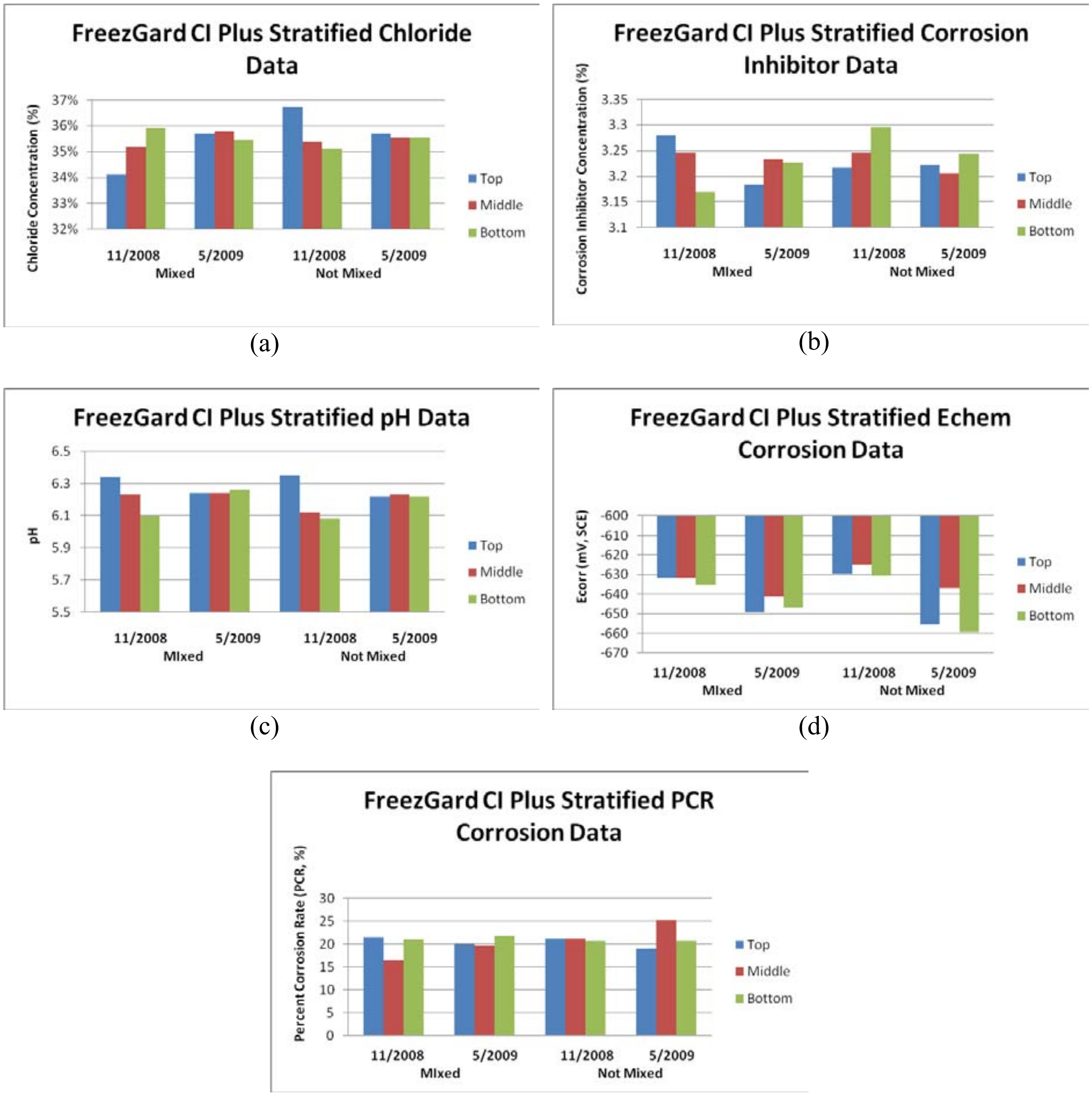
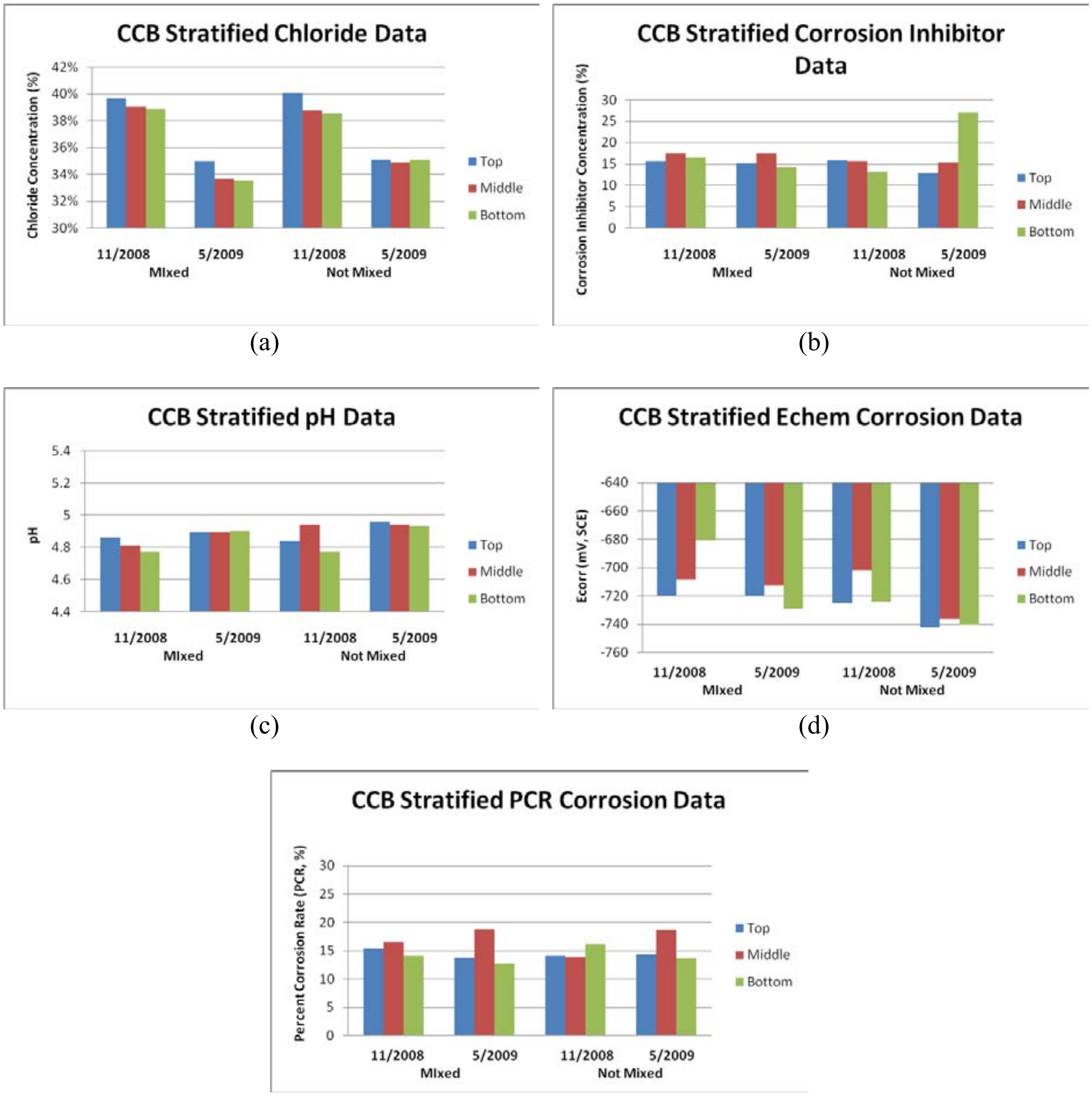
[10] For the 23% NaCl brine made from reagent-grade salt, the T_c (by DSC) and $IMC_{30°F,\ 60min}$ (by SHRP Ice Melting Test) was 21.8±0.1 ºF and 3.5 mL/mL respectively.



(a) (b) (c) (d) (e)

FIGURE 13 Properties of stratified samples obtained from the top, middle and bottom of the FreezGard deicer tanks: (a) chloride concentration; (b) inhibitor concentration; (c) pH; (d) E_{corr} of mild steel; and (e) *PCR*.

Figures 14(a) and 14(b) show that after the first seven months of storage both the mixed and non-mixed CCB deicer tanks featured the lowest chloride concentration at the bottom of the tank, whereas the inhibitor concentration along the tank depth showed little trend. The 13-months-old deicer samples at all depths of both CCB tanks featured lower chloride concentrations, relative to the 7-months-old deicer samples. Such decrease in the chloride concentrations at all depths was accompanied by a significant increase in the inhibitor concentration in the non-mixed bottom CCB samples. Figure 14(c) shows that after the first seven months of storage there was significant variability in the pH as a function of sampling depth whereas the effect of mixing action was unclear. The 13-months-old deicer samples from both CCB deicer tanks featured slightly higher pH and more homogeneity along the tank depth, relative to those in the 7-months-old deicer samples. Figures 14(d) and 14(e) suggest that there was little difference in the corrosivity of CCB deicer samples to mild steel regardless of the mixing action. On average, the mild steel coupons in the 13-months-old deicer samples from both CCB deicer tanks featured slightly lower corrosion potentials, relative to those in the 7-months-old deicer samples.

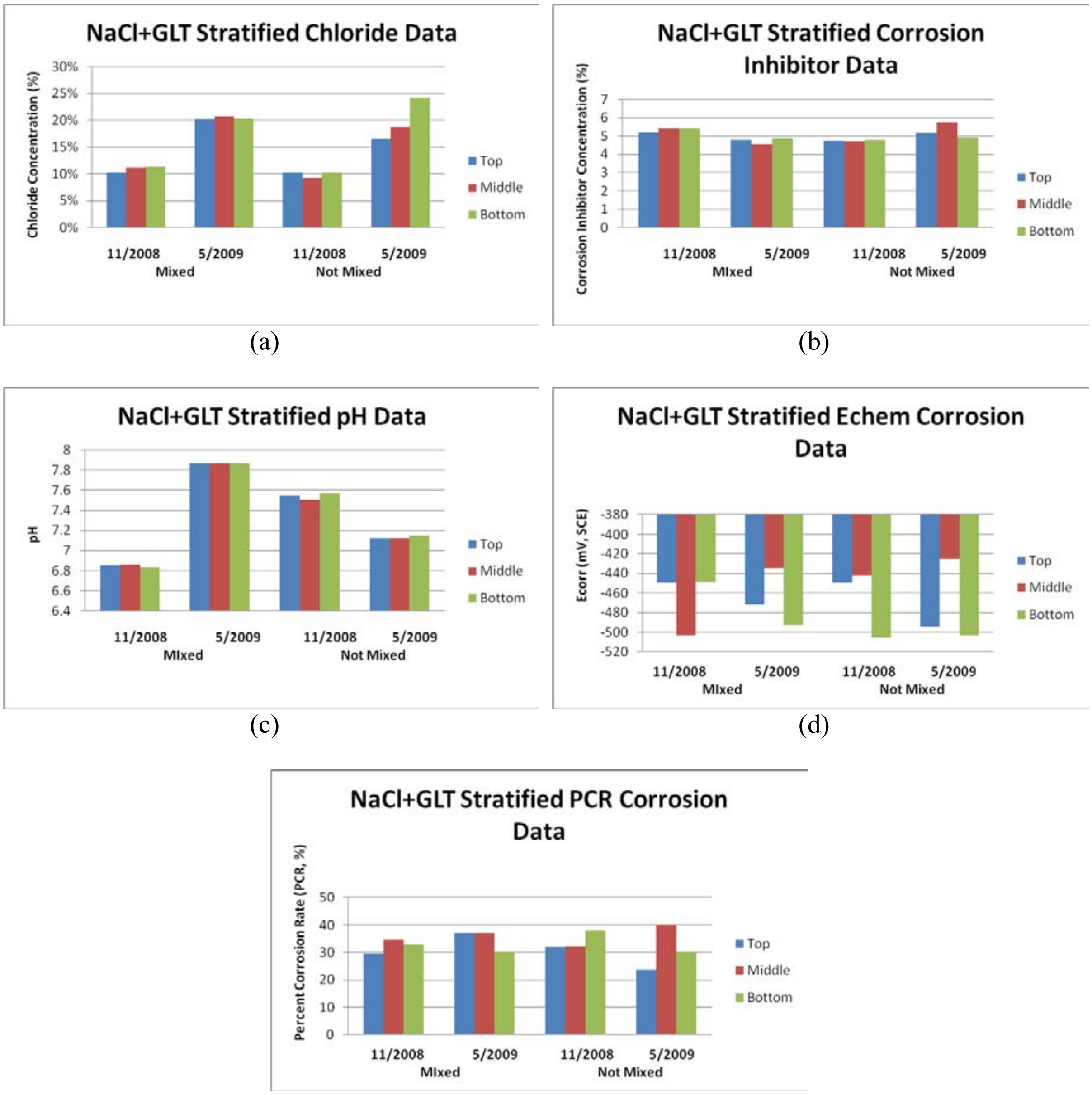


(a) (b)

(c) (d)

(e)

FIGURE 14 Properties of stratified samples obtained from the top, middle and bottom of the CCB deicer tanks: (a) chloride concentration; (b) inhibitor concentration; (c) pH; (d) E_{corr} of mild steel; and (e) *PCR*.



(a) (b) (c) (d) (e)

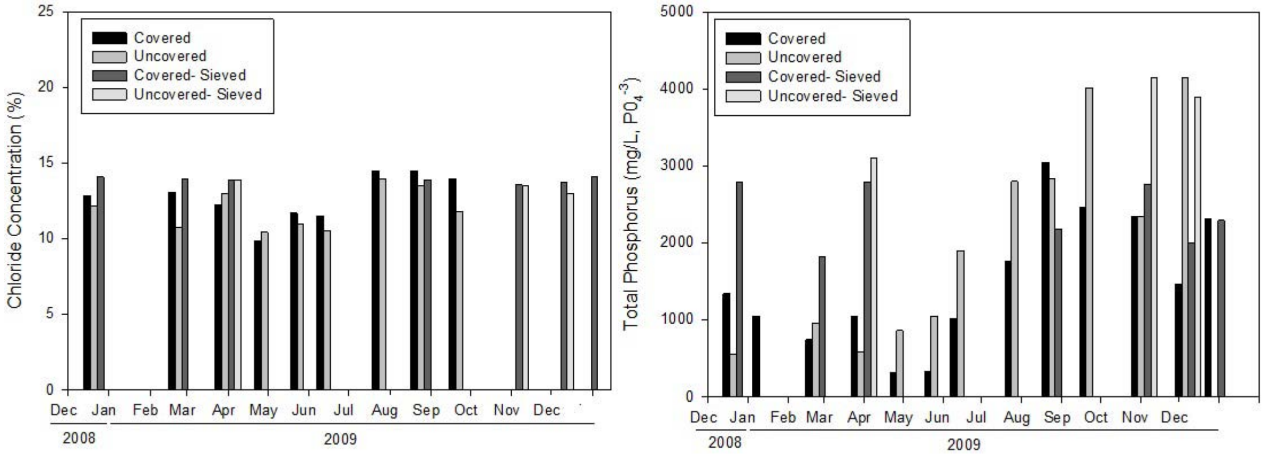
FIGURE 15 Properties of stratified samples obtained from the top, middle and bottom of the NaCl+GLT deicer tanks: (a) chloride concentration; (b) inhibitor concentration; (c) pH; (d) E_{corr} of mild steel; and (e) *PCR*.

Figures 15(a) and 15(b) show that after the first seven months of storage the non-mixed NaCl+GLT deicer tank featured similarly low chloride concentrations (about 10%) yet slightly lower inhibitor concentrations, relative to the mixed tank. After 13 months of storage, the mixed NaCl+GLT deicer tank featured uniformly higher chloride concentrations (about 20%). In the non-mixed tank, the 13-months-old deicer samples featured generally higher chloride and inhibitor concentrations relative to the 7-months-old samples, with the highest chloride and inhibitor concentrations seen at the bottom and middle of the tank respectively. Figure 15(c) shows that after the first seven months of storage both the mixed and non-mixed tanks featured relatively uniform pH along the tank depth, averaged at 6.85 and 7.5 respectively. After 13 months of storage both the mixed and non-mixed tanks featured relatively uniform pH along the tank depth, averaged at 7.85 and 7.1 respectively. Figures 15(d) and 15(e) suggest that there was little difference in the corrosivity of NaCl+GLT deicer samples to mild steel regardless of the mixing action. The corrosion data from NaCl+GLT stratified deicer samples were highly variable and no apparent trend could be identified as a function of sampling depth or date.

2.2.6. Longevity of NaCl-based IceSlicer under Storage

This section presents the temporal evolution of properties of the solid deicer, NaCl-based IceSlicer, over the months of field storage monitoring, including the chloride and inhibitor concentrations, corrosion parameters (E_{corr} and PCR), pH, electrical conductivity, and performance parameters (T_{c} and $IMC_{30°\text{F}}$). The IceSlicer data are presented separately for the following reasons. (1) The IceSlicer field monitoring lasted from December 2008 to December 2009, whereas the monitoring of the liquid deicers lasted from April 2008 to May 2009, for logistical reasons. (2) The IceSlicer samples were not collected every month during field monitoring, due to the difficulty of sampling the field solid deicer piles during winter weather. (3) The inhibitor package used for this specific IceSlicer formulation exhibited a solubility issue, which was later confirmed by the vendor. (4) Some of the collected samples were not fully analyzed in light of the inhibitor solubility issue and the time and funding constraints, per the decision by the Steering Committee in November 2009. It should be cautioned that the vendor thus no longer markets this specific product formulation and all the data provided in this report are purely for research purposes.

Figure 16 presents the change of chloride and inhibitor concentrations over the time period of IceSlicer deicer storage. Note that the concentrations were based on the 23% IceSlicer solution, instead of its solid form. With few exceptions, the IceSlicer samples from the covered pile generally featured slightly higher chloride concentrations and significantly lower inhibitor concentrations, relative to those from the uncovered pile. While the chloride concentration in both covered and uncovered piles remained relatively consistent over the 12 months of field storage, the inhibitor concentration in both piles tended to increase over time. This may be related to the inhibitor solubility issue, that is, the solubility of inhibitor improved over the storage duration. The sieving of the solid deicer sample prior to testing did not make significant difference in its chloride concentration but tended to increase its inhibitor concentration reading. Finally, the fluctuations in the measured concentrations can be partly explained by the sampling variabilities inherent in the ASTM D 632 method used to collect the solid deicer from the field storage piles.



(a) (b)

FIGURE 16 Temporal evolution of (a) chloride and (b) inhibitor concentrations in the IceSlicer piles. Note that the concentrations were based on the 23% IceSlicer solution, instead of its solid form.

Figure 17 presents the change of deicer corrosivity over the time period of the IceSlicer deicer storage. It shows that during the field storage months the corrosion potential of mild steel (E_{corr}) fluctuated between -500 mV (SCE) and -600 (SCE), regardless of the storage condition. The deicer corrosivity to steel (*PCR*) fluctuated between 60 and 100, regardless of the storage condition or the sieving of the deicer sample. During the 12 months of field sampling and monitoring, the *PCR* of the IceSlicer solid deicer samples all remained well above 30%, indicating unacceptable corrosivity levels under the specific storage conditions investigated. The storage time showed little effect on the corrosivity of the IceSlicer deicer.

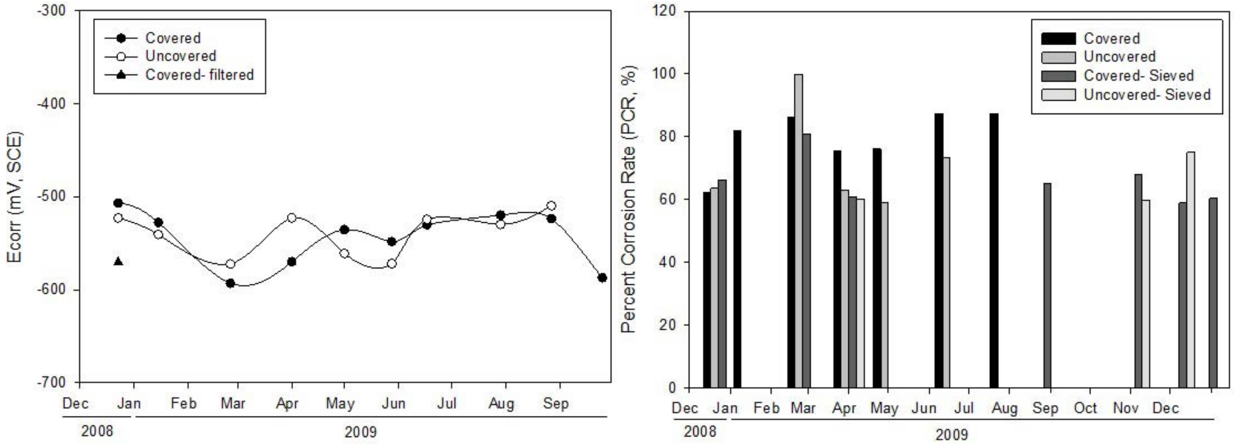


FIGURE 17 Temporal evolution of deicer corrosivity to steel (indicated by E_{corr} and *PCR*) in the NaCl+GLT deicer tanks.

The IceSlicer solid deicer samples from the first 12 months of field storage were also made into 23 wt.% aqueous solution prior to their pH and DSC measurements. During the field storage months the pH of IceSlicer samples (after being made into 23 wt.% aqueous solution) from covered and uncovered piles showed little difference and both remained within 4.8±0.3[11]. Note that such low pH readings do not necessarily indicate high acidity, since the high chloride concentrations in the IceSlicer samples could have interfered with the readings by the pH probe. As indicated in Appendix G, the pH readings of deicer solutions tended to be lower in the presence of high salt concentrations.

The DSC-derived characteristic temperature (T_c) and ice melting capacity ($IMC_{30^{\circ}\mathrm{F},\,60\mathrm{min}}$) of the IceSlicer deicer samples remained very consistent over the duration of sampling, within 27.6±4.2 ºF and 3.6±0.7 mL/mL for the covered samples and 26.1±2.3 ºF and 3.2±0.6 mL/mL for the uncovered samples respectively. For the 23% NaCl brine made from reagent-grade salt, the T_c (by DSC) and $IMC_{30^{\circ}\mathrm{F},\,60\mathrm{min}}$ (by SHRP Ice Melting Test) was 21.8±0.1 ºF and 3.5 mL/mL respectively. These data suggest that the 23% IceSlicer brine had slightly higher working temperature and lower ice melting capacity at 30ºF, relative to the NaCl+GLT liquid deicer and the 23% NaCl solution[12]. The uncovered IceSlicer samples featured slightly lower ice melting capacity yet also slightly lower working temperature, relative to the covered IceSlicer samples. In other words, regardless of the storage condition, the IceSlicer deicer did not lose its quality over the 12 months of field storage.

2.2.7. Monitoring of IceSlicer Cistern Samples

This section presents the temporal evolution of properties of IceSlicer leachate solution collected from the cistern attached to the uncovered IceSlicer pile, over the months of field storage monitoring. Figure 18 indicates that the chloride and inhibitor concentrations in the cistern steadily increased in the first five months, attributable to the concurrent leaching of both chloride and inhibitor from the uncovered IceSlicer pile. In the following three months (April-July 2009), the chloride and inhibitor concentrations in the cistern steadily decreased, likely due to the overflow of the cistern caused by significant rain precipitation as shown in Figure 6. As such, the inhibitor-to-chloride concentration ratio in the cistern remained fairly consistent in the first eight months of monitoring. The dramatic increase in the inhibitor-to-chloride ration in the cistern thereafter cannot be readily explained due to the lack of sufficient data points. Yet the low inhibitor concentrations in the cistern during August to November 2009 may be correlated with the high inhibitor concentrations in the uncovered pile shown in Figure 17(b), both suggesting that <u>the leaching rate of chloride from the uncovered pile exceeded that of the corrosion inhibitor.</u>

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[11] The pH reading of the 23% IceSlicer samples after the 1:4 dilution was approximately 6.1.

[12] While these laboratory data suggest that the brine made from IceSlicer are not as effective as the brine made from regular white salt, the relative performance of IceSlicer to white salt may depend on the field scenario where the color, albedo properties, particle size, longevity, etc. of the solid deicers may significantly affect their performance.

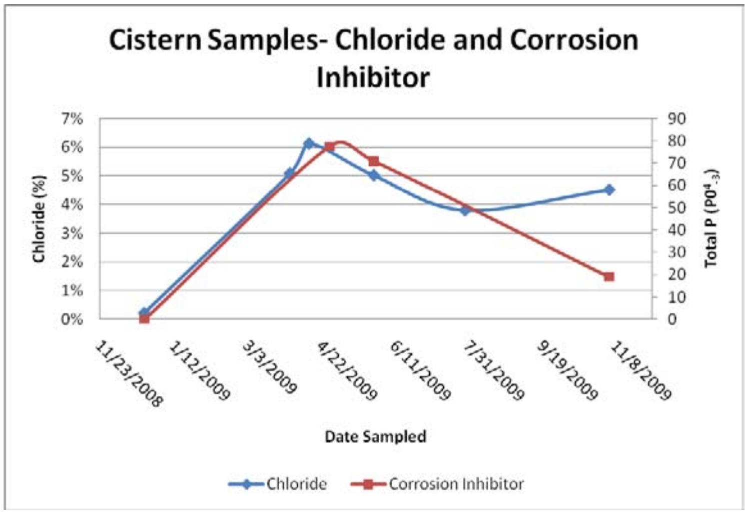


FIGURE 18 Temporal evolution of chloride and inhibitor concentrations in the IceSlicer cistern.

Figure 19 shows that the pH of IceSlicer leachate solution was uniform along the sampling depth in the cistern (i.e., no stratification). The data also show that the pH of leachate solution fluctuated between 5.3 and 6.2 over the months of monitoring.

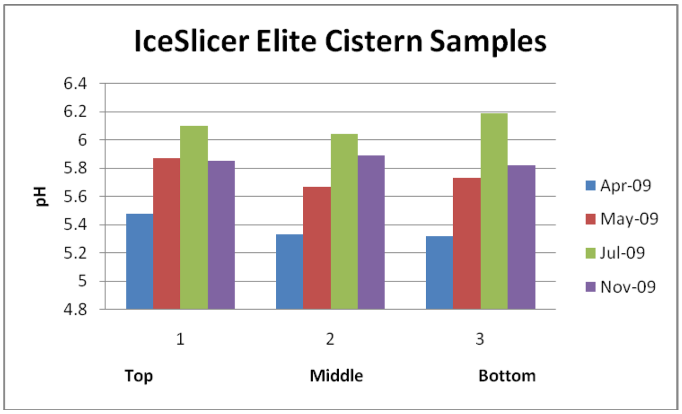


FIGURE 19 Temporal evolution of pH in the IceSlicer cistern.

2.2.8. Inhibitor Degradation under Laboratory Conditions

This section presents the results and discussion related to the laboratory study of inhibitor degradation, which examined the change in the inhibitor concentration in the four deicers after their exposure at a given temperature and UV intensity for a certain time period (as shown in Table 2).

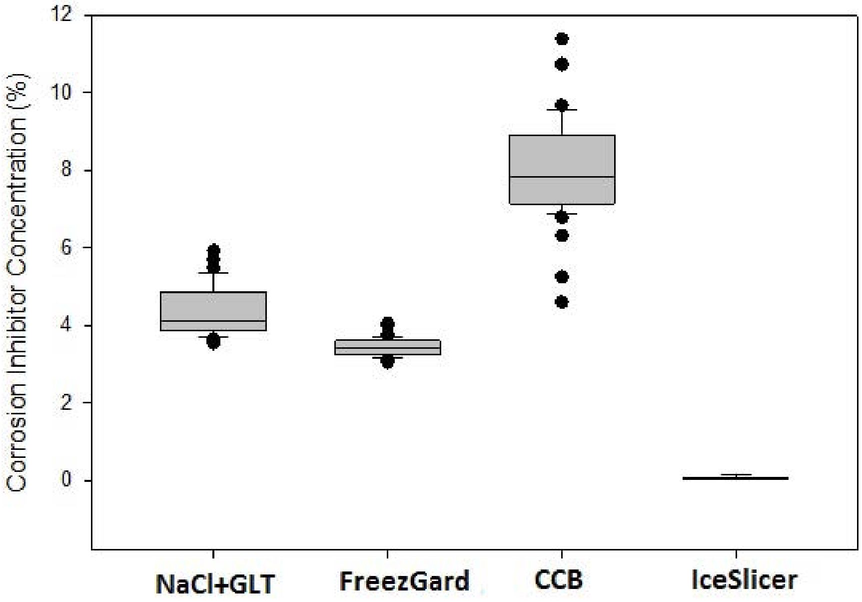


FIGURE 20 Box plot showing the corrosion inhibitor concentration following various exposure experiments as detailed in Table 3.

Figure 20 shows the measured corrosion inhibitor concentration following various exposure experiments as detailed in Table 3, with the data grouped by the deicer type. For the NaCl+GLT deicer, the inhibitor concentration after the various heat-UV exposure experiments averaged at 4.2%, which is slightly above the initial concentration measured at 3.9%. For the FreezGard deicer, the inhibitor concentration after the various heat-UV exposure experiments averaged at 3.5%, which is slightly above the initial concentration measured at 3.4%. These, along with the limited scatter seen in the post-exposure inhibitor concentrations, suggest very limited degradation of GLT or FreezGard inhibitors under the investigated conditions and some water evaporation from the liquid deicer samples. For the CCB deicer, the inhibitor concentration after the various heat-UV exposure experiments averaged at 7.9%, which is significantly below the initial concentration measured at 10.2%. This, along with the significant scatter seen in the post-exposure CCB inhibitor concentration, confirms the significant degradation of this inhibitor by the combined action of heat and UV light under the investigated conditions. For the IceSlicer solid deicer, the inhibitor concentrations were too low to make reliable conclusions about any possible inhibitor degradation.

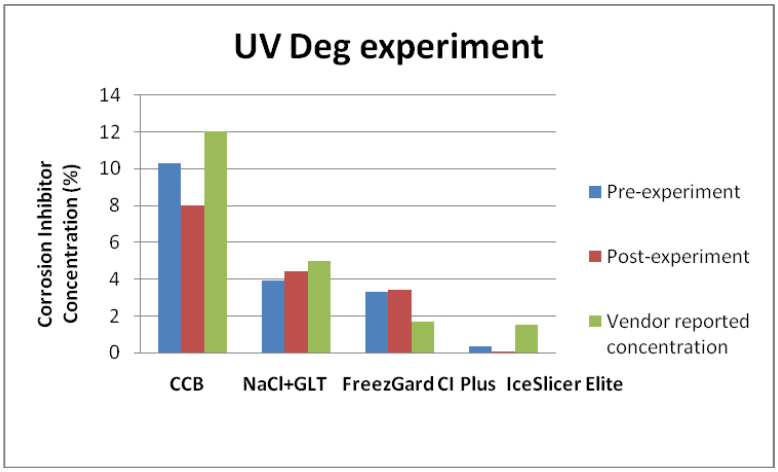


FIGURE 21 Inhibitor concentration in deicers before and after the laboratory degradation experiments.

In light of the variability introduced by the water evaporation during the exposure tests, it was impossible to establish a quantitative model (as planned) to correlate inhibitor degradation with exposure conditions and deicer type. As such, all of the data were grouped for each deicer product as shown in Figure 21. Figure 21 further confirms very limited degradation of GLT or FreezGard inhibitors and significant degradation of CCB inhibitor under the investigated conditions. For the IceSlicer solid deicer, the inhibitor concentrations were too low to make reliable conclusions about any possible inhibitor degradation.

Note that the most severe exposure conditions during the laboratory degradation experiments entailed the air temperature of 40ºC (104ºF) and 96 hours. The peak intensity of the simulated UV-A (315-400 nm) and UV-B (280-315 nm) long-wave radiation was no more than 6.0 kW/m^2. While higher temperature and higher UV intensity could have led to more significant degradation of corrosion inhibitors, it would become unrealistic simulation of the field storage conditions where the highest average weekly air temperature was about 70ºF (see Figure 5) and the maximum daily solar radiation at the storage site (prior to the blocking by the storage tanks or the building cover) was 1.2 kW/m^2 (see Figure 7). For the CCB deicer, the blocking of UV light by the storage tanks was likely beneficial in preventing its inhibitor degradation over the 14-month field storage monitoring period.

2.2.8. Correlating the Electrochemical Corrosion Data with the PNS/NACE Corrosion Data of Liquid Deicers

ARTIFICIAL NEURAL NETWORK AS A MODELING TOOL

An artificial neural network (ANN) was used to achieve better understanding of the complex correlation between the electrochemically obtained corrosion data (along with solution conductivity) and the gravimetrically obtained corrosion data. These corrosion data were mostly obtained by testing the field storage samples of the three liquid deicers.

Furthermore, a few standard solutions of each deicer were prepared by mixing the vendor-provided non-inhibited deicer and the corresponding corrosion inhibitor at various known concentrations.

ANNs provide non-parametric, data-driven, self-adaptive approaches to information processing. They are powerful in tackling complex, non-linear problems and have been successfully used to model, predict, control and optimize non-linear systems. ANNs offer several advantages over traditional model-based methods [5] such as multi-regression. First, ANNs are robust and can produce generalizations from experience even if the data are incomplete or noisy, given that over-fitting is avoided with expert intervention. Second, ANNs can learn from examples and capture subtle functional relationships among case data. Prior assumptions about the underlying relationships in a particular problem, which in the real world are usually implicit or complicated, need not be made. Third, ANNs provide universal approximation functions flexible in modeling linear and nonlinear relationships. As such, ANNs have been successfully utilized to predict the compressive strength of concrete, to predict the electrochemical behavior of steel in various chloride solutions and the chloride binding, chloride profiles, and chloride permeability in concrete, to recognize the OCP behavioral pattern of steel in concrete, and to predict the time-to-onset of rebar corrosion and the life of concrete structures [6].

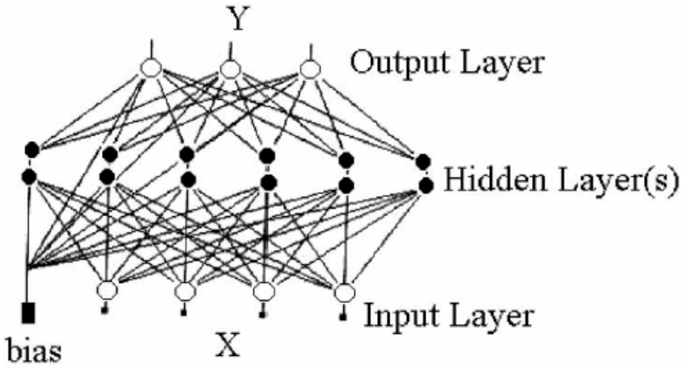


FIGURE 22 A typical multi-layer feed-forward ANN architecture.

The ANN paradigm adopted in this study was the multi-layer feed-forward neural network, of which a typical architecture is shown in Figure 22. The nodes in the input and output layers consist of independent variables and response variable(s), respectively. One or two hidden layers are included to model the dependency based on the complexity of relationship(s). For a feed-forward network, signals are propagated from the input layer through the hidden layer(s) to the output layer, and each node in a layer is connected in the forward direction to every node in the next layer. Every node simulates the function of an artificial neuron. The inputs are linearly summated utilizing connection weights and bias terms and then transformed via a non-linear transfer function.

In this study, a modified back propagation (BP) algorithm was employed for the ANN training, in which a sigmoid function in Equation (1) was used as the nonlinear transfer function and the sum of the mean squared error (SMSE) in the output layer as the convergence criteria.

$$f(x) = \left(1 + e^{-x}\right)^{-1} \tag{1}$$

All the data for input and output were normalized based on Equation (2), where X_i and NX_i are the i^{th} value of factor X before and after the normalization, and X_{min} and X_{max} are the minimum and maximum value of factor X, respectively.

$$NX_i = \frac{(x_i - x_{\min} + 0.1)}{(X_{\max} - X_{\min} + 0.1)} \tag{2}$$

All the connection weights and bias terms for nodes in different layers were initially randomized and then iteratively adjusted based on certain learning rules. For each given sample, the inputs were forwarded through the network until they reached the output layer producing output values, which were then compared with the target values. Errors were computed for the output nodes and propagated back to the connections stemming from the input layer. The weights were systematically modified to reduce the error at the nodes, first in the output layer and then in the hidden layer(s). The changes in weights involved a learning rate and a momentum factor (0.9 and 0.5 respectively for this study) and were usually in proportion to the negative derivative of the error term. The learning process was continued with multiple samples until the prediction error converged to an acceptable level. The selection of layers and nodes took into consideration driving the SMSE as small as possible and the training process as efficient as possible.

TABLE 4 Corrosion data used for ANN training and testing (highlighted) respectively.

Deicer Type	Relative i_{corr}	Relative E_{corr} (mV)	Solution Conductivity (mS)	PCR
1	0.63	16.8	5.1	21.3
1	0.70	40.1	9.8	28.1
1	0.68	28.2	14.4	25.5
1	0.84	81.4	18.7	24.3
1	1.25	60.8	24.1	28.0
1	1.00	0.0	14.7	93.3
3	0.76	40.9	7.5	41.7
3	1.00	144.6	14.9	28.2
3	1.05	39.8	22.6	15.7
3	0.81	55.5	28.2	14.5
3	0.98	133.6	34.6	10.0
3	0.83	33.2	22.8	45.9
2	0.48	230.0	7.9	34.5
2	0.45	329.9	15.7	21.0
2	0.53	225.8	23.7	15.9
2	0.85	287.6	30.4	10.6
2	1.39	187.4	36.9	13.5
2	1.03	7.0	25.0	87.1
2	0.65	155.3	131.1	15.0
2	0.83	16.9	130.8	13.1
2	1.08	134.7	131.2	13.6
2	1.06	220.0	130.6	16.4
2	0.85	257.6	131.5	12.2
2	1.12	166.3	131.5	13.1
2	0.23	-9.2	131.6	15.5
2	0.51	1.1	131.7	11.8
2	1.89	54.5	132.4	17.3
2	0.47	0.0	133.4	15.4
2	1.00	10.7	132.5	16.5
2	0.97	38.7	132.5	14.1
2	0.18	5.1	132.6	14.5
2	0.99	10.7	133.9	22.8
2	0.19	7.2	132.1	21.9
2	1.34	88.7	133.5	7.1
2	0.22	-13.9	132.8	17.7
2	0.89	194.7	132.6	17.7
2	0.46	-0.6	133.4	13.7
2	0.41	7.0	132.4	18.8
2	0.41	-9.8	132.1	12.7
2	0.22	4.2	132.1	13.1
2	1.05	213.5	132.4	11.0
2	1.11	21.8	131.0	14.6
2	1.37	172.7	132.2	15.7
2	0.98	225.7	132.8	15.7
2	0.85	250.6	132.1	12.4
2	0.74	234.9	129.2	15.3
2	0.27	-0.8	123.9	17.6
2	1.17	30.1	133.0	11.5
2	1.34	37.0	133.4	13.2
2	0.29	-5.9	134.0	14.1
2	0.86	17.3	134.6	13.9
2	0.63	-5.0	134.1	16.1
2	0.32	-8.6	133.9	16.6
2	0.15	-0.2	121.5	24.5
2	0.20	-0.8	122.2	12.7
2	1.71	74.5	128.7	10.0
2	0.35	-31.6	132.0	18.1
2	0.36	-31.6	130.8	13.5
2	0.37	-23.0	135.1	14.4
2	0.55	-17.0	134.1	18.7
2	0.46	-20.7	123.7	13.6
2	1.01	4.9	130.7	11.4
3	1.74	97.0	99.0	18.4
3	2.28	176.4	98.4	14.2
3	1.62	82.2	98.8	13.9
3	1.44	94.6	99.0	16.2
3	1.50	89.5	98.2	15.9
3	3.16	169.2	98.8	17.4
3	2.85	57.9	98.8	18.4
3	1.14	71.0	99.2	19.0
3	1.46	87.8	99.8	21.6
3	1.68	87.8	99.3	16.6
3	1.19	84.1	99.5	21.2
3	2.23	105.0	99.2	19.4
3	1.69	107.8	99.7	23.5
3	2.88	73.3	100.6	27.2
3	3.00	65.4	99.4	17.1
3	1.73	85.3	98.8	26.8
3	1.88	65.1	99.6	17.5
3	3.32	70.3	100.2	20.0
3	2.30	78.3	99.8	19.7
3	2.16	72.7	99.5	21.9
3	2.04	96.2	98.9	21.2
3	1.84	67.8	104.0	23.0
3	2.61	139.7	98.0	16.9
3	1.55	81.8	97.2	15.5
3	1.09	97.7	99.6	16.5
3	3.43	135.9	98.9	15.5
3	3.51	131.0	98.0	17.6
3	2.81	52.9	98.5	17.2
3	3.03	74.3	100.3	22.5
3	1.39	89.9	100.0	21.3
3	1.48	94.8	100.6	21.2
3	1.22	88.9	100.0	20.8
3	0.99	78.4	99.7	16.6
3	0.93	86.1	97.8	28.0
3	2.71	85.7	98.9	26.2
3	2.25	71.4	100.6	14.3
3	3.18	69.6	99.6	27.8
3	1.65	69.5	98.2	15.1
3	3.03	63.8	99.6	19.1
3	2.70	82.6	100.3	25.3
3	3.30	59.9	99.6	20.8
3	2.85	99.4	99.9	17.2
1	0.11	346.7	145.0	1.6
1	1.18	-94.7	131.7	28.0
1	0.52	292.6	157.5	16.5
1	0.88	226.9	167.6	21.7
1	0.64	297.1	173.2	25.3
1	0.43	308.3	189.6	16.4
1	0.60	277.3	196.7	17.4
1	0.41	212.1	199.9	31.1
1	0.55	243.7	200.0	35.5
1	0.62	270.0	191.5	29.4
1	0.54	216.1	193.3	34.6
1	0.59	270.7	192.2	32.7
1	0.57	225.7	200.0	35.6
1	0.94	243.9	200.0	31.7
1	0.83	226.2	200.0	25.8
1	0.24	257.6	200.0	27.8
1	0.69	223.6	200.0	36.0
1	0.83	176.6	200.0	40.5
1	0.53	247.5	200.0	37.0
1	0.66	284.7	200.0	37.0
1	0.62	226.9	200.0	30.3
1	0.33	217.2	200.0	30.7
1	0.58	267.9	200.0	33.5
1	0.41	315.7	146.8	27.8
1	0.99	196.7	200.0	33.6
1	0.46	283.0	136.6	17.1
1	0.30	258.9	143.9	20.7
1	0.62	253.6	200.0	19.0
1	1.00	187.8	200.0	34.7
1	0.36	255.8	189.0	26.4
1	0.65	271.1	200.0	36.1
1	0.61	270.0	200.0	32.2
1	0.40	277.5	200.0	32.4
1	0.52	213.7	200.0	38.0
1	0.53	259.4	200.0	35.9
1	0.78	260.8	200.0	33.2
1	0.82	237.8	200.0	22.0
1	0.25	235.5	200.0	32.7
1	0.72	232.9	200.0	34.6
1	0.75	177.8	200.0	37.8
1	0.49	225.3	187.5	23.8
1	0.59	294.1	197.3	40.2
1	0.69	216.1	200.0	30.3
1	0.45	157.0	200.0	31.0

ANN MODEL FOR CORRELATING THE TWO DEICER CORROSION TESTS

ANN was used to establish a predictive model correlating the two sets of corrosion data. The first set consists of deicer type, corrosion current density i_{corr} and potential E_{corr} (relative to those of steel in the 3% of 23% NaCl brine solution respectively, obtained from a potentiodynamic weak polarization test after 24 hours of continuous immersion) and solution conductivity. Note that for modeling purpose, the deicer type (a qualitative factor) was given a numerical value for each level (1 for NaCl+GLT^{TM}, 2 for CCB^{TM}, and 3 for Freezgard^{TM} respectively). When the ANN model was established, all the predictions were made with the deicer type strictly fixed at the levels given, without any attempt for interpolation or extrapolation (which would have been unreasonable). The second set consists of the *PCR* obtained from the PNS/NACE weight loss test after 72 hours of cyclic immersion. The data used for training and testing are presented in Table 4, with 141 and 7 records respectively. Through trial and error, a 4-7-1 BP ANN model was trained to allow for a reasonable training error and a reasonable testing error, i.e., SMSE for training and testing at 0.05 and 0.03 respectively.

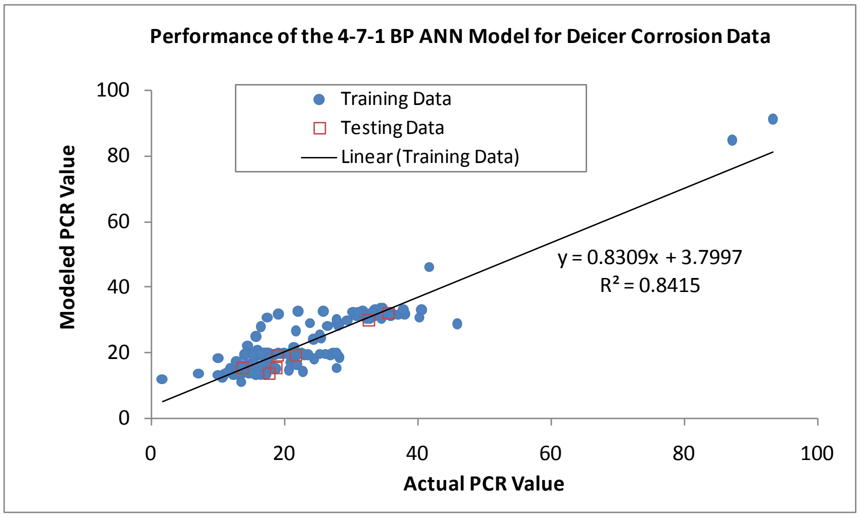
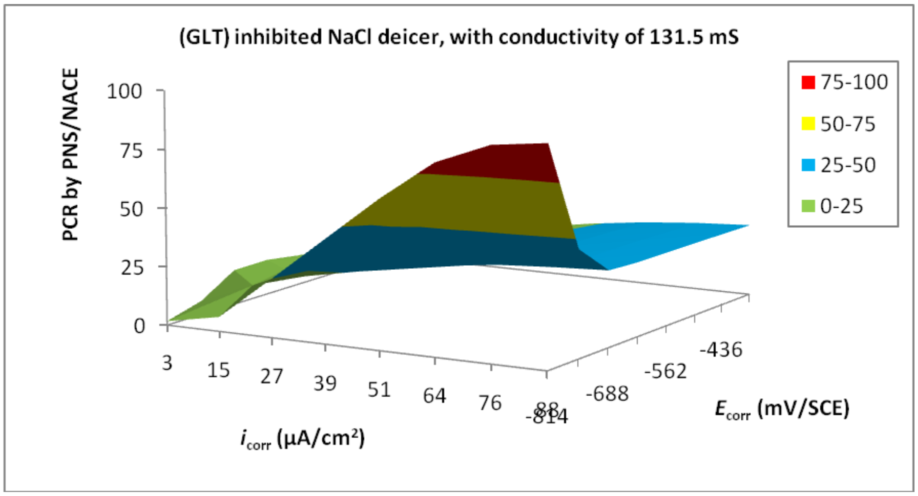


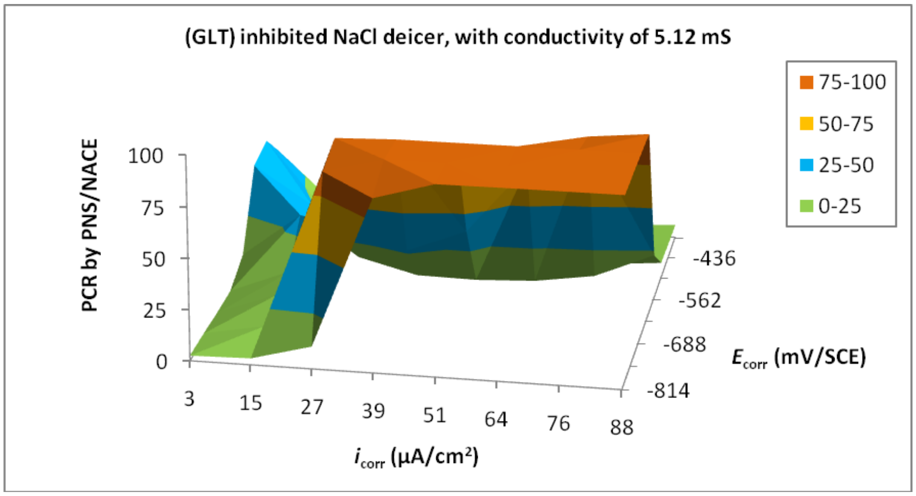
FIGURE 23 Relationship between the measured *PCR* of steel in deicer samples and the *PCR* modeled by the corrosion ANN model.

Figure 23 shows the relationship between experimental and modeled *PCR* values of steel in deicers. From the training and testing results, it appears that the established ANN model has relatively good "memory" and the trained matrices of interconnected weights and bias reflect the hidden functional relationship well. As such, the ANN model was reasonably suitable for predicting the *PCR* value of unknown samples within the ranges of the modeling data. Once the empirical ANN model was trained and tested, it was used to predict the *PCR* as a function of various independent variables.

In Figure 23, the R-square of this correlation was relatively high (0.84), whereas a perfect correlation would be 1.0. This disparity could be derived from experimental errors as well as from the difference in the type of steel coupons used in the two different corrosion tests. Ways to improve the R-square may include: inclusion of an additional solution characteristic (other than electrical conductivity) as model input factor, inclusion of more data points for training the model, and use of the same type of steel for both corrosion tests.



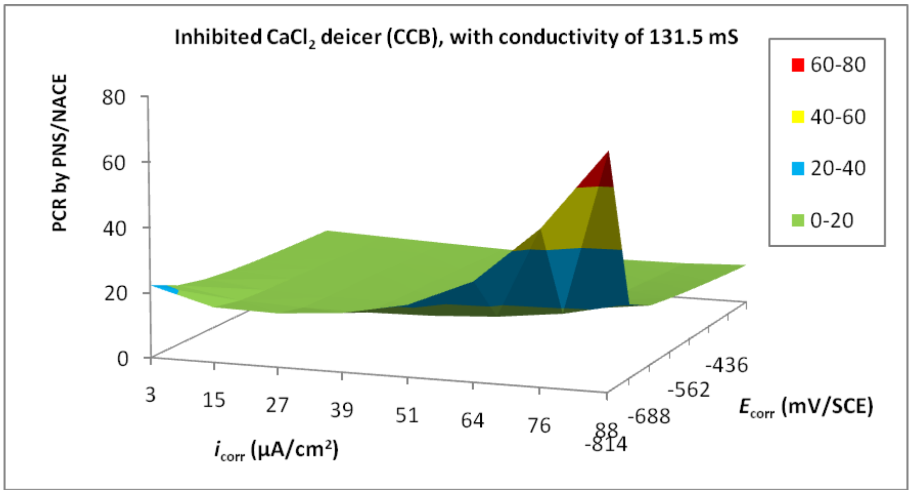
(a)



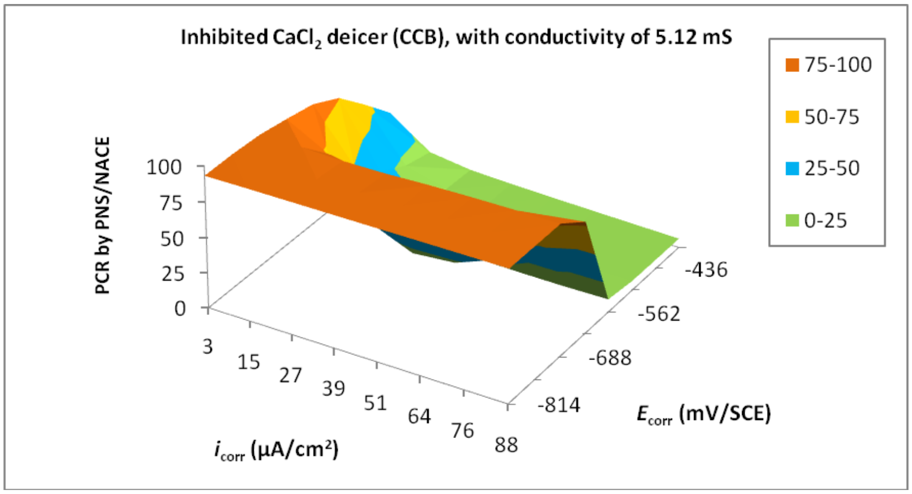
(b)

FIGURE 24 Predicted *PCR* as a function of i_{corr} and E_{corr} for GLT-inhibited NaCl deicer, with conductivity of (a) 131.5 mS/cm, or (b) 5.12 mS/cm.

Figure 24 presents the predicted *PCR* value a function of electrochemical corrosion data (i_{corr} and E_{corr}) for GLT-inhibited NaCl deicers, with a relatively high conductivity (a) and a low conductivity (b) respectively. According to the model predictions, for the inhibited NaCl deicer with a relatively high conductivity, the *PCR* value would increase as the i_{corr} increases or as the E_{corr} decreases. For the inhibited NaCl deicer with a low conductivity, such trends generally remain, except in the ranges where low i_{corr} values are coupled with high E_{corr} values.



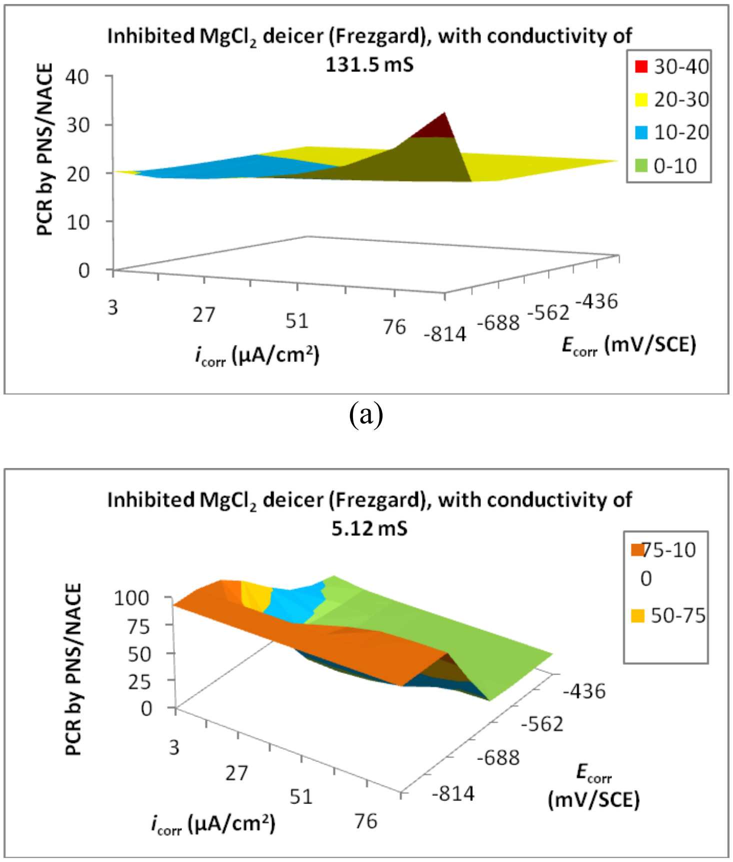
(a)



(b)

FIGURE 25 Predicted *PCR* as a function of i_{corr} and E_{corr} for inhibited $CaCl_2$ deicer (CCB^{TM}), with conductivity of (a) 131.5 mS/cm, or (b) 5.12 mS/cm.

Figure 25 presents the predicted *PCR* value a function of electrochemical corrosion data (i_{corr} and E_{corr}) for inhibited $CaCl_2$ deicer, with a relatively high conductivity (a) and a low conductivity (b) respectively. According to the model predictions, for the inhibited $CaCl_2$ deicer with a r elatively high conductivity, the *PCR* value would increase as the i_{corr} increases or as the E_{corr} decreases. For the inhibited $CaCl_2$ deicer with a low conductivity, however, the *PCR* value would increase as the i_{corr} decreases or as the E_{corr} decreases.



(a)

(b)

FIGURE 26 Predicted *PCR* as a function of i_{corr} and E_{corr} for inhibited $MgCl_2$ deicer (Freezgard^{TM}), with conductivity of (a) 131.5 mS/cm, or (b) 5.12 mS/cm.

Figure 26 presents the predicted *PCR* value a function of electrochemical corrosion data (i_{corr} and E_{corr}) for inhibited $MgCl_2$ deicer, with a relatively high conductivity (a) and a low conductivity (b) respectively. According to the model predictions, for the inhibited $MgCl_2$ deicer with a relatively high conductivity, the *PCR* value would increase as the i_{corr} increases or as the E_{corr} decreases. For the inhibited $MgCl_2$ deicer with a low conductivity, however, the *PCR* value would increase as the i_{corr} decreases or as the E_{corr} decreases. These trends may be the joint outcome of multiple mechanisms at work, including the inhibitory role of rust layer formed during the immersion process and the role of corrosion inhibitor and possibly other additives in the deicers.

A collective examination of Figures 24, 25 and 26 reveals that high E_{corr} values generally corresponded with low *PCR* values. The E_{corr} value higher than -562 mV (vs. SCE) generally corresponded to *PCR* values lower than 30. It should be noted, however, that an E_{corr} value lower than -562 mV_{SCE} does not necessarily indicate a *PCR* value higher than 30. As such, the electrochemical test could be used as a quality assurance tool for rapid assessment of deicer corrosivity to mild steel.

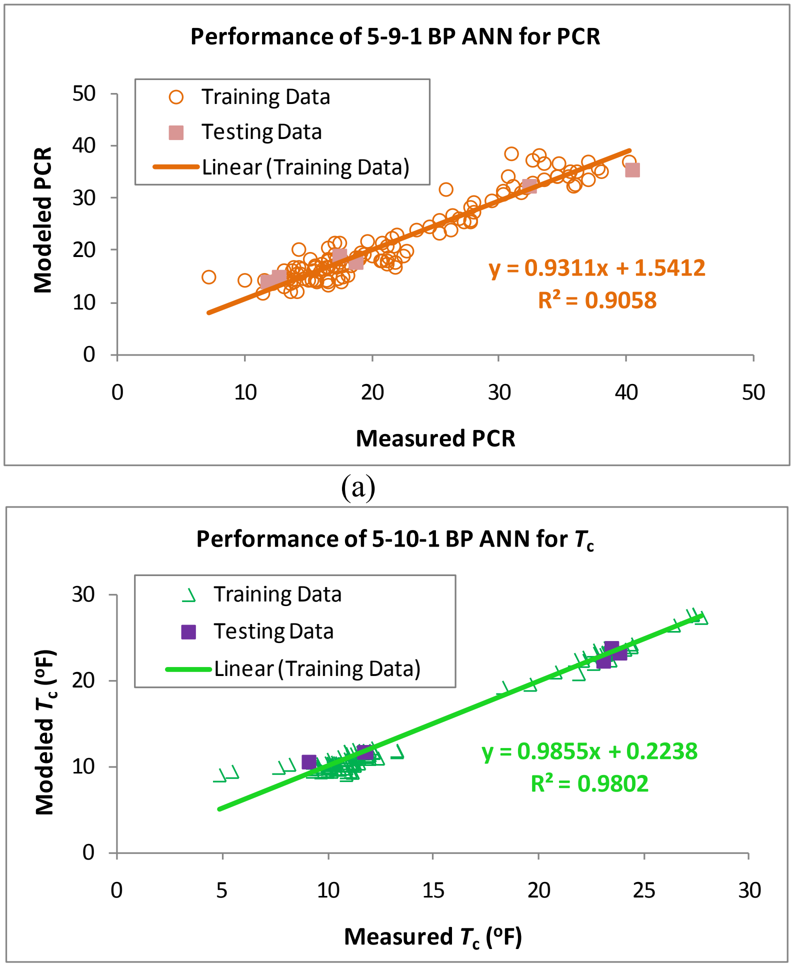
ANN has demonstrated great potential in finding meaningful, logical results from the noisy data associated with the metallic corrosion experiments. According to the ANN modeling, there are strong correlations between the two sets of data, whereas the trends differ as a function of the deicer type and the solution conductivity. As such, for any unknown solution derived from the three deicers, once we subject it to the electrochemical testing (24-hr continuous immersion) and obtain the E_{corr} and i_{corr} data, which coupled with the measured conductivity of the solution, would give us the predicted *PCR* value (instead of running the 72-hour cyclic immersion PNS/NACE test). As such, the electrochemical test could serve as a supplement to the PNS/NACE test or for rapid quality assurance of deicers.

2.2.9. Correlating the Composition with the Corrosivity and Performance of Liquid Deicers

This section presents two ANN models that were established to achieve better understanding of the complex correlation between the deicer composition (deicer type, chloride and inhibitor concentrations, pH, and electrical conductivity) and the deicer corrosivity (in *PCR*) and performance (in T_c) respectively. These data were mostly obtained by testing the field storage samples of the three liquid deicers. Furthermore, a few standard solutions of each deicer were prepared by mixing the vendor-provided non-inhibited deicer and the corresponding corrosion inhibitor at various known concentrations. A total of 126 deicer samples were tested using DSC and they shared similar ice melting capacity at 30ºF regardless of deicer composition. All the DSC-derived $IMC_{30°\mathrm{F}}$ values remained within 3.79±0.14 mL/mL; and this lack of diversity disqualified $IMC_{30°\mathrm{F}}$ as an output factor for ANN modeling.

The data set used for the training and testing of the two ANN models include 120 and 6 records respectively. Through trial and error, a 5-9-1 model and a 5-10-1 model were used to capture the relationship between the deicer composition and the *PCR* and the T_c respectively. The training and testing SMSE was 0.03 and 0.02 respectively for the *PCR* model and 0.006 and 0.004 respectively for the T_c model.

Figures 27(a) and 27(b) show the strong correlations between experimental and modeled *PCR* and T_c values respectively for the deicer samples, indicated by the high R-square values (0.91 and 0.98 respectively). From the training and testing results, it appears that the established ANN models have relatively good "memory" and the trained matrices of interconnected weights and bias reflect the hidden functional relationship well. As such, the ANN models were reasonably suitable for predicting the *PCR* and T_c values of unknown samples within the ranges of the modeling data. Once the empirical ANN models were trained and tested, they were used to predict the *PCR* and T_c as a function of chloride and inhibitor concentrations.

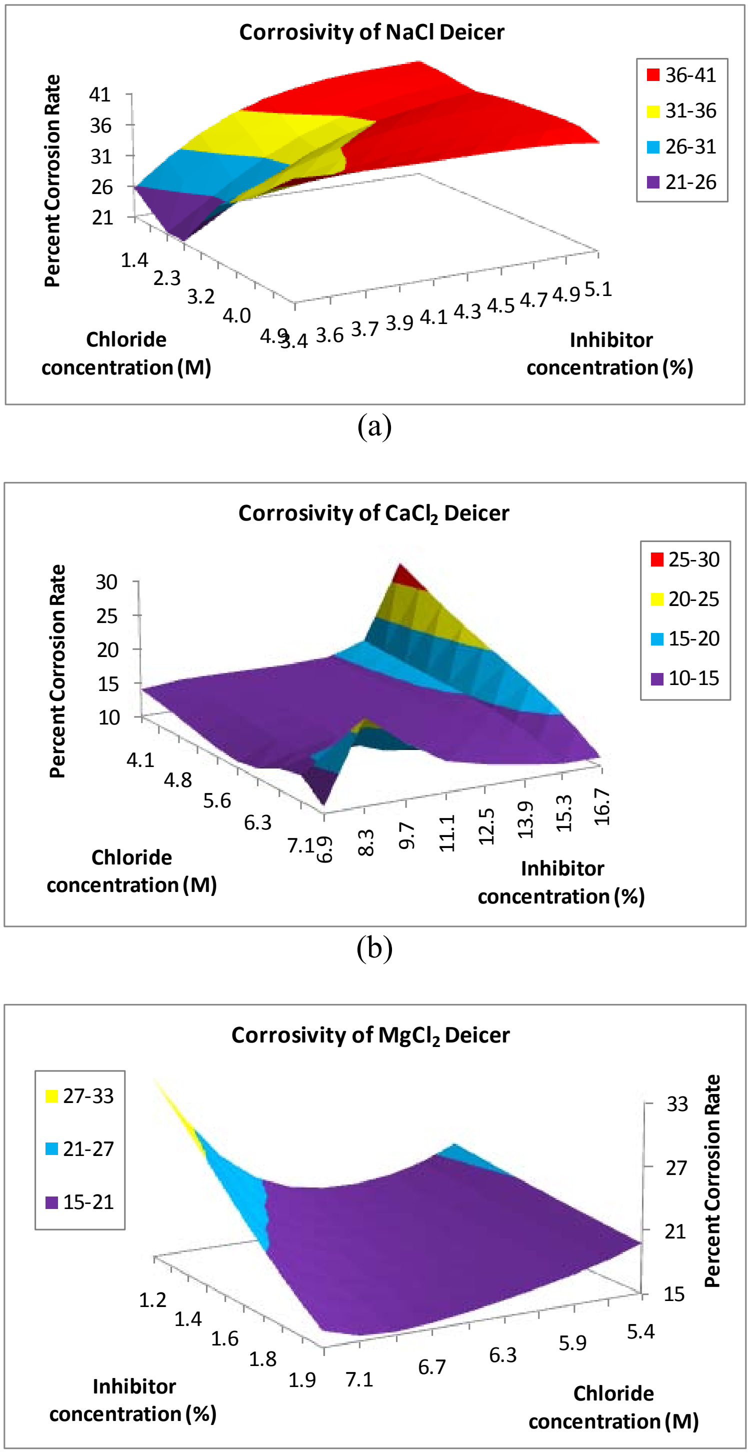


(a)

(b)

FIGURE 27 Relationship between the measured and modeled (a) PCR and (b) T_c in deicer samples.

Figure 28 presents the predicted *PCR* value a function of chloride and inhibitor concentrations for the three liquid deicers, with pH and conductivity fixed at the median levels for each deicer, which were 7.56 and 200.0 mS respectively for NaCl+GLT, 4.92 and 132.1 m S/cm respectively for CCB, and 6.24 and 99.4 m S/cm respectively for FreezGard. According to the model predictions, there was no straightforward relationship between the deicer corrosivity with the chloride or inhibitor concentrations, at least in the ranges investigated (as shown in Figure 29). For NaCl+GLT, the lowest *PCR* values are predicted to fall in formulations with both relatively low inhibitor concentration (e.g., 3.4%) and intermediate chloride concentration (e.g., 2.3 M [Cl^-]). For CCB, the *PCR* values are generally predicted to be low except in formulations with both very high inhibitor concentration (e.g., 16.7%) and low chloride concentration (e.g., 4.1 M [Cl^-]). For FreezGard, the *PCR* values are generally predicted to be low except in formulations with both very low inhibitor concentration (e.g., 1.2%) and very high chloride concentration (e.g., 7.1 M [Cl^-]).

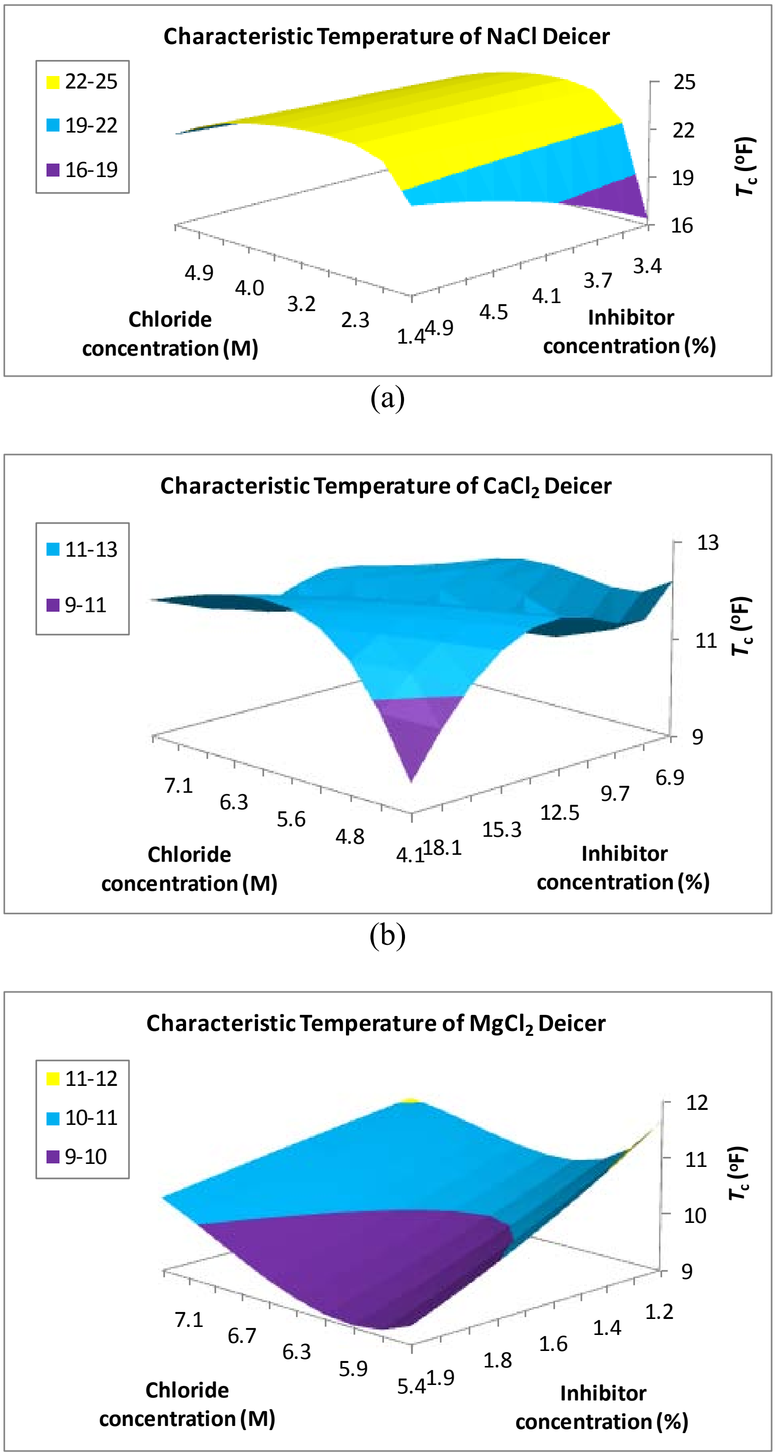


(a)

(b)

(c)

FIGURE 28 Predicted *PCR* as a function of chloride and inhibitor concentrations for (a) NaCl+GLT, (b) CCB, and (c) FreezGard, with pH and conductivity fixed at the median levels for each deicer.



(a)

(b)

(c)

FIGURE 29 Predicted T_c as a function of chloride and inhibitor concentrations for (a) NaCl+GLT, (b) CCB, and (c) FreezGard, with pH and conductivity fixed at the median levels for each deicer.

Figure 29 presents the predicted T_c value a function of chloride and inhibitor concentrations for the three liquid deicers, with pH and conductivity fixed at the median levels for each deicer. According to the model predictions, the lowest T_c values are predicted to fall in formulations with both low inhibitor concentration (e.g. 3.4%) and low chloride concentration (e.g., 1.4 M [Cl^-]) for NaCl+GLT deicer. For CCB, the lowest T_c values are predicted to fall in formulations with both high inhibitor concentration (e.g. 18.1%) and low chloride concentration (e.g., 4.1 M [Cl^-]). For FreezGard, the lowest T_c values are predicted to fall in formulations with both high inhibitor concentration (e.g. 1.9%) and intermediate chloride concentration (e.g., 6.0 M [Cl^-]).

To further explore the effect of corrosion inhibitors on the suppression of freezing point temperature or the effectiveness of deicers, Table 5 presents the DSC-derived performance characteristics of corrosion inhibitor, non-inhibited brine, and inhibited brine for the three liquid deicers. Note that strong deicers are generally expected to feature low T_c and high ΔH values. As shown in Table 5, the GLT inhibitor used alone or as additive to the NaCl-based deicer showed little benefit in suppressing effective temperature or in providing ice melting capacity. The inhibitor packages used in the CCB and FreezGard deicers slightly increased the effective temperature of their respective brine (which is undesirable[13]) and showed little effect on the ice melting capacity. However, different from GLT, these inhibitor packages showed some limited ice melting capacity when used alone, as indicated by their T_c and high ΔH values.

TABLE 5 DSC-derived performance characteristics of corrosion inhibitor, non-inhibited brine, and inhibited brine for the three liquid deicers.

Deicer Products	Heat Flow (J/g)	Characteristic Temperature (T_c, °F)	ΔH (J/g)
NaCl+GLT (with 4.3% inhibitor)	144.3±18.9	21.4	201
Non-inhibited 23% straight salt brine (provided by the MDT)	152.7±4.4	21.4	192
Non-inhibited 23% NaCl brine (made from reagent-grade NaCl)	165.0±1.8	21.8	180
Corrosion inhibitor (GLT) only	333.9±8.3	34.2	0.1
CCB ($CaCl_2$-based, with 11.1% inhibitor)	154.3±1.6	13.7	191
Non-inhibited CCB brine (provided by the vendor)	142.8±2.6	11.5	202
Corrosion inhibitor only	246.6±6.4	31.9	87
FreezGard ($MgCl_2$-based, with 2.4% inhibitor)	135.3±5.7	11.2	210
Non-inhibited FeezGard Brine (provided by the vendor)	130.4±5.1	10.3	215
Corrosion inhibitor only	165±38.3	32.6	169

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[13] This may be the result of some negative interactions between the corrosion inhibitor and the chlorides and/or other impurities.

2.3. Conclusions

This study investigated the longevity of corrosion inhibitors and the performance of corrosion-inhibited deicer products under various storage conditions. Multiple established analytical methods were used to monitor the temporal evolution of the identified deicer properties under field storage, by randomly sampling the solid or liquid deicers periodically and analyzing them in the laboratory. The key findings are presented as follows.

1. Three liquid deicers ($MgCl_2$-based FreezGard, Calcium Chloride with Boost - CCB, and NaCl+GLT) and one solid deicer (NaCl-based IceSlicer) were selected for the field storage monitoring and the key properties tested include the chloride and inhibitor concentrations, corrosion parameters (E_{corr} and PCR), pH, electrical conductivity, and performance parameters (T_c and $IMC_{30^{\circ}\mathrm{F}}$). None of liquid deicers lost their quality over the 14 months of field storage, regardless of the storage condition (mixed or non-mixed). The NaCl-based solid deicer did not lose its quality over the 12 months of field storage, regardless of the storage condition (covered or uncovered). For all four deicers, the observed fluctuations in their properties seem to be non-seasonal but more likely attributable to the sampling and measuring variabilities. No significant degradation of corrosion inhibitor or loss of chlorides was seen during the months of field storage.

2. From an accelerated UV-degradation study conducted in the laboratory, the effect of exposure conditions (temperature, UV intensity, and time) on the resulting inhibitor concentration was generally insignificant for the NaCl+GLT and FreezGard deicers but significant for the CCB deicer. For the CCB deicer, the blocking of UV light by the storage tanks was likely beneficial in preventing its inhibitor degradation over the 14-month field storage monitoring period. For the IceSlicer solid deicer, the inhibitor concentrations were too low to make reliable conclusions about any possible inhibitor degradation.

3. The GLT inhibitor used alone or as additive to the NaCl-based deicer showed no benefit in suppressing effective temperature or in providing ice melting capacity. The inhibitor packages used in the CCB and FreezGard deicers slightly increased the effective temperature of their respective brine and showed little effect on the ice melting capacity (based on the *DSC* data). However, different from GLT, these inhibitor packages showed some limited ice melting capacity when used alone. In a word, while these inhibitors demonstrated their effectiveness in corrosion inhibition, they showed no side benefits in deicer performance.

4. During the field storage months the average chloride and inhibitor concentrations in the FreezGard deicer generally remained within 35.6±0.8% and 1.7±0.3% respectively. The inhibitor-to-chloride concentration ratio in the mixed and non-mixed FreezGard tanks was highly consistent over the months of field storage and both averaged at 1:21. During the 14 months of field sampling and monitoring, the *PCR* of the FreezGard deicer remained below 30%, indicating PNS-acceptable

corrosivity levels under the specific storage conditions investigated. The DSC-derived T_c and $IMC_{30°F,\ 60min}$ of the FreezGard deicer samples remained very consistent within 10.2±1.2 ºF and 3.7±1.1 mL/mL (snowmelt/deicer) respectively.

5. There was a significant difference in corrosion inhibitor concentration between mixed and non-mixed CCB tanks. The average inhibitor concentration in mixed and non-mixed CCB tanks generally remained within 9.3±1.7% and 11.2±3.3% respectively, with the mixed tanks showing lower readings and less data variability. During the 14 months of field sampling and monitoring, the *PCR* of the CCB deicer remained below 30%, indicating PNS-acceptable corrosivity levels under the specific storage conditions investigated. The DSC-derived T_c and $IMC_{30°F,\ 60min}$ of the CCB deicer samples remained very consistent within 11.2±1.2 ºF and 3.8±0.1 mL/mL (snowmelt/deicer) respectively, suggesting similar performance characteristics to FreezGard.

6. There was a significant difference in corrosion inhibitor concentration between mixed and non-mixed NaCl+GLT tanks. The average inhibitor concentration in mixed and non-mixed NaCl+GLT tanks generally remained within 3.8±0.2% and 4.3±0.4% respectively, again with the mixed tank showing lower readings and less data variability. The inhibitor-to-chloride concentration ratio in the mixed and non-mixed NaCl+GLT tanks was highly variable over the months of field storage and averaged at 1:4.0 and 1:3.4 respectively. NaCl+GLT was the only liquid deicer to have non-passing PCR corrosion scores, suggesting potential shelf-life issues. The DSC-derived T_c and $IMC_{30°F,\ 60min}$ of the NaCl+GLT deicer samples remained very consistent within 23.5±1.9 ºF and 3.8±0.2 mL/mL (snowmelt/deicer) respectively, suggesting higher T_c and similar $IMC_{30°F}$ relative to the $MgCl_2$- or $CaCl_2$-based liquid deicers.

7. The properties of stratified samples obtained from the top, middle and bottom of the mixed and non-mixed deicer tanks were also measured every six months or so during the field storage, which shed light on the effect of mixing on the homogeneity of each liquid deicer in the storage tanks.

8. With few exceptions, the IceSlicer samples from the covered pile generally featured slightly higher chloride concentrations and significantly lower inhibitor concentrations, relative to those from the uncovered pile. While the chloride concentration in both covered and uncovered piles remained relatively consistent over the 12 months of field storage, the inhibitor concentration in both piles tended to increase over time. The deicer corrosivity to steel (*PCR*) fluctuated between 60 and 100, regardless of the storage condition or the sieving of the deicer sample, indicating unacceptable corrosivity levels under the specific storage conditions investigated. The inhibitor-to-chloride concentration ratio in the cistern attached to the uncovered pile remained fairly consistent in the first eight months of monitoring. Yet the low inhibitor concentrations in the cistern during last four months may be correlated with the high inhibitor concentrations in the uncovered

pile, both suggesting that the leaching rate of chloride from the uncovered pile exceeded that of the corrosion inhibitor.

9. ANN has demonstrated great potential in finding meaningful, logical results from the noisy data associated with the metallic corrosion experiments. One ANN model was established to correlate the corrosion data from the electrochemical test method with those from the PNS/NACE test method (featuring a R-square of 0.84). Two additional ANN models were established to achieve better understanding of the complex correlation between the deicer composition (deicer type, chloride and inhibitor concentrations, pH, and electrical conductivity) and the deicer corrosivity (in *PCR*) and performance (in T_c) respectively. According to the ANN modeling, there are strong correlations inherent in the deicer samples (indicated by the R-square values of 0.91 and 0.98 for *PCR* and T_c respectively), whereas the trends differ as a function of the deicer type.

10. High E_{corr} values generally corresponded with low *PCR* values. The E_{corr} value higher than -562 mV (vs. SCE) generally corresponded to *PCR* values lower than 30. It should be noted, however, that an E_{corr} value lower than -562 mV_{SCE} does not necessarily indicate a *PCR* value higher than 30. As such, the electrochemical test could be used as a quality assurance tool for rapid assessment of deicer corrosivity to mild steel.

2.4. References

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CHAPTER 3 INHIBITOR LONGEVITY AND DEICER PERFORMANCE AFTER PAVEMENT APPLICATION DURING WINTER STORMS

In the field environment, both chloride and inhibitor in the deicer product may be lost to the environment or diluted over time once applied on the roadway. This chapter presents the methodology, results and discussion pertinent to the investigation of the longevity of corrosion inhibitors and the performance of corrosion-inhibited deicer products after pavement application during winter storms. The field operational tests included the daily sampling of deicer residuals on the pavement for seven days after deicer application for a black ice event, a m an-made snow event, and a natural snow event respectively. Subsequently, the analytical methods established previously (see Chapter 2) were used to analyze the properties of pavement-collected samples in the laboratory.

3.1. Experimental

3.1.1. Deicers of Interest

The field operation tests (FOTs) involved three liquid deicers of interest to the project sponsors. These include the inhibited NaCl liquid deicer, the inhibited $CaCl_2$ liquid deicer (Calcium Chloride with Boost, or CCB^{TM}), and the inhibited $MgCl_2$ liquid deicer (FreezGard CI Plus^{TM}). They represent deicer products under selected PNS categories, with individual chloride and inhibitor concentrations provided in Table 6. Note that these deicers were slightly different from the ones used for the field storage study (as shown in Table 1), since they were prepared from a new batch.

TABLE 6 Chloride and inhibitor concentrations of the deicer products for the field operational tests, as stated by the vendor or measured independently.

Deicer Product	Salt Concentration (by vendor)	Corrosion Inhibitor Concentration (by vendor)	Salt Concentration (by WTI)	Corrosion Inhibitor Concentration (by WTI)	Inhibitor to Chloride Ratio
NaCl+GLT	23%	5%	18.8%	4.7%	1:4.0
CCB	31+%	12%	30.3%	16.2%	1:1.9
FreezGard	29-31%	1.7%	36.2%	1.2%	1:30.2

Note that the salt concentrations reported by WTI were calculated based on the elemental concentrations of cations (Na, Ca, or Mg) measured using the inductively-coupled plasma (ICP), whereas the vast majority of the salt concentrations reported in this project were calculated based on ion-selective sensor measurements of chloride concentration. The inhibitor concentrations in the three deicers were measured by WTI using the UV-vis method.

3.1.2. Laboratory Testing

All the deicer residual samples collected from the field pavement were stored in the refrigerator. Prior to laboratory testing, they were removed from cold storage and allowed to reach room temperature (21 to 23°C). For each deicer property, at least three duplicate samples were tested or at least three readings were taken (e.g., pH and electrical conductivity). Note that unlike the field storage samples, the pavement-collected deicer samples were not diluted prior to any laboratory test.

MEASURING CHLORIDE AND INHIBITOR CONCENTRATIONS IN DEICER SAMPLES

As detailed in Chapter 2, we also used custom-made chloride ion-selective sensors to quickly measure the chloride concentration in pavement-collected deicer samples. Note that since the chloride concentrations in the pavement-collected deicer samples tended to be much lower than those in the field storage samples, the calibration curve of chloride sensors were established using standard solutions with much diluted chloride concentrations. The samples were tested however, without dilution prior to the UV-vis measurements.

We used UV-vis to collect the full spectrum (190 to 750 nm) data of each pavement-collected deicer sample. Due to the very low inhibitor concentrations and potential interference from contaminants in the pavement-collected deicer samples, it was often infeasible to identify the characteristic peak of the corrosion inhibitor. For instance, Figure 30 presents the measured UV-vis spectra of samples collected over the 7 days after deicer application for the black ice event: (a) from the control lane (with no deicer applied); (b) from the CCB section. The presence of inhibitor from the CCB section samples was subtle and difficult to quantify. To enhance the inhibitor signal in the pavement-collected samples, it was necessary to analyze the UV-vis data using the first-order derivative method. As shown in Figure 31, such treatment did facilitate the identification of the characteristic peak attributed to the CCB inhibitor (the peaks around 268 nm).

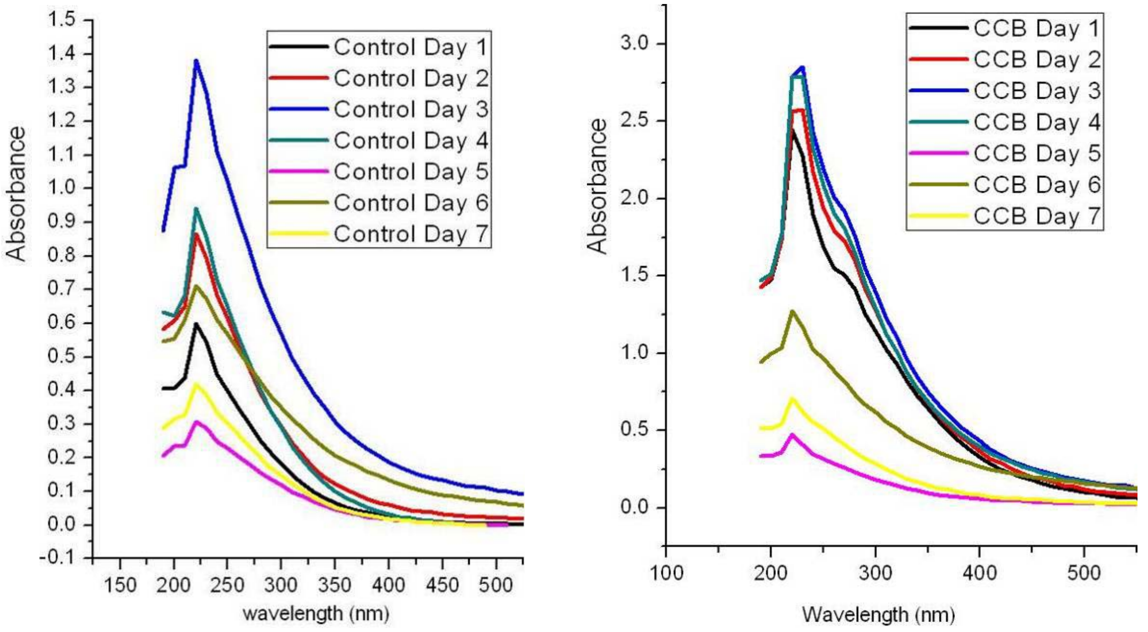
MEASURING PH, CONDUCTIVITY, AND PERFORMANCE OF DEICER SAMPLES

The pH of pavement-collected deicer solutions was determined following the ASTM D 1293 test method, using a Fisher Scientific® Accumet Basic AB15 pH meter. The conductivity of pavement-collected deicer solutions was measured using a Eutech Instruments® CON510 Bench Meter.

In this study, we conducted the DSC analysis of pavement-collected deicer samples following the method described in Chapter 2, which gives the characteristic temperature (T_c) and predicted ice melting capacity ($IMC_{30°F}$) for each sample. The samples were tested however, without being diluted by three times.

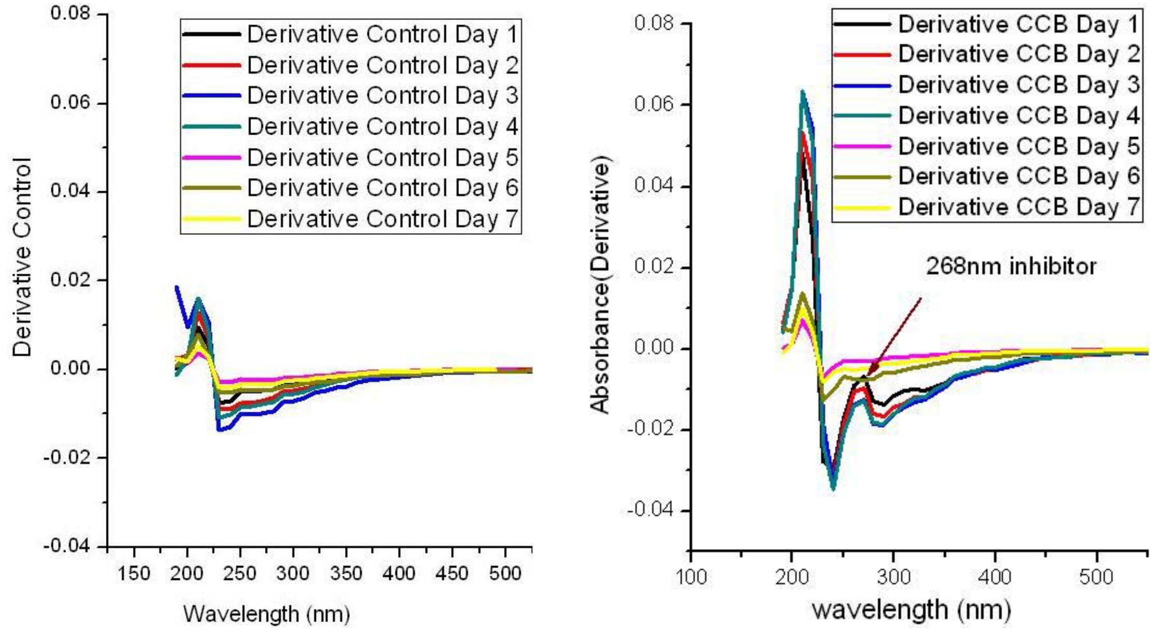
TESTING CORROSION OF DEICER SAMPLES TO METAL

As detailed in Chapter 2, the corrosion of pavement-collected deicer samples to steel was also tested using two different methods, one of which was a gravimetric method and the other was an electrochemical method.



(a) (b)

FIGURE 30 Measured UV-vis spectra of samples collected over the 7 days after deicer application for the black ice event: (a) from the control lane (with no deicer applied); (b) from the CCB lane.



(a) (b)

FIGURE 31 First-order derivative UV-vis spectra of samples collected over the 7 days after deicer application for the black ice event: (a) from the control lane (with no deicer applied); (b) from the CCB lane.

The samples were tested, however, without being diluted by 100:3 prior to the corrosion tests. For samples showing an electrical conductivity no more than 1.8 mS/cm, 0.372 grams of lithium perchlorate was added to 175 mL of such pavement-collected sample to make a 0.02 M supporting electrolyte.

3.1.3. Field Operational Tests

The field operational tests (FOTs) were conducted to detect the presence and concentration of residual chloride and corrosion inhibitor from each of three liquid deicers, over duration of seven days subsequent to their application onto asphalt pavement. To simulate realistic climatic and logistical situations, the FOTs were conducted at the at the TRANSEND facility at Lewistown, MT (as shown in Figure 32), which features unoccupied paved sections of an underutilized airport that enable side-by-side experiments in a safe and controlled field setting. This research and testing facility provides ample space and 4,500 feet of two-lane asphalt pavement, a weather station, snowplow and snowmakers (as shown in Figure 33), friction testing equipment, and winter maintenance applicators for both liquid and solid products.

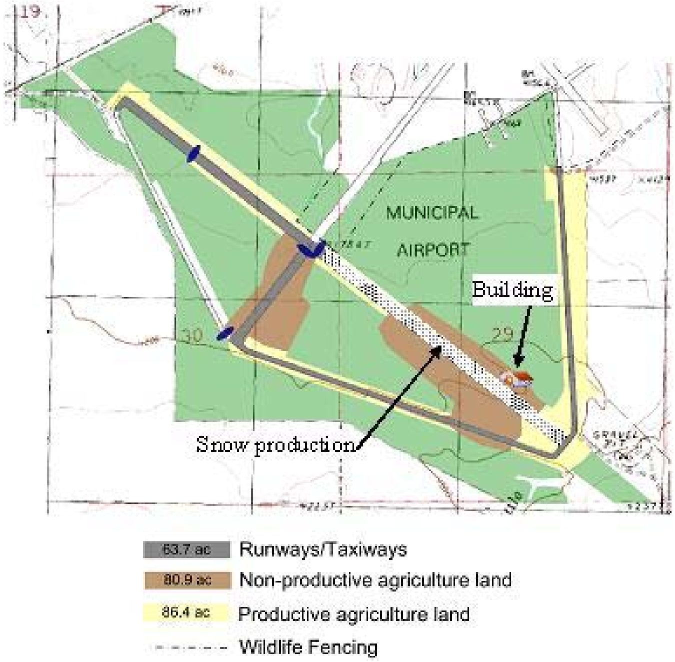


FIGURE 32 Marked aerial photo of the TRANSEND controlled field test-bed.

The FOTs were conducted for three winter storms, i.e., a black ice event, a man-made snow event, and a natural snow event respectively, the target and actual conditions for which are provided in Table 7. For this specific study, the effect of traffic on the fate and transport of chlorides and inhibitors was not simulated in order to minimize safety concerns and to reduce the number of variables for the FOTs. In addition to sampling deicer residuals from the pavement, we also took photographs of weather and pavement conditions at the time of sample collection. The photos (as shown in Appendix E) served to provide qualitative indication of the daily weather condition as well as the anti-icing performance, the latter of which was as a function of deicer type, storm type, and time after application. The detailed field reports are provided in Appendix D. In general, no significant difference in anti-icing performance was observed between the three liquid deicers, based on the periodical visual observations made during the two (man-made and natural snow) storm events. All three liquid deicers worked effectively for anti-icing applications under the investigated conditions, even though the field operational tests did not incorporate real or simulated traffic.


(a) (b)

FIGURE 33 (a) Snowplowing and (b) practice of snowmaking at the TRANSEND facility during the 2009-2010 winter season.

TABLE 7 Target and actual conditions for the three storm events.

	Black Ice Event	Man Made Snow Event	Natural Snow Event
Target Precipitation	No precipitation	Minimum 1 inch of snow	1-4 inches in the first 24 hours
Actual Precipitation	Total of 0.75″ of precipitation (mostly snow/ice) during day 4 to day 7.	1″ of man-made snow; a total of 0.26″ of natural snow during day 3 and day 4.	3.5-4″ in the first 24 hours; about 0.75″ of blowing snow on day 2.
Target Air Temperature	25-32 °F	15-25 °F	25-32 °F
Target Pavement Temperature	Less than 32 °F	Less than 25 °F	25-32 °F
Moisture Content in Snow (Average Density)	Not applicable	30-40% (24 lb/ft^3)	20-40% (19 lb/ft^3)
Target Deicer Application Rate	30 gallons/lane-mile	60 gallons/lane-mile	60 gallons/lane-mile
Actual Application Rate	33±5 gallons/l-m	53±4 gallons/l-m *	55±6 gallons/l-m *
Target Wind Speed	Not specified	Less than 6 mph	Not specified
Average Wind Speed	6 mph	9 mph	9 mph
Average Wind Direction	SSW to NNE (coming from 200°)	SW to NE (coming from 228°)	SSE to NNW (coming from 173°)

* These high application rates were for improved product recovery and subsequent analysis, and they are not representative of what should be applied.

The procedures of site preparation, deicer application, snowmaking, and sample collection are detailed in Appendix C. For each FOT, a test section within the paved surface area was chosen to accommodate four test lanes with dimensions of 12 feet by 100 feet and six 18-foot buffer zones. The 18-foot wide buffer zones were used to provide the separation needed to minimize contamination between test lanes. They also provided staging areas for the sampling activities. Prior to test section set-up and application of the liquid deicers, the entire test section was cleared and washed with high-pressure water to reduce the potential of contaminants being collected with the samples from the pavement.

Once the washing was complete and the drive surface was dry, the four test lanes were demarcated with orange and blue safety cones. Three of the test lanes were designated for the three deicer products and the fourth served as control (with no deicers applied). Subsequently, the three liquid deicers (CCB, FreezGard, and NaCl+GLT) were applied to delineated test lanes using the liquid applicator trailer at the pre-determined application rate (as shown in Table 7). To calculate more precisely the actual amount of liquid deicer applied for each test lane, three sets of five Petri-dishes were placed in the test sections to collect the deicer during application. Between each deicer application the entire application system was thoroughly flushed and cleaned to avoid potential cross-contamination.

Each test lane contained seven sampling plots, each of which represented a sampling day. The layout of sampling plots and sampling boxes for the black ice event and for the two snow events are shown in Figure 34. Each sampling box was constructed using a colored silicone sealant, which served as a dike extending above the pavement surface a minimum of 0.375 inches to prevent the deicer and liquids from flowing out of the sampling box.

For the black ice event, there was no snow-making activity or anticipated natural precipitation and no water or snow was added to the pavement surface to create the black ice. For the man-made snow event, three Turbocrystal$^{©}$ snow guns were placed around the test lanes based on current wind speed and direction, and snowmaking commenced immediately following the application of deicer products. For the natural snow event, deicers were applied prior to the predicted start of the natural snow precipitation. In the case of both snow events, the liquid deicer products served as anti-icers to prevent or weaken the bond of accumulated snow with the pavement surface.

Each sampling plot represented one of seven daily samplings. For the black ice event, the sample collection process began by first adding 1 L of de-ionized water to the 32 × 32 inches sampling box, as shown in Figure 35(a). The de-ionized water aimed to aid in deicer recovery and vacuum collection. For both snow events, the sample collection process began by first leveling off the snow cover in the sampling box to an exact depth of ½ inches, then collecting and melting the snow remaining in it. Subsequently, 0 to 1000 mL of de-ionized water was added to the 18 × 18 inches sampling box, depending on the amount of snowmelt water in the sampling box. In all cases, each sampling day would yield typically 1 L of liquids collected from the pavement, providing adequate volumes for laboratory testing.

Before the snowmelt or added de-ionized water was collected from the pavement surface, it was agitated with a clean 14-inch coarse bristle brush for a period of two minutes, as shown in Figure 35(b). Thereafter, the resultant liquid was vacuumed from the test surface using a small vacuum with a squeegee attachment as shown in Figure 36. After sampling of each test box was complete the vacuum hose, squeegee attachment, cylinder, and agitation brush were thoroughly rinsed with de-ionized water. Daily sampling continued up to seven days following the application of deicers.

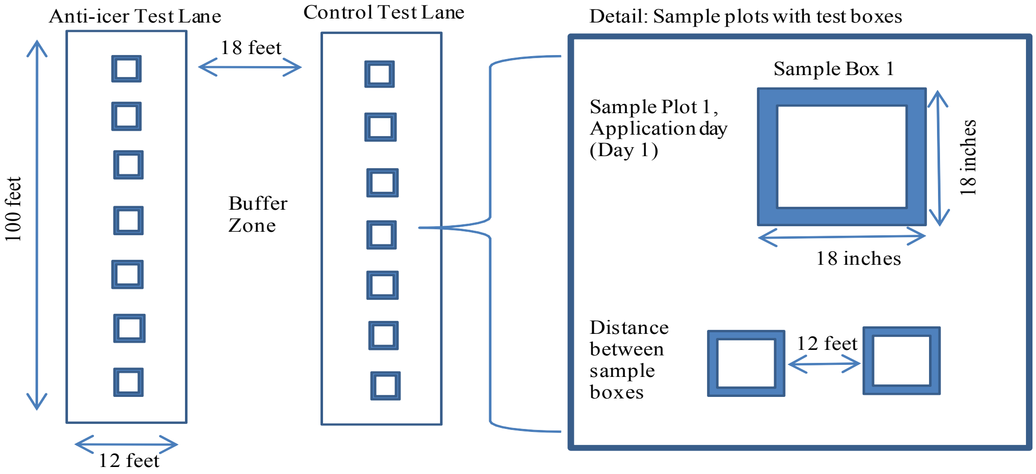


FIGURE 34 Diagram of test lanes and sampling plot layout. For the black ice event however, the boxes were of 32 by 32 inches.

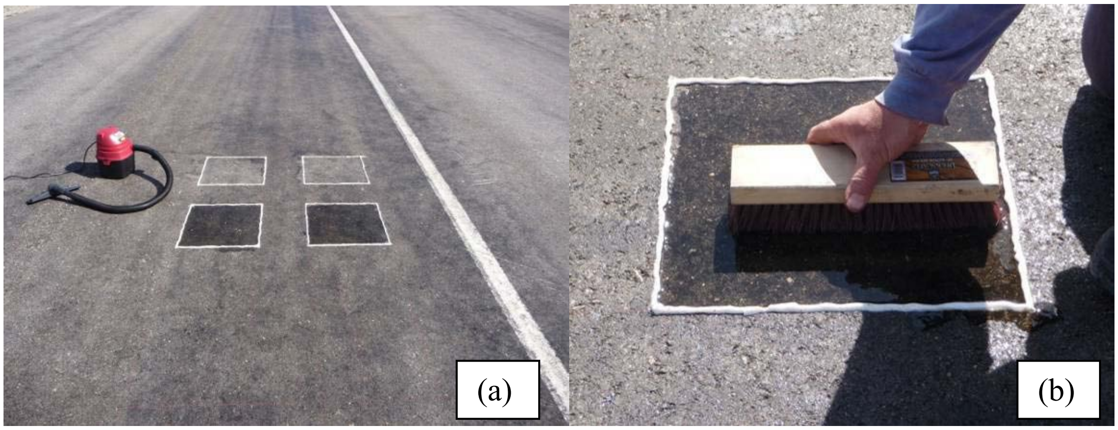


FIGURE 35 Sampling boxes shown (a) after addition of de-ionized water and (b) during the agitation step.

FIGURE 36 Sample collection using a vacuum with squeegee attachment.

METEOROLOGICAL DATA COLLECTION

During the FOTs, we monitored the air temperature and relative humidity (Campbell Scientific® CD215), wind speed and direction (Young® wind monitor 05103), barometric pressure (Setra® 278), and solar radiation (Apogee® PYR-P Pyranometer CS300) at the field site at Lewistown, MT. Pavement temperature was monitored using Omega® Type T thermocouples embedded at the asphalt pavement surface located 20 ft from the pavement edge as well at 15 inches below the asphalt pavement surface located 10 ft from the edge of the asphalt pavement. A Campbell Scientific® CR1000-XT data logger was used to capture and record readings from all the meteorological sensors.

3.2. Results and Discussion

3.2.1. Meteorological Conditions at the FOTs Site

This section presents the temporal evolution of meteorological conditions at the FOTs site for the three storm events at the TRANSEND facility at Lewistown, MT. Such information may help to explain the temporal evolution of chloride and inhibitor concentrations on the pavement, as detailed later. Table 8 provides the event log for deicer application, precipitation, and sampling during each of the three storm events. Note that the day-one sampling occurred 1.7 hours after deicer application for the black ice event. For the man-made snow event, it took 3.25 hours to obtain 1 inch of artificial snow in the sampling plots, and the day-one sampling did not occur until 15.3 hours after deicer application. For the natural snow event, the day-one sampling occurred 20.3 hours after deicer application since we had to wait 9.5 hours for the forecasted snow event to initiate and then another 8.5 hours for it to accumulate 3.5-4 inches of snow in the sampling plots.

TABLE 8 Event log of deicer application, precipitation and sampling for the storm events.

Winter Storm	Appln.	Sample Collection				Precipitation			
	Start	Day	Date	Start	Hr.	Form	Start	Finish	Accmln.
Black Ice Event 10-Feb-10 30 g/ln-m 58-min	9:43 AM	1	10-Feb-10	11:23 AM	1.7	-	-	-	-
		2	11-Feb-10	11:39 AM	25.9	-	-	-	-
		3	12-Feb-10	11:20 AM	49.6	natural snow/rain	-	-	Trace
		4	13-Feb-10	11:00 AM	73.3	natural snow	-	-	>1/4"
		5	14-Feb-10	11:40 AM	98.0	ice/natural snow	-	-	1/2"
		6	15-Feb-10	11:55 AM	122.2	-	-	-	-
		7	16-Feb-10	9:45 AM	144.0	natural snow	-	-	Trace
Man-Made Snow Event 19-Mar-10 60 g/ln-m 54-min	4:37 PM					artificial snow	10:30 PM		
		1	20-Mar-10	7:53 AM	15.3	artificial snow		1:45 AM	1.0"
		2	21-Mar-10	12:00 PM	43.4	-	-	-	-
		3	22-Mar-10	11:39 AM	67.0	natural snow	-	-	~1/8"
		4	23-Mar-10	11:21 AM	90.7	natural snow	-	-	~1/4"
		5	24-Mar-10	10:56 AM	114.3	-	-	-	-
		6	25-Mar-10	11:29 AM	138.9	-	-	-	-
		7	26-Mar-10	8:05 AM	159.5	natural snow	-	-	Trace
Natural Snow Event 12-Apr-10 60 g/ln-m 45-min	4:30 PM					-	-	-	-
		1	13-Apr-10	12:45 PM	20.3	natural Snow	2:00 AM	10:30 AM	3.5-4"
		2	14-Apr-10	10:30 AM	42.0	blowing snow	-	-	1/2-1"
		3	15-Apr-10	10:55 AM	66.4	-	-	-	-
		4	16-Apr-10	11:55 AM	91.4	-	-	-	-
		5	17-Apr-10	6:50 AM	110.3	-	-	-	-
		6	18-Apr-10	12:30 PM	140.0	-	-	-	-
		7	19-Apr-10	10:45 AM	162.2	-	-	-	-

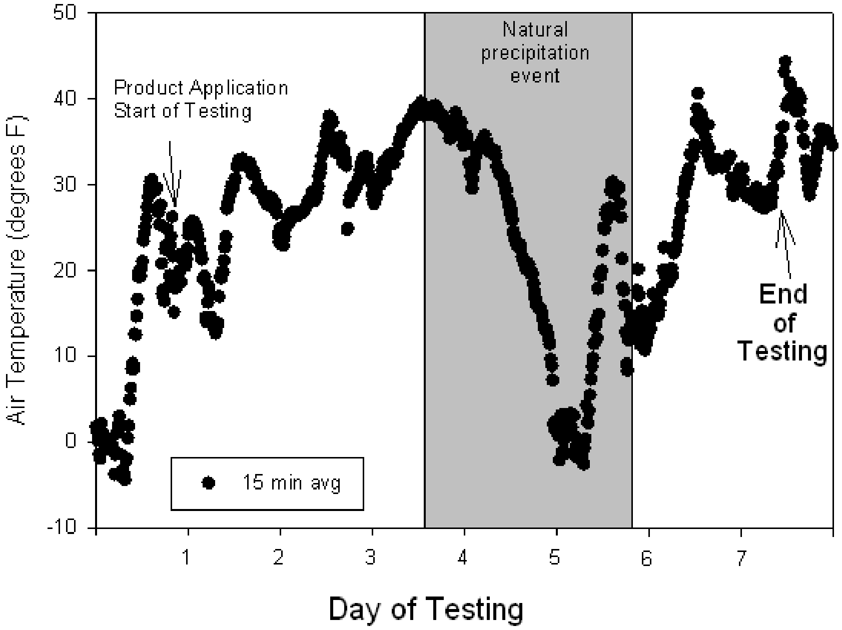


FIGURE 37 Temporal evolution of average air temperature during the black ice event.

BLACK ICE EVENT

Figure 37 presents the change of 15-min average air temperature over the time period of the black ice event. It shows that the air temperature fluctuated greatly with the hour (mostly between 0ºF and 40ºF). The air temperature on day 3 ranged between 28ºF and 38ºF, during which some rain precipitation occurred. On day 4 and day 5, the air temperature dropped to as low as -4 ºF, which corresponded to the precipitation of natural snow and ice. Figure 38 presents the change of temperature both at the pavement surface and at 15 inches under the pavement surface, over the time period of the black ice event. Note that the surface pavement thermocouple experienced a recording error during the night of day 5, which affected data collected for the last two days of the black ice event. The error was fixed shortly after completion of the black ice event. As shown in Figure 38, the temperature at 15 inches under the pavement surface remained fairly consistent, slightly below 32°F (0°C). The pavement surface temperature showed a trend of daily fluctuations mostly between 25ºF and 50ºF and gradually decreased over the first six days of the black ice event. There were many hours during which the pavement temperature dropped below 32ºF, indicating a frozen pavement scenario.

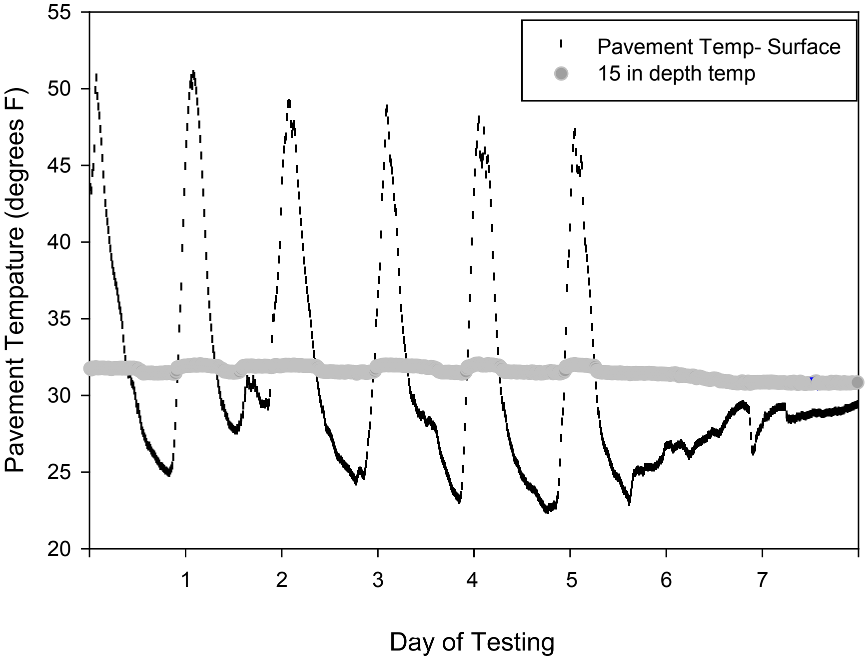


FIGURE 38 Temporal evolution of average pavement temperature during the black ice event.

Figure 39 presents the change of relative humidity, wind speed and air pressure over the time period of the black ice event. The relative humidity fluctuated greatly over the seven-day period, mostly between 35% and 90%, whereas the wind speed ranged between 0 and 20 mph. Note that the day 3 had some natural precipitation of rain, which corresponded with the high humidity readings (up to 90%) and high wind speeds (up to 21 mph). The air pressure at the test site ranged between 757 and 761 mmHg in the first two days, started to increase up to 769 mmHg by day 4, and then declined to 763 mmHg by day 7.

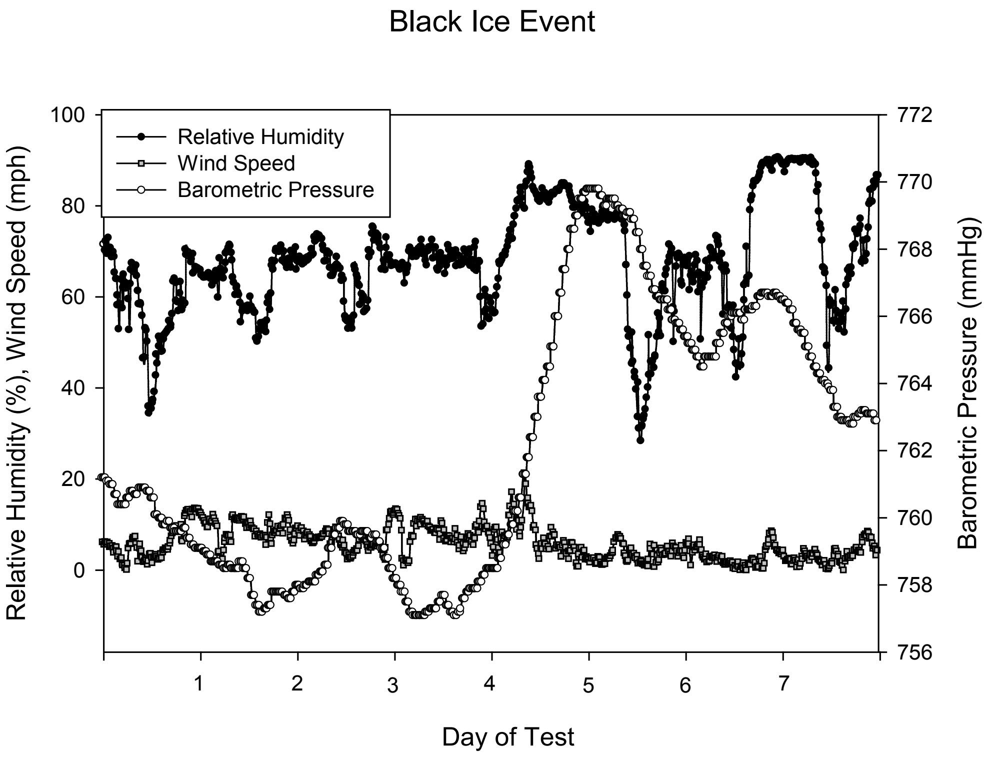


FIGURE 39 Temporal evolution of relative humidity, wind speed and air pressure during the black ice event.

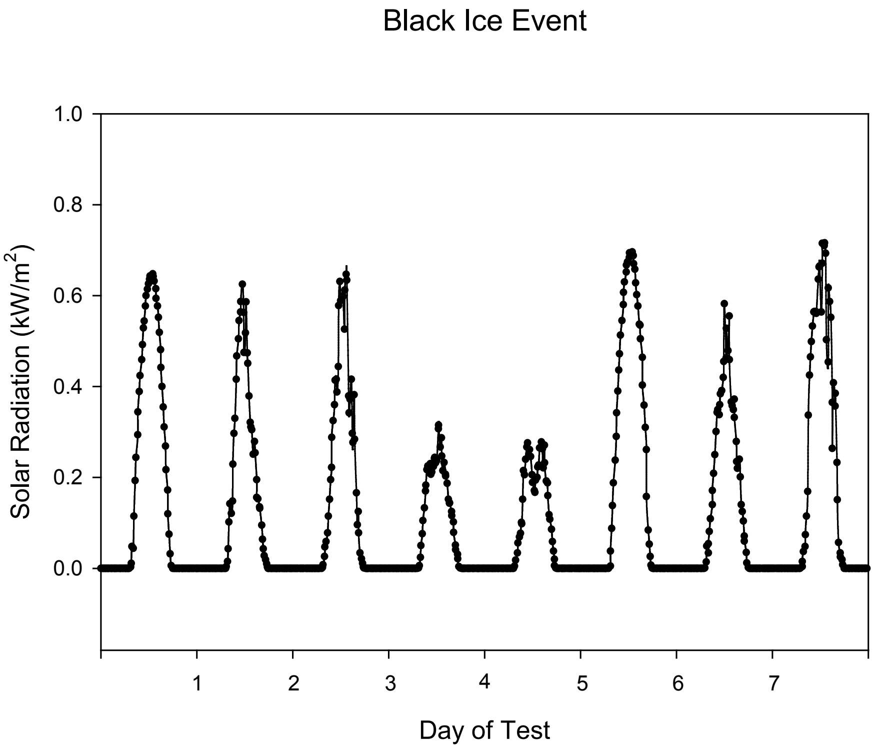


FIGURE 40 Temporal evolution of solar radiation during the black ice event.

Figure 40 presents the change of solar radiation over the time period of the black ice event, which showed a trend of daily fluctuations mostly between 0 and 0.65 kW/m^2. In general, the solar radiation at the test site was low during night time and high during day time. The maximum solar radiation on day 3 was no more than 0.3kW/m^2, due to the rain event.

MAN-MADE SNOW EVENT

Figure 41 presents the change of 15-min average air temperature over the time period of the man-made ice event. It shows that the air temperature fluctuated greatly with the hour (mostly between 20ºF and 60ºF). Immediately after the natural snow precipitation on day 3 and day 4, the air temperature dropped to the range of 34ºF and 46ºF.

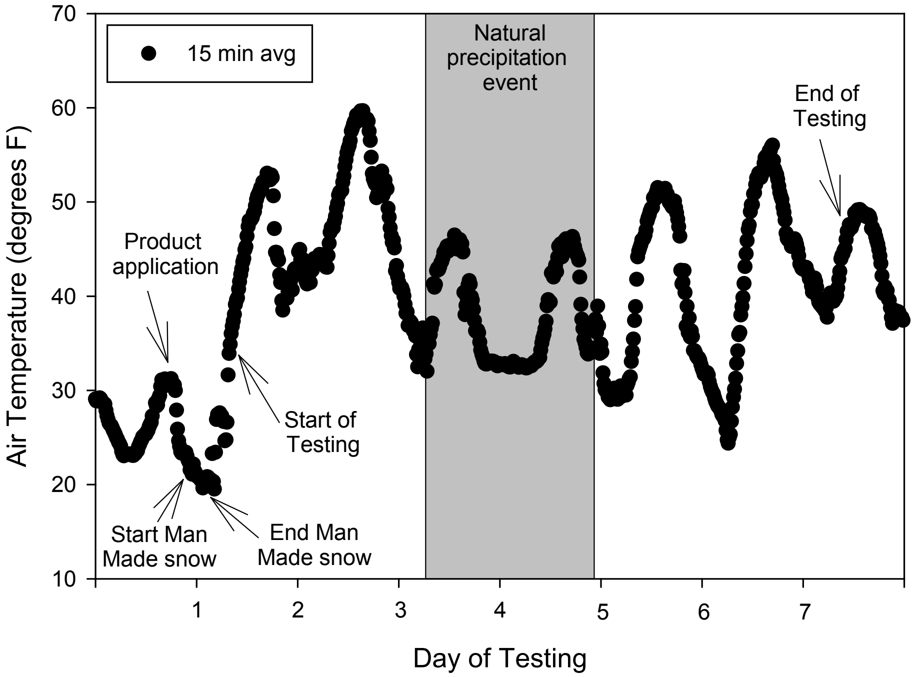


FIGURE 41 Temporal evolution of average air temperature during the man-made snow event.

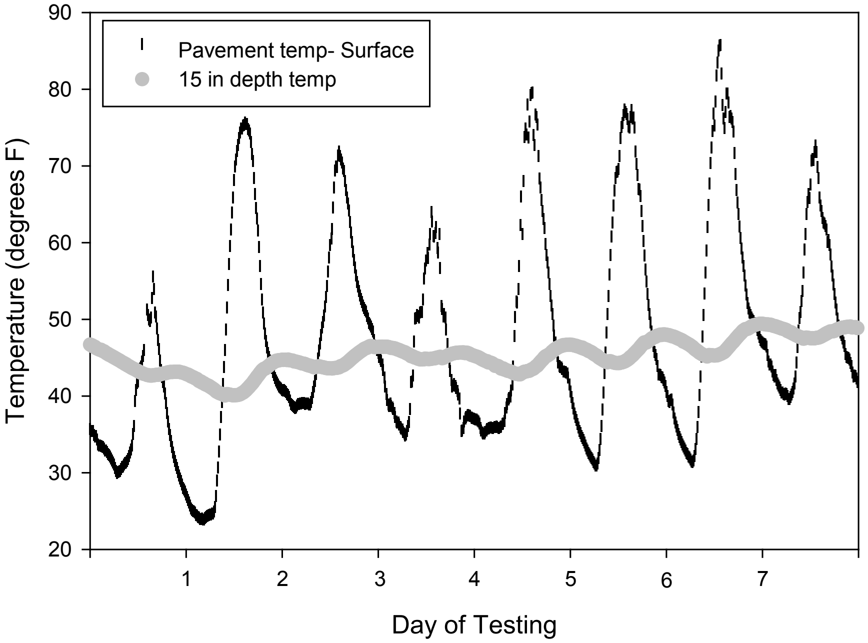


FIGURE 42 Temporal evolution of average pavement temperature during the man-made snow event.

Figure 42 presents the change of temperature both at the pavement surface and at 15 inches under the pavement surface, over the time period of the man-made snow event. It shows that the temperature at 15 inches under the pavement surface generally remained between 40°F and 46°F, suggesting that the ground was not frozen. This corresponded with the relatively high air temperatures shown in Figure 41. The pavement surface temperature showed a trend of daily fluctuations mostly between 25ºF and 80ºF and gradually increased during the seven days of monitoring, except for the two days when the natural snow precipitation occurred. There were some hours during which the pavement temperature dropped below 32ºF, indicating a frozen pavement scenario.

Figure 43 presents the change of relative humidity, wind speed and air pressure over the time period of the man-made snow event. The relative humidity fluctuated greatly over the seven-day period, mostly between 24% and 90%, whereas the wind speed ranged between 0 and 25 mph. The air pressure at the test site declined over the seven days of monitoring in a cyclic manner, in the range of 752 and 771 mmHg. The low pressure readings corresponded to day 3 and day 7, during which small amounts of natural snow precipitation occurred.

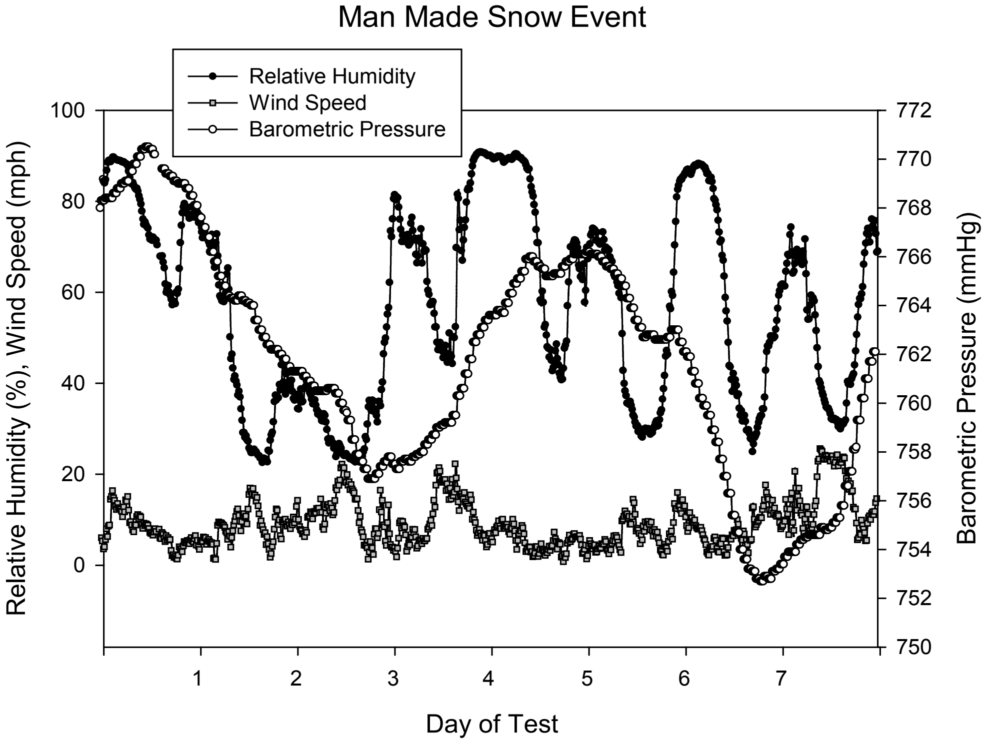


FIGURE 43 Temporal evolution of relative humidity, wind speed and air pressure during the man-made snow event.

Figure 44 presents the change of solar radiation over the time period of the man-made snow event, which showed a trend of daily fluctuations mostly between 0 and 0.95 kW/m^2. In general, the solar radiation at the test site was low during night time and high during day time.

NATURAL SNOW EVENT

Figure 45 presents the change of 15-min average air temperature over the time period of the natural snow event. It shows that the air temperature fluctuated greatly during the first three days of monitoring (mostly between 30ºF and 46ºF); thereafter, it showed a clear trend of daily fluctuations mostly between 30ºF and 65ºF. Note that the natural snow precipitation occurred during the first two days.

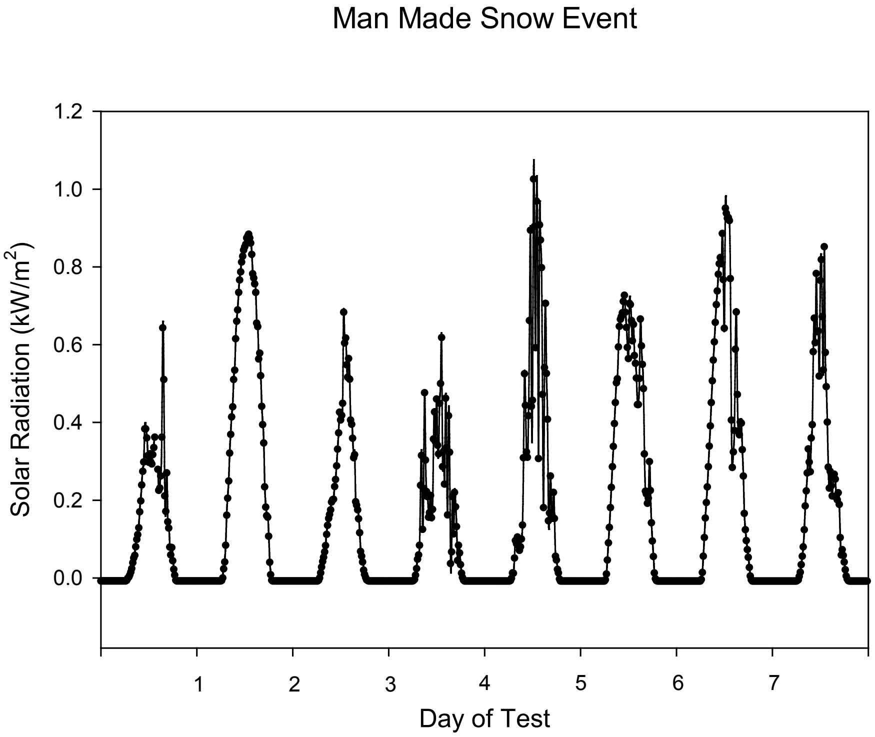


FIGURE 44 Temporal evolution of solar radiation during the man-made snow event.

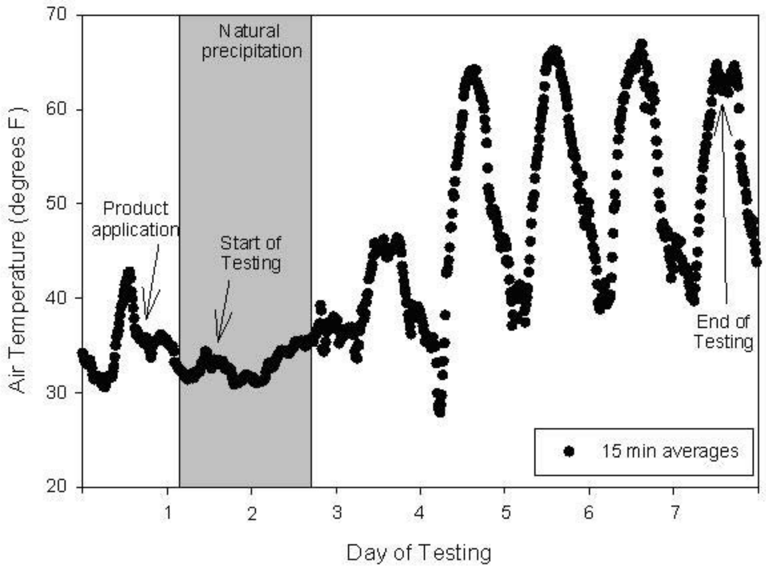


FIGURE 45 Temporal evolution of average pavement temperature during the natural snow event.

Figure 46 presents the change of temperature both at the pavement surface and at 15 inches under the pavement surface, over the time period of the natural snow event. It shows that the temperature at 15 inches under the pavement surface gradually decreased in the range of 38ºF and 48ºF in the first 3.5 days and then increased in the range of 38ºF and 56ºF in daily cycles, suggesting that the ground was not frozen. The pavement surface temperature showed a trend of daily fluctuations mostly between 35ºF and 95ºF, except for the days of natural snow precipitation during which the pavement temperature remained mostly near 36ºF, indicating a warm pavement scenario.

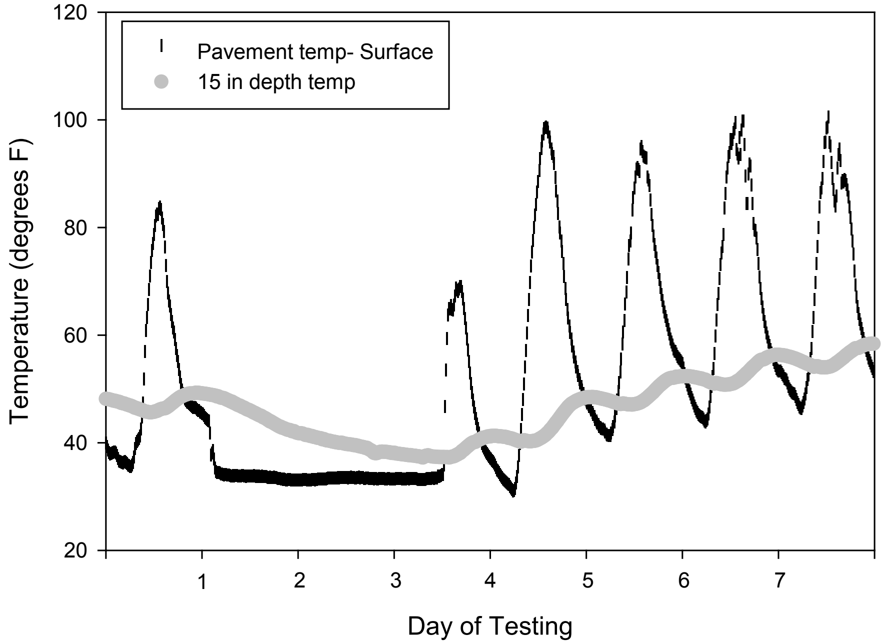


FIGURE 46 Temporal evolution of average pavement temperature during the natural snow event.

Figure 47 presents the change of relative humidity, wind speed and air pressure over the time period of the natural snow event. The relative humidity fluctuated greatly over the seven-day period, mostly between 29% and 90%, whereas the wind speed ranged between 0 and 26 mph. Note that during the days 1 to 3 natural precipitation of snow occurred, which corresponded with the high humidity readings (up to 90%) and high wind speeds (up to 26 mph). The air pressure at the test site fluctuated over the seven days of monitoring in the range of 752 and 771 mmHg, with the low pressure readings corresponded to the days with natural snow precipitation.

Figure 48 resents the change of solar radiation over the time period of the natural snow event, which showed a trend of daily fluctuations mostly between 0 and 1.0 kW/m^2. In general, the solar radiation at the test site was low during night time and high during day time.

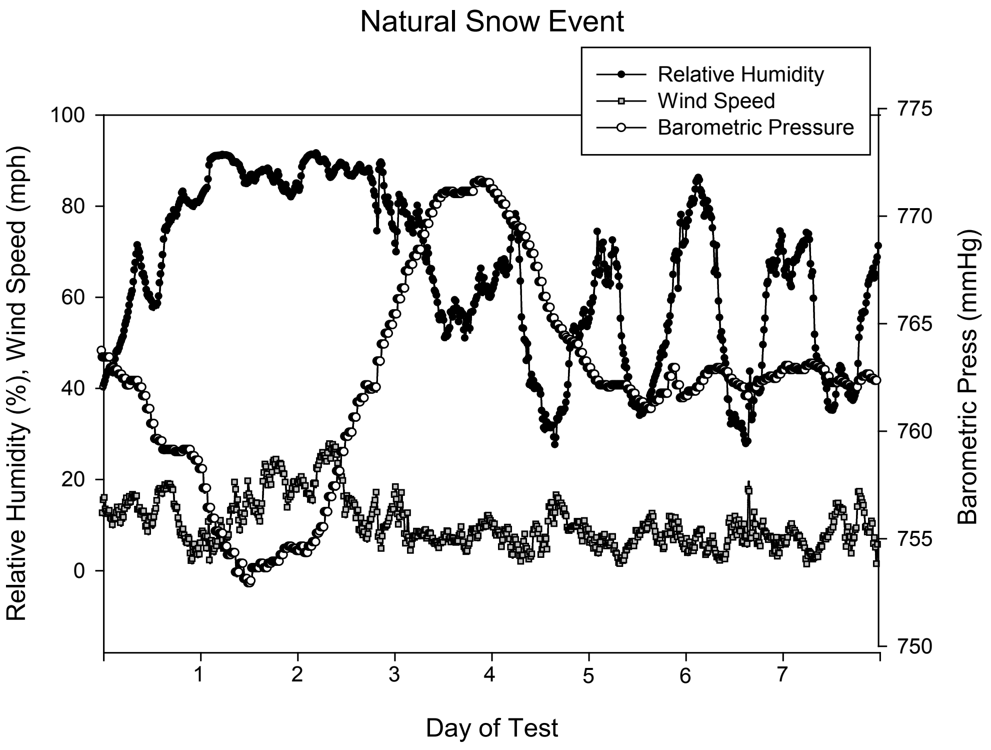


FIGURE 47 Temporal evolution of relative humidity, wind speed and air pressure during the natural snow event.

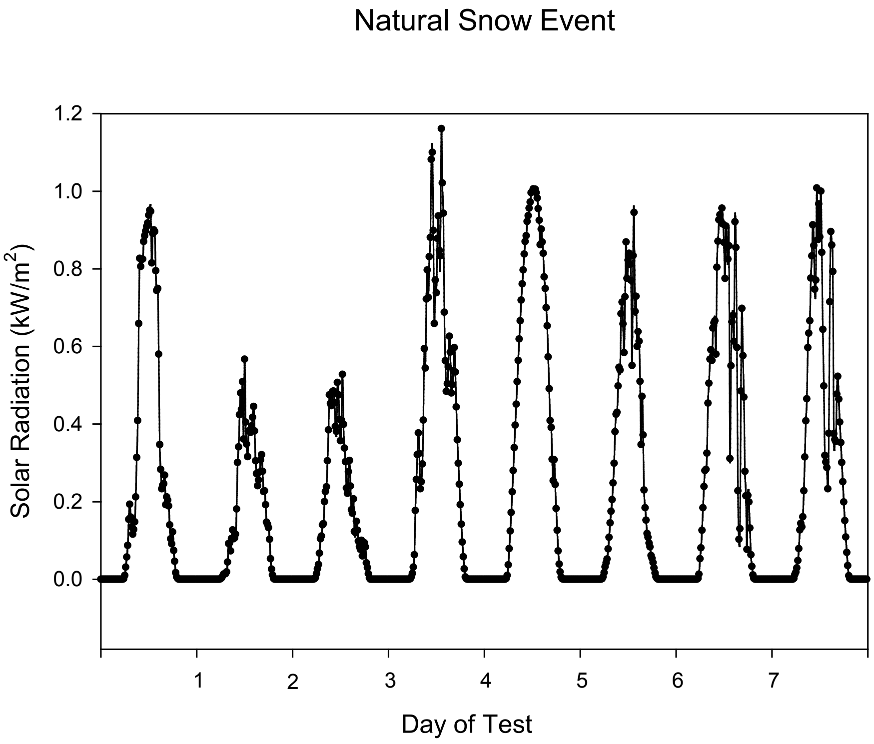


FIGURE 48 Temporal evolution of solar radiation during the natural snow event.

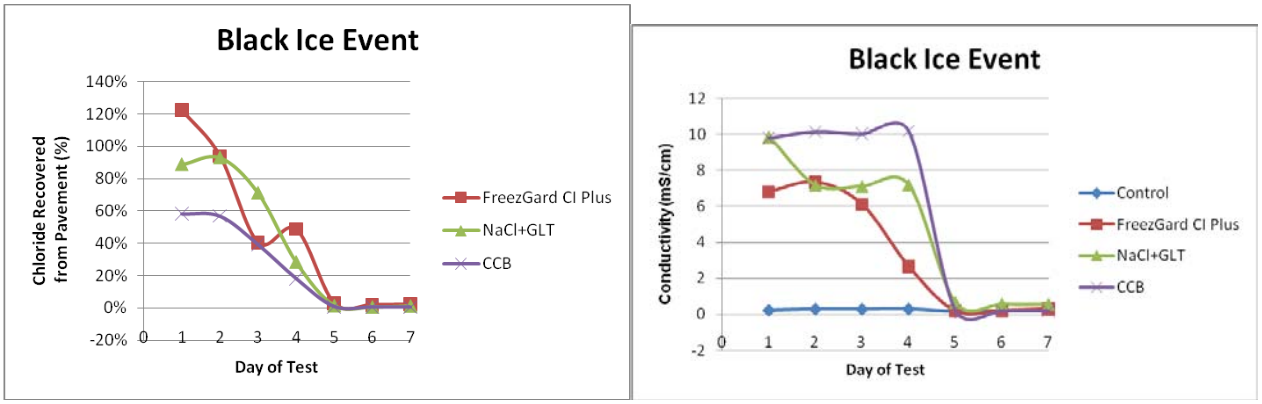
3.2.2. Longevity of Chlorides on the Pavement and Temporal Evolution of Solution Conductivity

This section presents the temporal evolution of chloride concentration and electrical conductivity of deicer residual solutions collected from the asphalt pavement surface, during the three winter storms.

For the black ice event, the target deicer application rate was 30 gallons/lane-mile, whereas the actual application rate for the three deicers was within 33±5 gallons/lane-mile based on the deicer solutions collected by the petri-dishes. As shown in Figure 49(a), during the first four days of the black ice event, the percent of chloride recovered from the pavement generally decreased over time for all three deicers (averaged between 30% and 90%). For the black ice event, the FreezGard and CCB deicer residuals generally showed the highest and lowest percent of chloride recovery respectively, while the NaCl+GLT deicer fell in between. The percent of chloride recovered from the pavement by day 4 was approximately 30%, 20%, and 50% for NaCl+GLT, CCB, and FreezGard respectively. Starting on day 5, the chloride recovery for all three deicers significantly dropped, attributable to the rain precipitation on day 3 and the snow precipitation on day 3 (trace amount), day 4 (>1/2″), and day 5 (1/2″), as shown in Table 8.

From the field storage study, we obtained the electrical conductivity data for the concentrated deicers, which were similar to the deicers used for the FOTs. The NaCl (14.8%) + GLT (4.1%) deicer had the highest electrical conductivity (~189.5 mS/cm), followed by the CCB (37.0% with 10.3% inhibitor, 130.6 mS/cm) and then the FreezGard (35.6% with 1.7% inhibitor, 99.4 mS/cm). These reported inhibitor concentrations slightly deviated from those initial concentrations reported in Table 1, since they were averaged from measurements taken over the 14 months of field monitoring. Note that the drinking water typically has an electrical conductivity of 0.05 to 0.5 mS/cm. As shown in Figure 49(b), the samples collected from the control test lanes (with no deicer applied) had very low electrical conductivity (0.2 mS/cm or lower), for all seven days of the black ice event, indirectly confirming the absence of any salt contamination.

During the first four days of the black ice event, the conductivity of deicer residuals recovered from the pavement mostly ranged between 2.5 and 10.0 mS/cm for all three deicers. Relative to the applied deicers, CCB, FreezGard, and NaCl+GLT residuals all showed more than one order of magnitude decrease in the solution conductivity on day one. Such decreases in the solution conductivity were partly attributable to the 1 L of de-ionized water used for sample collection and the loss of salt to the pavement. The conductivity of both FreezGard and NaCl+GLT residuals further decreased in the first four days. Starting on day 5, the solution conductivity for all three deicers dropped sharply, which corresponded well with the sharp drop in the percent of chlorides recovered shown in Figure 49(a).



(a) (b)

FIGURE 49 Temporal evolution of (a) chloride recovery efficiency and (b) electrical conductivity of samples collected from the asphalt pavement during the black ice event.

For the man-made snow event, the target deicer application rate was 60 gallons/lane-mile[14], whereas the actual application rate for the three deicers was within 53±4 gallons/lane-mile based on the deicer solutions collected by the petri-dishes. As shown in Figure 50(a), the FreezGard deicer residuals showed a 62% chloride recovery on day one and then dropped significantly down to less than 8% for the remaining six days of the man-made snow event. For the man-made snow event, the NaCl+GLT and FreezGard deicer residuals consistently showed the highest and lowest percent of chloride recovery respectively, while the CCB deicer fell in between. The percent of chloride recovered from the pavement by day 7 was approximately 20%, 16%, and 8% for NaCl+GLT, CCB, and FreezGard respectively. For NaCl+GLT and CCB, the percent of chloride recovered from the pavement generally decreased over time over the seven-day sampling period except for day 3 and day 4, averaged between 20% and 100%. All deicers had unusually low chloride recovery on day 3, which could be derived from the trace amount of natural snow precipitation received prior to sample collection[15].

As shown in Figure 50(b), the samples collected from the control test lanes (with no deicer applied) had low electrical conductivity (0.6 mS/cm or lower), for all seven days of the man-made snow event, indirectly confirming the absence of any salt contamination. Relative to the applied deicers, CCB, FreezGard, and NaCl+GLT residuals all showed nearly two orders of magnitude decrease in the solution conductivity on day one. The FreezGard deicer residuals showed a 4.2 mS/cm conductivity on day one and then dropped significantly down to lower than 1.2 mS/cm for the remaining six days of the man-made snow event (except for day 3 for unknown reasons). For the man-made snow event, the conductivity of NaCl+GLT and CCB deicer residuals fluctuated between 1.1 and 4.2 mS/cm, and day 3 and day 4 samples exhibited some unusually low conductivity readings. Relative to the applied deicers, FreezGard, CCB, and NaCl+GLT

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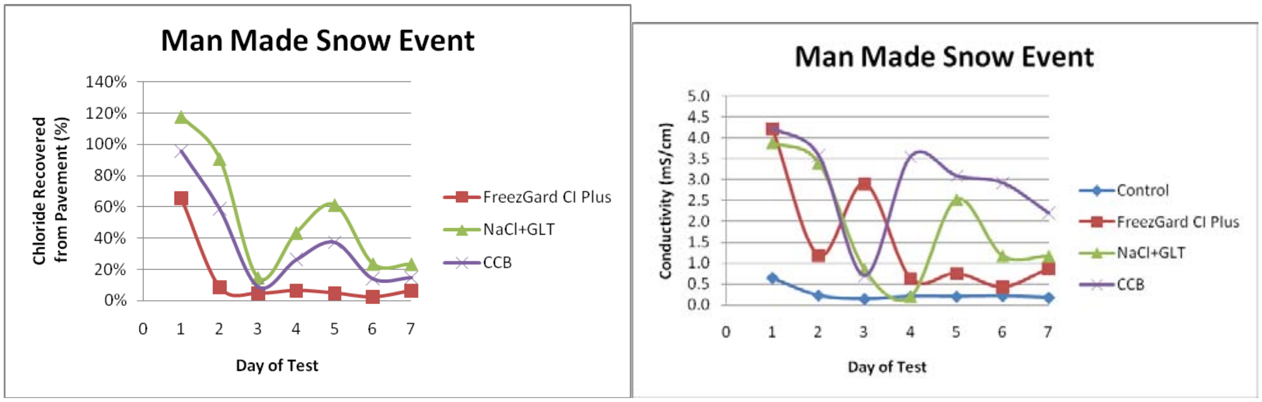
[14] This high application rate was for improved product recovery and subsequent analysis, and it is not representative of what should be applied.

[15] The deicer applied was working to melt the natural snow and hence was diluted.

residuals generally showed significant decrease in the solution conductivity over time. Such decreases in the solution conductivity were partly attributable to the de-ionized water or snowmelt used for sample collection and the loss of salt to the pavement.



(a) (b)

FIGURE 50 Temporal evolution of (a) chloride recovery efficiency chloride concentration and (b) electrical conductivity of samples collected from the asphalt pavement during the man-made snow event.

For the natural snow event, the target deicer application rate was 60 gallons/lane-mile[16], whereas the actual application rate for the three deicers was within 55±6 gallons/lane-mile based on the deicer solutions collected by the petri-dishes. As shown in Figure 51(a), the FreezGard deicer residuals showed a 4.1% chloride recovery on day one and then dropped significantly down to less than 0.5% for the remaining six days of the natural snow event. The natural snow event, the NaCl+GLT and FreezGard deicer residuals consistently showed the extremely low chloride recovery (no more than 0.7%) for all seven days during the natural snow event. The percent of chloride recovered from the pavement was less than 0.7% by day 6 and less than 0.5% by day 7, for all three deicers. The very low recovery of chlorides for all three deicers corresponded to the very low electrical conductivity of the collected deicer residuals from the pavement shown in Figure 51(b), which averaged at 0.08 mS/cm, similar to that of the samples collected from the control test lanes. Relative to the applied deicers, CCB, FreezGard, and NaCl+GLT residuals all showed about three orders of magnitude decrease in the solution conductivity on day one.

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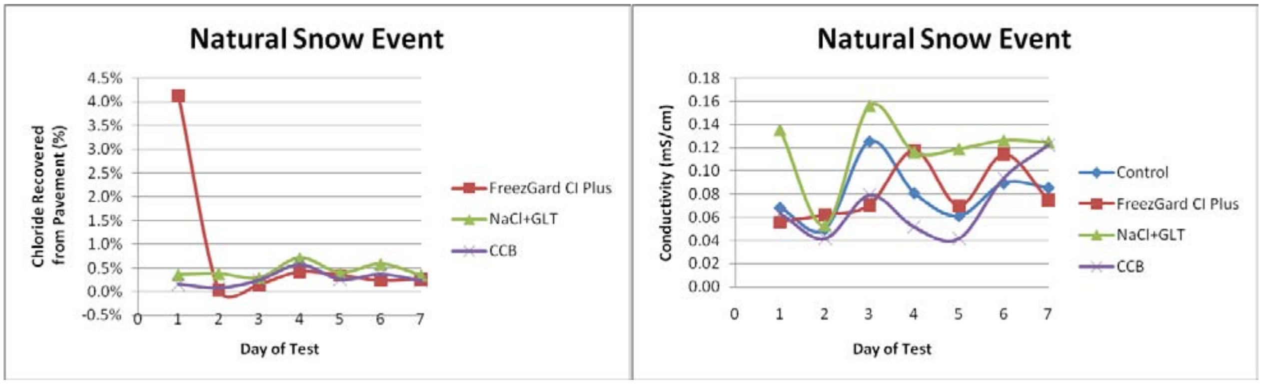
[16] This high application rate was for improved product recovery and subsequent analysis, and it is not representative of what should be applied.



(a) (b)

FIGURE 51 Temporal evolution of (a) chloride recovery efficiency chloride concentration and (b) electrical conductivity of samples collected from the asphalt pavement during the natural snow event.

A number of mechanisms may have accounted for the much lower chloride recovery from the pavement during the natural snow event, relative to the man-made snow event. First of all, the pavement temperature during the natural snow event (Figure 46) was consistently higher than that during the man-made snow event (Figure 42) or the black ice event (Figure 38). More importantly, the pavement surface temperature remained above the freezing point temperature of water (32°F), whereas the other two events had some hours during which the pavement surface was frozen. The warm and unfrozen pavement condition greatly accelerated and facilitated the migration of deicer solutions down to the pavement microstructure (see Figure 46).

FIGURE 52 Photo showing the upward migration of deicer up to 2 inches of snow cover.

Secondly, the sampling boxes for the natural snow event received more precipitation, which included 3.5-4″ of natural snow in the first 24 hours and about 0.75″ of blowing snow on day 2. For the man-made snow event, however, the sampling boxes only received 1″ of artificial snow and a total of 0.26″ of natural snow during day 3 and day 4. Thirdly, we leveled off the sampling boxes down to ½ inch before sample collection, which particularly in the natural snow event, prevented significant amounts of deicers from being collected. As shown in Figure 52, the deicer seemed to have migrated up to 2 inches of snow cover, whereas only the ½ inch of snow above the pavement surface was collected for analysis. Fourthly, the day-one sampling for the natural snow event occurred 20.3 hours after deicer application (relative to 15.3 hours and 1.7 hours for the man-made snow event and the black ice event respectively), which allowed more time for the applied deicers to migrate down to the pavement microstructure.

Figure 53 shows box plots of chloride recovery (in percentage) for the FreezGard, NaCl+GLT, and CCB test lanes for the three storm events: Black Ice (BI), Man Made snow event (MM), and Natural Snow event (NS). Each box plot was established using the chloride concentration of deicer residuals collected over the seven-day sampling period, for the given deicer and the given storm event. The results indicate that there was greater variability in the percent of chloride recovered during the black ice event for all three deicers and during the man-made snow event for NaCl+GLT and CCB.

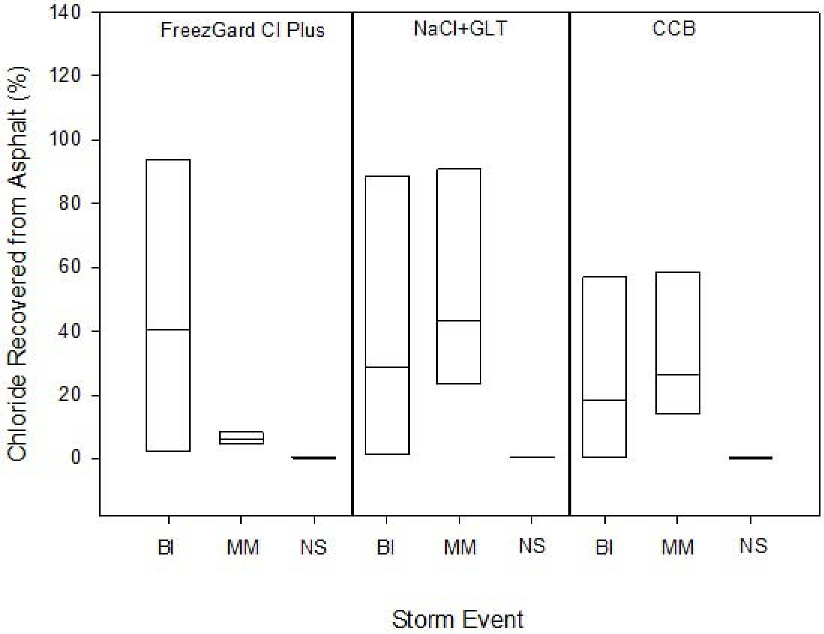
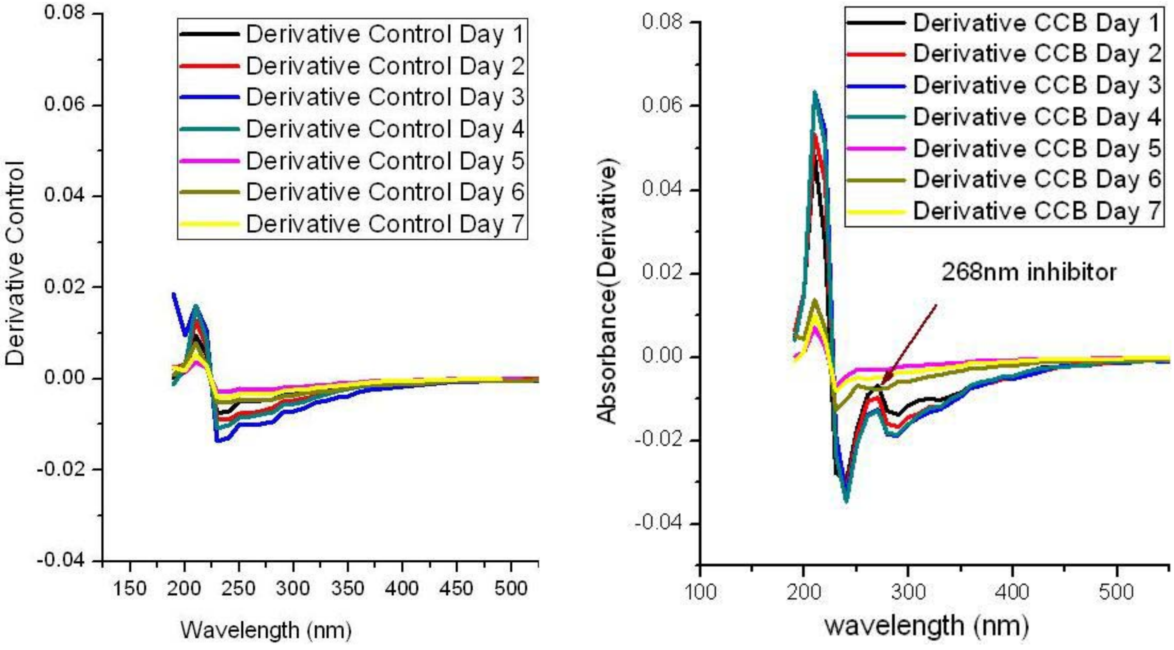


FIGURE 53 Box plot of chloride recovery efficiency on the asphalt pavement over the 7 days of sampling for each storm event.

3.2.3. Longevity of Corrosion Inhibitors on the Pavement and Temporal Evolution of Solution pH

This section presents the temporal evolution of inhibitor concentration and pH of deicer residual solutions collected from the asphalt pavement surface, during the three winter storms. Figure 54, Figure 55, and Figure 56 present the first-order derivative UV-vis spectra of both control and CCB samples collected over the 7 days after deicer application for the black ice event, for the man-made snow event, and for the natural snow event, respectively.

For the black ice event, Figure 54(a) indicates that samples collected from the control lane did not show any significant peak near 268 nm, which was the characteristic peak attributable to the corrosion inhibitor in the CCB deicer. Figure 54(b) shows that there was a significant peak near 268 nm for the deicer residuals collected from the asphalt pavement, which could not longer be detected for the later samples. This sudden drop in the inhibitor concentration starting on day 5 corresponded well with the sudden drops observed in both the chloride recovery efficiency and the electrical conductivity of samples collected from the asphalt pavement (shown in Figure 49).

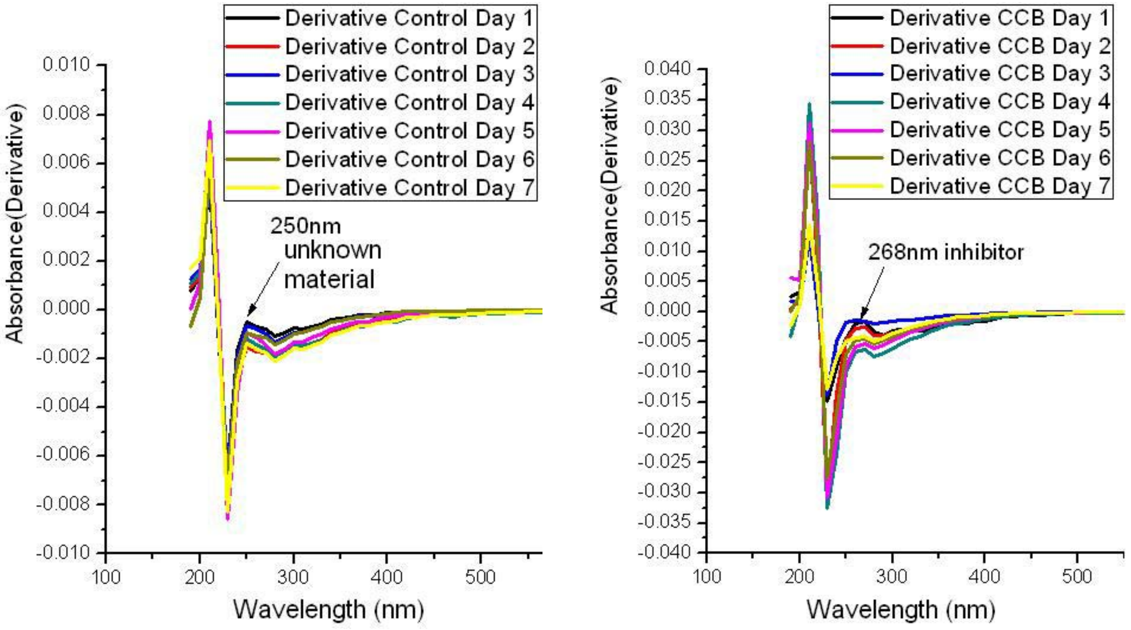


(a) (b)

FIGURE 54 First-order derivative UV-vis spectra of samples collected over the 7 days after deicer application for the black ice event: (a) from the control lane (with no deicer applied); (b) from the CCB lane.

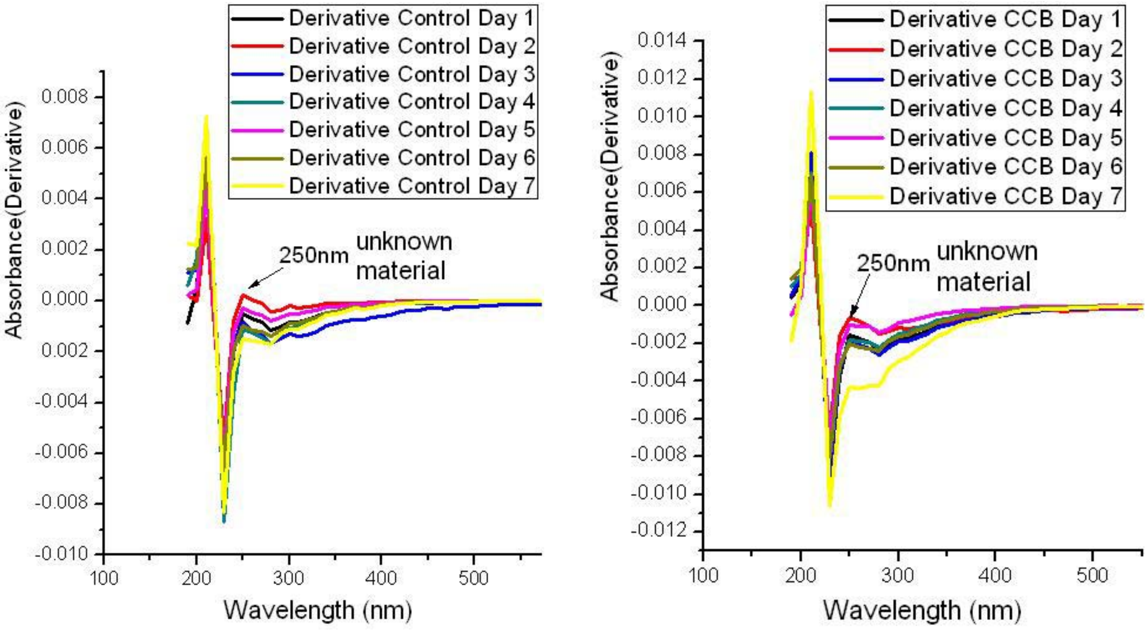
For the man-made snow event, Figure 55(a) indicates that samples collected from the control lane showed significant peak near 250 nm, which was not the characteristic peak of the corrosion inhibitor but attributable to unknown material (likely components of the asphalt mix). Figure 55(b) shows that there was a significant peak near 268 nm for the deicer residuals collected from the asphalt pavement, which remained detectable for the seven-day sampling period. The presence of corrosion inhibitor up to day 7 corresponded well with the data in both the chloride recovery efficiency and the electrical conductivity of samples collected from the asphalt pavement (shown in Figure 50).

For the natural snow event, Figure 56(a) indicates that samples collected from the control lane showed significant peak near 250 nm, which was not the characteristic peak of the corrosion inhibitor but attributable to unknown material (likely components of the asphalt mix). Figure 56(b) shows that there was a significant peak near 250 nm for the deicer residuals collected from the asphalt pavement, but no peak detectable near 268 nm. The absence of corrosion inhibitor throughout the seven-day sampling period corresponded well with the data in both the chloride recovery efficiency and the electrical conductivity of samples collected from the asphalt pavement (shown in Figure 51).



(a) (b)

FIGURE 55 First-order derivative UV-vis spectra of samples collected over the 7 days after deicer application for the man-made snow event: (a) from the control lane (with no deicer applied); (b) from the CCB lane.



(a) (b)

FIGURE 56 First-order derivative UV-vis spectra of samples collected over the 7 days after deicer application for the natural snow event: (a) from the control lane (with no deicer applied); (b) from the CCB lane.

From the field storage study, we obtained the pH data for the concentrated deicers, which were similar to the deicers used for the FOTs. The NaCl (14.8%) + GLT (4.1%) deicer had the highest pH (~7.6), followed by the FreezGard (35.6% with 1.7% inhibitor, pH 6.3) and then the CCB (37.0% with 10.3% inhibitor, pH 5.0). Note that drinking water typically has a pH nearly neutral, i.e., 7.0. As shown in Figure 57, the samples collected from the control test lanes (with no deicer applied) had pH values averaged around 7.0 and the pH readings fluctuated as a function of storm type and sampling time, indirectly confirming the presence of contaminants from the asphalt pavement. As discussed earlier, the electrical conductivity of the control samples was consistently low (see Figures 49b, 50b, and 51b), suggesting that the contaminants contained little to no salt.

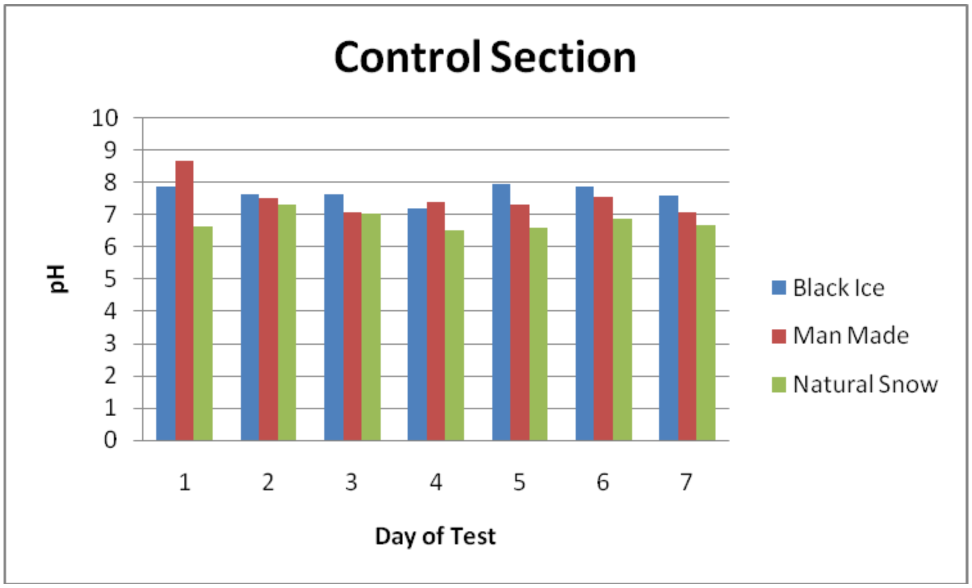


FIGURE 57 pH of samples from the control test lane for each storm

Figure 58 illustrates the change of inhibitor concentration and relative pH of samples collected from the FreezGard deicer test lanes over the sampling period. As shown in Figure 58(a), the corrosion inhibitor concentration in the natural snow event FreezGard residuals fluctuated between 0.5% and 1.2% during the seven-day sampling period (but not detected in day-one sample[17]). This translates to inhibitor recovery efficiencies between 42% and 100% in light of the 1.2% inhibitor concentration in the applied FreezGard deicer. Up to 83% of the FreezGard inhibitor was recovered from the pavement seven days after the deicer application. Such unusually high inhibitor recovery efficiencies for the natural snow event present a significant contrast to the extremely low chloride recovery (no more than 0.7%) shown in Figure 51. The FreezGard inhibitor signals for the black ice event and man-made event were not detectable for unknown reasons (e.g., possible contamination by asphalt components). The samples collected

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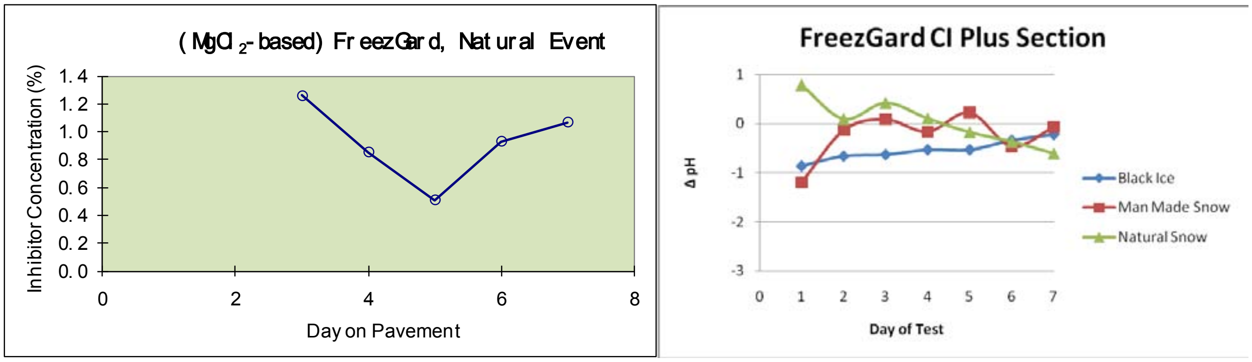
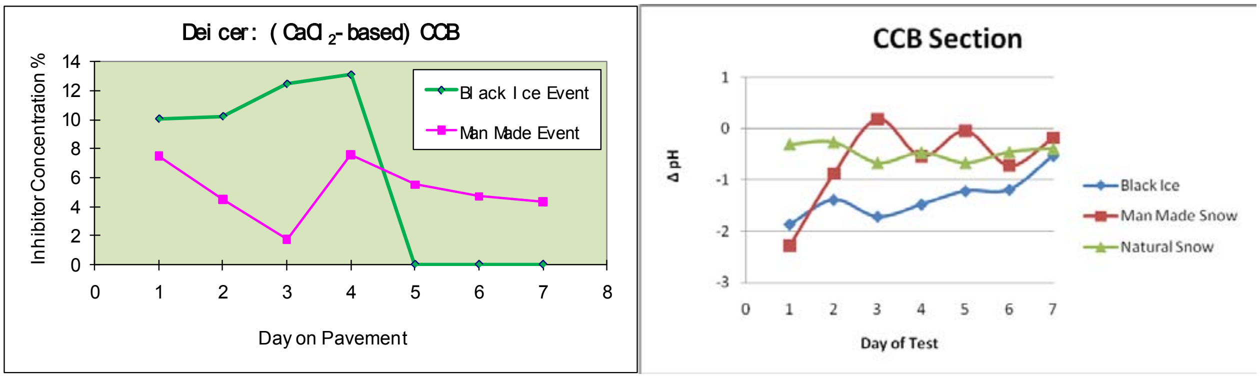
[17] One could assume that the inhibitor was present in day-one sample, even though it was not detected for unknown reasons (e.g., possible contamination by asphalt components). The data in Figure 58(a) shows that the inhibitor concentration decreased in the first five days (likely a result of dilution by snow precipitation) and then rebounded (likely a result of pavement drying-out).

from the FreezGard test lanes had pH values ranging between 6.0 and 7.4. As shown in Figure 58(b), the pH of FreezGard samples (relative to the control samples) generally increased over time during the black ice event as well as during the man-made snow event (particularly in the first two days) but decreased over time during the natural snow event. Note that the applied FreezGard deicer had a pH of 6.3.



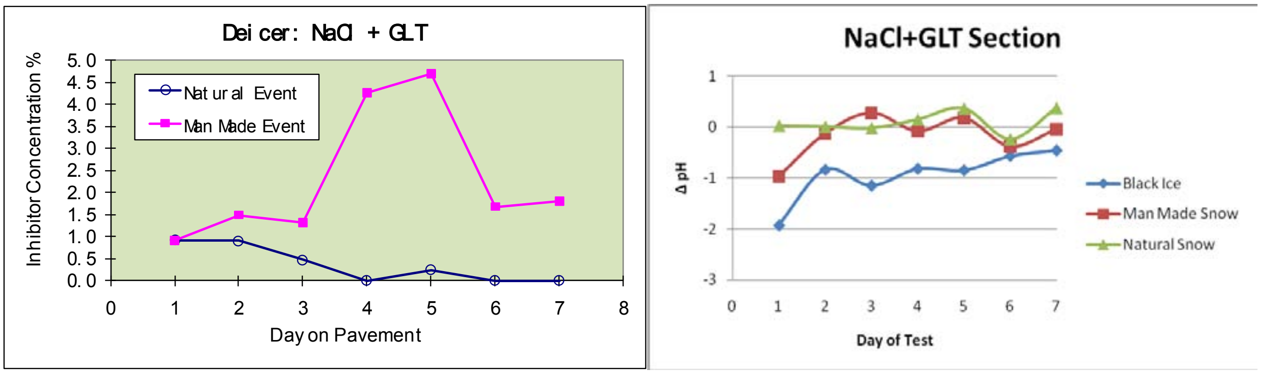
(a) (b)

FIGURE 58 Temporal evolution of (a) inhibitor concentration and (b) relative pH of samples collected from the FreezGard deicer test lanes. Note that the FreezGard inhibitor signals for the black ice event and man-made event were not detectable for unknown reasons.



(a) (b)

FIGURE 59 Temporal evolution of (a) inhibitor concentration and (b) pH of samples collected from the CCB deicer test lanes. Note that the CCB inhibitor signals for the natural snow event were not detectable for unknown reasons.



(a) (b)

FIGURE 60 Temporal evolution of (a) inhibitor concentration and (b) pH of samples collected from the NaCl+GLT deicer test lanes. Note that the GLT inhibitor signals for the black ice event were not detectable for unknown reasons.

Figure 59 illustrates the change of inhibitor concentration and pH of samples collected from the CCB deicer test lanes over the sampling period. As shown in Figure 59(a), the corrosion inhibitor concentration in the CCB residuals fluctuated between 10% and 13% during the first four days of the black ice event. This translates to inhibitor recovery efficiencies between 62% and 80% in light of the 16.2% inhibitor concentration in the applied CCB deicer. Up to 80% of the CCB inhibitor was recovered from the pavement four days after the deicer application. The sudden drop in the inhibitor concentration starting on day 5 corresponded well with the sudden drops observed in both the chloride recovery efficiency and the electrical conductivity of samples collected from the asphalt pavement (shown in Figure 49). For the man-made snow event, the inhibitor concentration in the CCB residuals fluctuated between 1.8% and 7.5% during the seven-day sampling period, equivalent to a recovery efficiency of 11% to 46%. Up to 26% of the CCB inhibitor was recovered from the pavement seven days after the deicer application. The CCB inhibitor signals for the black ice event were not detectable for unknown reasons (e.g., possible contamination by asphalt components). The samples collected from the CCB test lanes had pH values ranging between 5.7 and 7.2. As shown in Figure 59(b), the pH of CCB samples (relative to the control samples) generally increased over time during the black ice event as well as during the man-made snow event (particularly in the first three days) but fluctuated over time during the natural snow event. Note that the applied CCB deicer had a pH of 5.0.

Figure 60 illustrates the change of inhibitor concentration and pH of samples collected from the NaCl+GLT deicer test lanes over the sampling period. As shown in Figure 60(a), the corrosion inhibitor concentration in the NaCl+GLT residuals fluctuated between 0.8% and 4.7% during the seven days of the man-made snow event. This translates to inhibitor recovery efficiencies between 17% and 100% in light of the 4.7% inhibitor concentration in the applied NaCl+GLT deicer. Up to 38% of the GLT inhibitor was recovered from the pavement seven days after the deicer application. For the natural snow event, the inhibitor concentration in the NaCl+GLT residuals gradually decreased over time, from 0.9% (equivalent to 19% recovery) to below detection limit. Up to 21% and 4% of the GLT inhibitor was recovered from the pavement one day and five days after the deicer application respectively. The GLT inhibitor signals for the black ice event were not detectable for unknown reasons (e.g., possible contamination by asphalt components). The samples collected from the NaCl+GLT test lanes had pH values ranging between 5.9 and 7.5. As shown in Figure 60(b), the pH of NaCl+GLT samples (relative to the control samples) generally increased over time during the black ice event as well as during the man-made snow event (particularly in the first three days) but fluctuated over time during the natural snow event (particularly in the last four days). Note that the applied NaCl+GLT deicer had a pH of 7.6.

It should be cautioned that the inhibitor concentration data of pavement-collected samples had much more noise in them than the chloride concentration data, since the pavement contaminants tended to contribute to the UV absorption near the characteristic peak of the corrosion inhibitors. Such interference was illustrated in by the 250-nm peaks shown in Figure 55 and Figure 56. One lesson learned was that among the three investigated products the darker the deicer product (e.g., CCB), the more detectable the corrosion inhibitor was. When the pavement-collected samples were too dilute, there was too much noise in the UV-vis data to allow reasonable detection or quantification of the corrosion inhibitor.

The statistical analysis of the pH data revealed that there was a significant difference between the pH of control samples and FreezGard samples ($p=0.03$) and NaCl+GLT samples ($p=0.04$) from the pavement collection during the man-made snow event. Additionally, for FreezGard there was a significant difference in the pH of pavement residuals between the man-made snow event and the natural snow event ($p=0.02$). Either the amount of liquid added to the test lanes in the form of artificial snow affected the pH of the collected samples, or more likely the exposure of pavement to various amounts and types of precipitation affected how much pavement contaminants got into the collected samples. FreezGard, and to a lesser extent NaCl+GLT, showed the greatest change in pH as snow/water quantities were increased.

3.2.4. Temporal Evolution of Solution Corrosivity on the Pavement

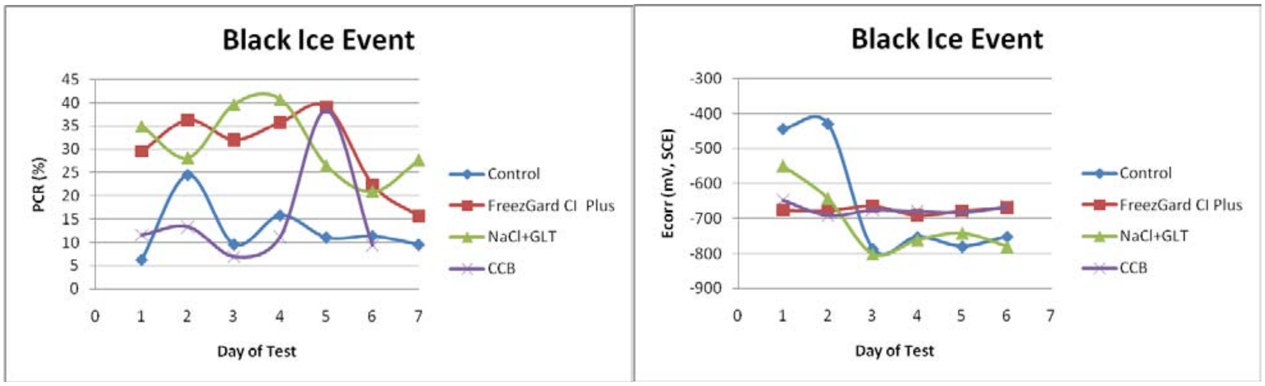
This section presents the temporal evolution of corrosivity of deicer residual solutions collected from the asphalt pavement surface, during the three winter storms. Note that unlike the field storage samples, the pavement-collected deicer samples were not diluted by 100:3 before the corrosion tests. The temporal evolution of *PCR* and E_{corr} should shed light on the relative presence of chlorides to inhibitors on the pavement, even though such data seems to evade interpretation. It should be cautioned that during the PNS/NACE test 25 percent of the weight loss data (21 out of 84 samples) failed to pass the quality control test of RSD<3% within a triplicate run. This phenomenon repeated during a second run of the same test, implying inherent issue in the test coupons. Due to the high variability between triplicate corrosion coupons, the *PCR* data are presented herein for reference purpose only. The E_{corr} data were also slightly compromised since some of the very dilute pavement-collected samples had too low electrical conductivity and had to add a supporting electrolyte to enable the electrochemical testing.

For the black ice event, Figure 61(a) indicates that samples collected from the control lane showed *PCR* values between 6 and 24, which confirms the presence of pavement contaminants being collected for the PNS/NACE test. The un-diluted samples collected from the deicer test lanes had *PCR* values ranging between 7 and 40, showing no clear relationship with storm type or deicer type. In general, the lower *PCR* values tended to occur at the end of the black ice event. The *PCR* of residuals recovered from the pavement by day 4 was approximately 40, 15 and 35 for NaCl+GLT, CCB, and FreezGard respectively. Note that the relative corrosivity of deicer solutions on the field pavement differed from that of them tested in the laboratory, where the *PCR* was 32, 21, and 16 for NaCl+GLT, CCB, and FreezGard respectively.

Figure 61(b) shows that the corrosion potential of steel in the control and NaCl+GLT samples decreased significantly from -450 mV (SCE) and -550 mV (SCE) respectively to nearly -800 mV (SCE) during the first three days of the black ice event and then remained around -770 mV (SCE) for the remaining four days. In contrast, the corrosion potential of steel in the CCB and FreezGard samples remained around -690 mV (SCE) through the seven-day sampling period.

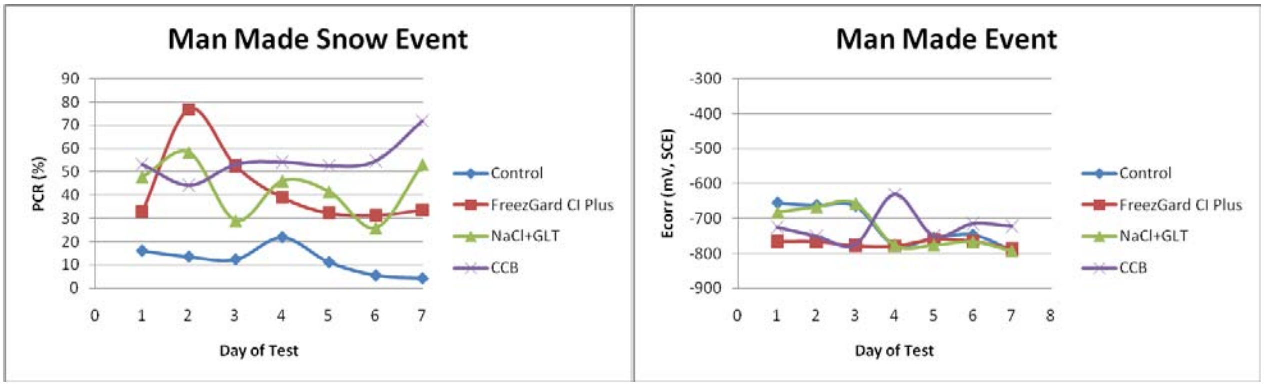
As shown in Figure 62(a), the un-diluted samples collected from the deicer test lanes during the man-made snow event featured the greatest number of non-passing *PCR* values: FreezGard (7/7), CCB (7/7), and NaCl+GLT (5/7). This could be partly attributed to the generally low inhibitor concentrations that remained on the pavement (shown in Figures 58 to 60), coupled with the relatively high chloride concentrations that remained on the pavement (shown in Figure 50). Figure 62(a) indicates that samples collected from the control lane showed *PCR* values between 4 and 21, which confirms the presence of pavement contaminants. The *PCR* values showed no clear relationship with storm type, deicer type or sampling time. The *PCR* of residuals recovered from the pavement by day 7 was approximately 51, 72 and 31 for NaCl+GLT, CCB, and FreezGard respectively.

Figure 62(b) shows that the corrosion potential of steel in the control and NaCl+GLT samples decreased significantly from -650 mV (SCE) and -625 mV (SCE) respectively to nearly -800 mV (SCE) during the first four days of the man-made snow event and then remained around -770 mV (SCE) for the remaining three days. In contrast, the corrosion potential of steel in the FreezGard samples remained around -780 mV (SCE) through the seven-day sampling period, whereas that in the CCB samples peaked on day 4 at -640 mV (SCE).



(a) (b)

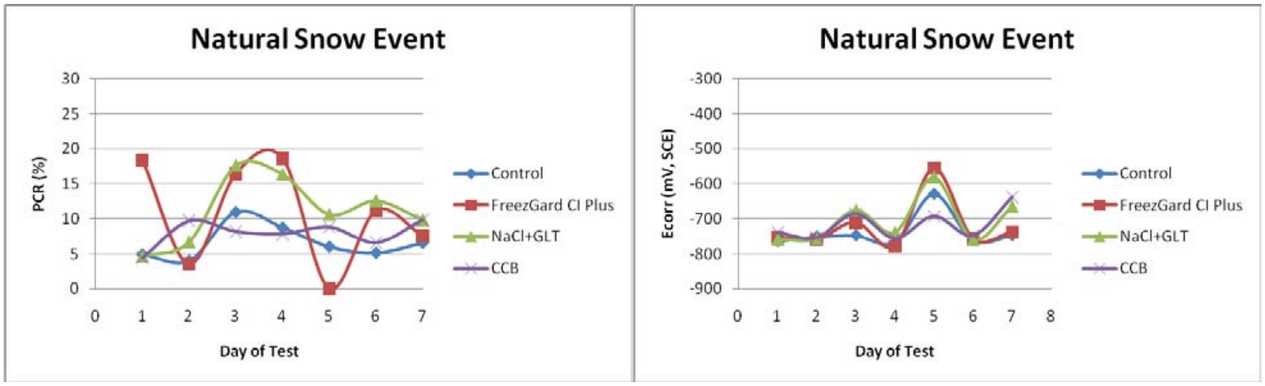
FIGURE 61 Temporal evolution of (a) *PCR* and (b) E_{corr} of samples collected from the asphalt pavement during the black ice event.



(a) (b)

FIGURE 62 Temporal evolution of (a) *PCR* and (b) E_{corr} of samples collected from the asphalt pavement during the man-made snow event.

As shown in Figure 63(a), the un-diluted samples collected from the deicer test lanes during the natural snow event featured the lowest *PCR* values, all of which remained well below the PNS-specified 30%. This could be attributed to the extremely low chloride concentrations that remained on the pavement (shown in Figure 51). Figure 63(a) indicates that samples collected from the control lane showed *PCR* values between 4 and 11, which confirms the presence of pavement contaminants. The *PCR* values showed no clear relationship with storm type or deicer type. In general, the higher *PCR* values tended to occur in the middle of the natural snow event. The *PCR* of residuals recovered from the pavement by day 1 was approximately 7, 10 and 18 for NaCl+GLT, CCB, and FreezGard respectively. Figure 63(b) shows that the corrosion potential of steel in all deicer samples first peaked on day 3 and then on day 5, for unknown reasons.



(a) (b)

FIGURE 63 Temporal evolution of (a) *PCR* and (b) E_{corr} of samples collected from the asphalt pavement during the natural snow event.

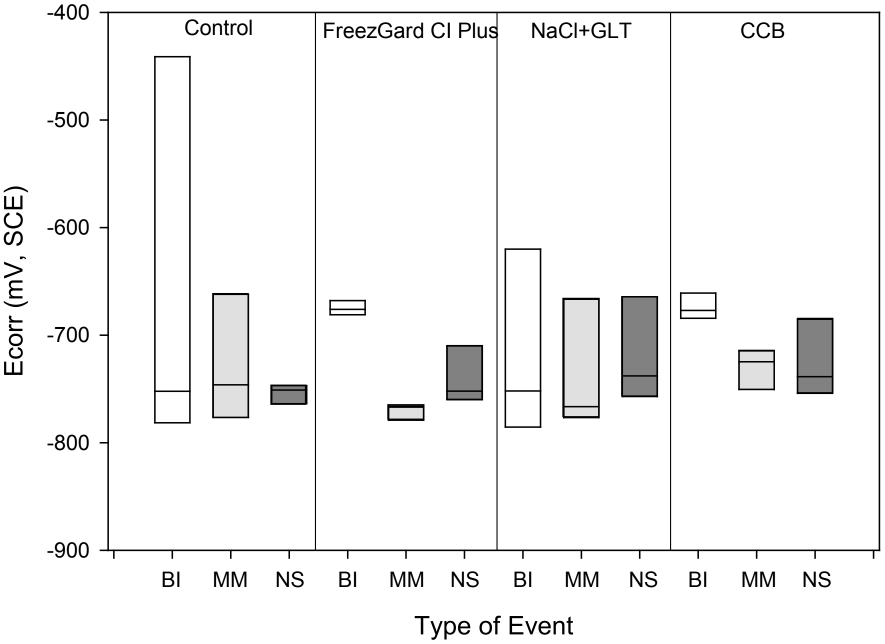


FIGURE 64 Box plot of E_{corr} of steel in samples recovered from the asphalt pavement over the 7 days of sampling for each storm event.

Out of the seven test days for the three events, NaCl+GLT had the greatest number of passing *PCR* values (14/21), followed by CCB (13/21) and FreezGard (11/21).

Note that E_{corr} is affected by the steel/electrolyte interface (e.g., oxygen availability, presence of inhibitor film relative to Cl^- ions). As discussed in Chapter 2, high E_{corr} values generally corresponded with low *PCR* values. The E_{corr} value higher than -562 mV_{SCE} generally corresponded to *PCR* values lower than 30. It should be noted, however, that an E_{corr} value lower than -562 mV_{SCE} does not necessarily indicate a *PCR* value higher than 30.

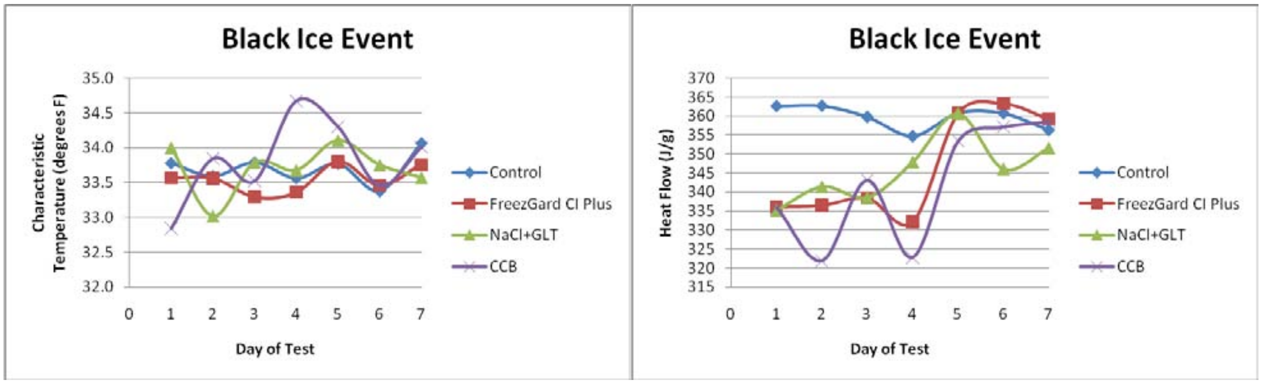
Figure 64 shows box plots of E_{corr} of steel in samples recovered from the control, FreezGard, NaCl+GLT, and CCB test lanes for the three storm events: Black Ice (BI), Man Made snow event (MM), and Natural Snow event (NS). The E_{corr} data of steel in control samples suggest that the natural snow event and the black ice event collected the least and the most amount of contaminants from pavement respectively, while the man-made snow event fell in between. The E_{corr} data indicate that the NaCl+GLT performed consistently across the three storm events. The natural snow event had the less variability in the E_{corr} across the three deicers, followed by the man-made snow event, and then the black ice event.

3.2.5. Temporal Evolution of Deicer Performance on the Pavement

This section presents the temporal evolution of the performance of deicer residual solutions collected from the asphalt pavement surface, during the three winter storms. Note that unlike the field storage samples, the pavement-collected deicer samples were not diluted by 3:1 before the DSC measurements.

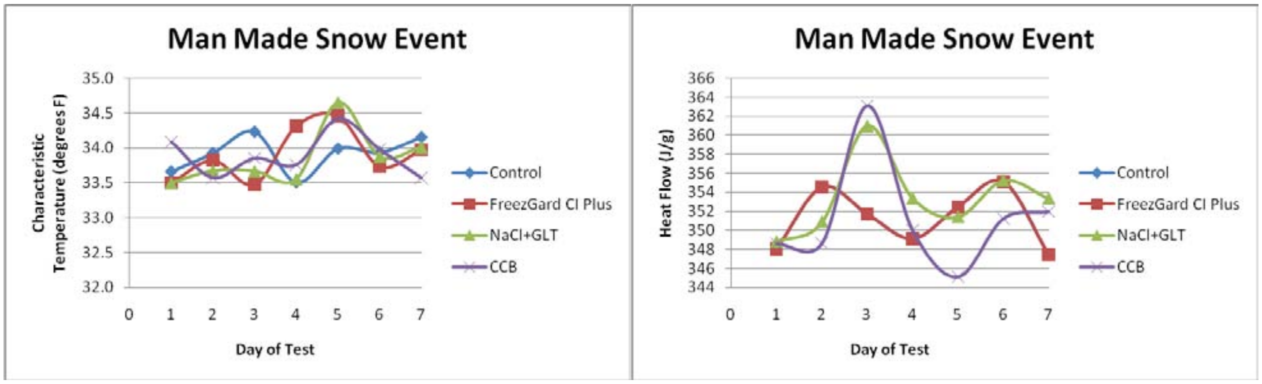
For the black ice event, Figure 65 indicates that samples collected from the control lane showed an average characteristic temperature (T_c) of 33.6°F and heat flow (H) of 360 J/g. These are similar to the T_c and H of de-ionized water, measured at 34.45°F and 345.1 J/g respectively, following the established DSC method. According to the statistical analysis, there was a significant difference between the H values for control samples and those of FreezGard ($p=0.002$), NaCl+GLT ($p=0.02$), and CCB ($p=0.001$). In general, the un-diluted samples collected from the deicer test lanes during the first three or four days had slightly lower T_c and H values, corresponding to the presence of deicer residuals as indicated by the chloride data shown in Figure 49. All the T_c and H values, however, remained above 32.8°F and 322 J/g respectively, suggesting very limited benefits of such residuals on suppressing the freezing point temperature and on ice melting. Note that strong deicers are generally expected to feature low T_c and low H values.

For both snow events, Figure 66 and Figure 67 indicate that samples collected from the control lane showed an average T_c of more than 33.6°F and H of more than 350 J/g. These are similar to the T_c and H of de-ionized water, measured at 34.45°F and 345.1 J/g respectively, following the established DSC method. In general, the un-diluted samples collected from the deicer test lanes featured similar T_c and H values to those from the control lanes and exhibited no clear relationship with storm type, deicer type or sampling time. One exception was that the T_c of FreezGard samples from the man-made snow event was significantly higher than the T_c of those from the natural snow event ($p=0.02$), for unknown reasons.



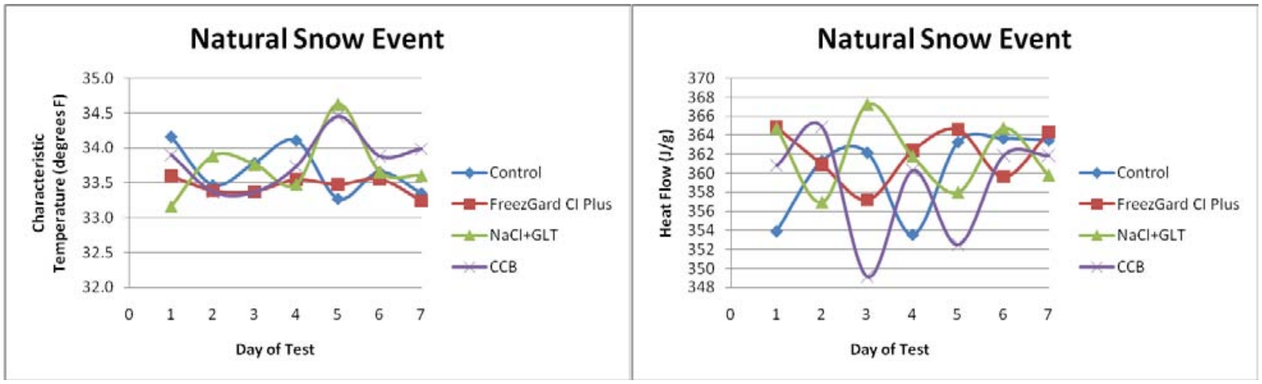
(a) (b)

FIGURE 65 Temporal evolution of (a) T_c and (b) H of samples collected from the asphalt pavement during the black ice event.



(a) (b)

FIGURE 66 Temporal evolution of (a) T_c and (b) H of samples collected from the asphalt pavement during the man-made snow event.



(a) (b)

FIGURE 67 Temporal evolution of (a) T_c and (b) H of samples collected from the asphalt pavement during the natural snow event.

In general, the heat flow (H) appeared to be most sensitive to changes between products and storms, more so than the characteristic temperature (T_c).

It should be noted that for the NaCl+GLT deicer, the as-applied product featured the T_c, ΔH, and predicted $IMC_{30^\circ F,\,60min}$ of 21.7ºF, 200.7 J/g, and 3.63 mL/mL (snowmelt/sample) respectively. Yet most of its pavement-collected residuals featured T_c values between 33.0 and 34.7 ºF and ΔH values between -1 and -22 J/g, which were unable to be used to predict meaningful $IMC_{30^\circ F,\,60min}$ values. The only exceptions are the pavement residuals collected from the first three days of the black ice event, which featured T_c values (33.6, 33.0 and 33.8 ºF respectively) and positive ΔH values (10.3, 3.6, and 6.4 J /g respectively), corresponding to predicted $IMC_{30^\circ F,\,60min}$ of 0.82, -0.06, and 0.42 mL/mL for day-1, day-2, and day-3 samples respectively.

Similarly, for the CCB deicer, the as-applied product featured the T_c, ΔH, and predicted $IMC_{30^\circ F,\,60min}$ of 13.7ºF, 190.7 J/g, and 3.77 mL/mL (snowmelt/sample) respectively. Yet most of its pavement-collected residuals featured T_c values between 32.8 and 34.7 ºF and ΔH values between -4 and -20 J/g, which were unable to be used to predict meaningful $IMC_{30^\circ F,\,60min}$ values. The only exceptions are the pavement residuals collected from the first four days of the black ice event, which featured T_c values (33.2, 33.8, 33.5 and 34.7 ºF respectively) and positive ΔH values (7.8, 23.2, 1.9, and 22.3 J/g respectively), corresponding to predicted $IMC_{30^\circ F,\,60min}$ of 0.58, 1.51, -0.63, and 1.46 mL/mL for day-1, day-2, day-3, and day-4 samples respectively.

For the FreezGard deicer, the as-applied product featured the T_c, ΔH, and predicted $IMC_{30^\circ F,\,60min}$ of 11.2ºF, 209.7 J/g, and 3.90 mL/mL (snowmelt/sample) respectively. Yet most of its pavement-collected residuals featured T_c values between 33.2 and 34.5 ºF and ΔH values between -3 and -20 J/g, which were unable to be used to predict meaningful $IMC_{30^\circ F,\,60min}$ values. The only exceptions are the pavement residuals collected from the first four days of the black ice event, which featured T_c values (33.4, 33.6, 33.3 and 33.4 ºF respectively) and positive ΔH values (18.6, 8.5, 6.6, and 12.8 J/g respectively), corresponding to predicted $IMC_{30^\circ F,\,60min}$ of 1.21, 0.66, 0.45, and 1.02 mL/mL for day-1, day-2, day-3, and day-4 samples respectively.

Note that the equation using the DSC data to predict the $IMC_{30^\circ F,\,60min}$ was derived on the basis of laboratory testing of concentrated chloride-based deicers, and may not be suitable for extrapolation to highly-diluted chloride brines or deicer samples containing too many contaminants.

3.3. Conclusions

This study investigated the longevity of corrosion inhibitors and the performance of corrosion-inhibited deicer products, by daily sampling of deicer residuals on the pavement for seven days after deicer application for a black ice event, a man-made snow event, and a natural snow event respectively. To simulate realistic climatic and logistical situations, the field operational tests were conducted at the TRANSEND facility at Lewistown, MT. Subsequently, the analytical methods established previously were used to analyze the properties of pavement-collected samples in the laboratory. The key findings are presented as follows.

1. In general, no significant difference in anti-icing performance was observed between the three liquid deicers, based on the periodical visual observations made during the two (man-made and natural snow) storm events. All three liquid deicers worked effectively for anti-icing applications under the investigated conditions, even though the field operational tests did not incorporate real or simulated traffic.

2. The samples collected from the control test lanes (with no deicer applied) seemed to contain contaminants that affect their UV-vis spectrum, pH, and corrosion data, yet their low chloride concentration and low conductivity suggested the absence of salt. The E_{corr} data of steel in control samples suggest that the natural snow event and the black ice event collected the least and the most amount of contaminants from pavement respectively, while the man-made snow event fell in between.

3. Out of the seven test days for the three events, NaCl+GLT had the greatest number of passing *PCR* values (14/21), followed by CCB (13/21) and FreezGard (11/21).

4. A number of mechanisms may have accounted for the much lower chloride recovery from the pavement during the natural snow event, relative to the man-made snow event, including warmer pavement temperature, more precipitation, loss of deicer to the leveling-off step, and more time waited before day-one sampling.

5. The longevity of the corrosion inhibitor and chlorides of liquid deicers after pavement application depended on the deicer type, storm type, and likely other field factors. In general, the fate and transport of the corrosion inhibitor differed from those of the chlorides, in which dilution by precipitation and likely wicking of the deicer into the pavement and the top snow layer contributed to the loss of inhibitor and chlorides. UV-degradation, if any, might have played a minor role.

6. The black ice event featured a total of 0.75″ of precipitation (mostly snow/ice) during day 4 to day 7. The percent of chloride recovered from the pavement by day 4 was approximately 30%, 20%, and 50% for NaCl+GLT, CCB, and FreezGard respectively. Starting on day 5, the chloride recovery for all three deicers significantly dropped, attributable to the rain precipitation on day 3 and the snow precipitation on day 3 (trace amount), day 4 (>1/2″), and day 5 (1/2″). Up to 80% of the CCB inhibitor was recovered from the pavement four days after the deicer application. The *PCR* of residuals recovered from the pavement by day 4 was approximately 40, 15 and 35 for NaCl+GLT, CCB, and FreezGard respectively. Note that the relative corrosivity of deicer solutions on the field pavement differed from that of them tested in the laboratory, where the *PCR* was 32, 21, and 16 for NaCl+GLT, CCB, and FreezGard respectively.

7. The man-made snow event featured 1″ of artificial snow and a total of 0.26″ of natural snow during day 3 and day 4. The percent of chloride recovered from the pavement by day 7 was approximately 20%, 16%, and 8% for NaCl+GLT, CCB, and FreezGard

respectively. Up to 38% and 26% of the inhibitors were recovered from the pavement seven days after the application of NaCl+GLT and CCB respectively. The *PCR* of residuals recovered from the pavement by day 7 was approximately 51, 72 and 31 for NaCl+GLT, CCB, and FreezGard respectively. The un-diluted samples collected from the deicer test lanes during the man-made snow event featured the greatest number of non-passing *PCR* values. This could be partly attributed to the generally low inhibitor concentrations that remained on the pavement, coupled with the relatively high chloride concentrations that remained on the pavement. The *PCR* values showed no clear relationship with storm type, deicer type or sampling time.

8. The natural snow event featured 3.5-4″ of natural snow in the first 24 hours and about 0.75″ of blowing snow on day 2. The percent of chloride recovered from the pavement was less than 0.7% by day 6 and less than 0.5% by day 7, for all three deicers. Up to 21% and 4% of the GLT inhibitor was recovered from the pavement one day and five days after the deicer application respectively. Up to 83% of the FreezGard inhibitor was recovered from the pavement seven days after the deicer application. Such unusually high inhibitor recovery efficiencies for the natural snow event present a significant contrast to the extremely low chloride recovery. The *PCR* of residuals recovered from the pavement by day 1 was approximately 7, 10 and 18 for NaCl+GLT, CCB, and FreezGard respectively. The un-diluted samples collected from the deicer test lanes during the natural snow event featured the lowest *PCR* values, all of which remained below the PNS-specified 30%. This could be attributed to the extremely low chloride concentrations that remained on the pavement. The *PCR* values showed no clear relationship with storm type or deicer type.

CHAPTER 4 CONCLUSIONS AND IMPLEMENTATION RECOMMENDATIONS

4.1 Conclusions

This study investigated the longevity of corrosion inhibitors and the performance of corrosion-inhibited deicer products under various storage conditions. Multiple established analytical methods were used to monitor the temporal evolution of the identified deicer properties under field storage, by randomly sampling the solid or liquid deicers periodically and analyzing them in the laboratory. The key findings are presented as follows.

1. Three liquid deicers ($MgCl_2$-based FreezGard, Calcium Chloride with Boost - CCB, and NaCl+GLT) and one solid deicer (NaCl-based IceSlicer) were selected for the field storage monitoring and the key properties tested include the chloride and inhibitor concentrations, corrosion parameters (E_{corr} and PCR), pH, electrical conductivity, and performance parameters (T_c and $IMC_{30°F}$). None of liquid deicers lost their quality over the 14 months of field storage, regardless of the storage condition (mixed or non-mixed). The NaCl-based solid deicer did not lose its quality over the 12 months of field storage, regardless of the storage condition (covered or uncovered). For all four deicers, the observed fluctuations in their properties seem to be non-seasonal but more likely attributable to the sampling and measuring variabilities. No significant degradation of corrosion inhibitor or loss of chlorides was seen during the months of field storage.

2. From an accelerated UV-degradation study conducted in the laboratory, the effect of exposure conditions (temperature, UV intensity, and time) on the resulting inhibitor concentration was generally insignificant for the NaCl+GLT and FreezGard deicers but significant for the CCB deicer. For the CCB deicer, the blocking of UV light by the storage tanks was likely beneficial in preventing its inhibitor degradation over the 14-month field storage monitoring period. For the IceSlicer solid deicer, the inhibitor concentrations were too low to make reliable conclusions about any possible inhibitor degradation.

3. The GLT inhibitor used alone or as additive to the NaCl-based deicer showed no benefit in suppressing effective temperature or in providing ice melting capacity. The inhibitor packages used in the CCB and FreezGard deicers slightly increased the effective temperature of their respective brine and showed little effect on the ice melting capacity (based on the *DSC* data). However, different from GLT, these inhibitor packages showed some limited ice melting capacity when used alone. In a word, while these inhibitors demonstrated their effectiveness in corrosion inhibition, they showed no side benefits in deicer performance.

4. During the field storage months the average chloride and inhibitor concentrations in the FreezGard deicer generally remained within 35.6±0.8% and 1.7±0.3% respectively. The inhibitor-to-chloride concentration ratio in the mixed and non-mixed FreezGard tanks was highly consistent over the months of field storage and

both averaged at 1:21. During the 14 months of field sampling and monitoring, the *PCR* of the FreezGard deicer remained below 30%, indicating PNS-acceptable corrosivity levels under the specific storage conditions investigated. The DSC-derived T_c and $IMC_{30°F,\ 60min}$ of the FreezGard deicer samples remained very consistent within 10.2±1.2 ºF and 3.7±1.1 mL/mL (snowmelt/deicer) respectively.

5. There was a significant difference in corrosion inhibitor concentration between mixed and non-mixed CCB tanks. The average inhibitor concentration in mixed and non-mixed CCB tanks generally remained within 9.3±1.7% and 11.2±3.3% respectively, with the mixed tanks showing lower readings and less data variability. During the 14 months of field sampling and monitoring, the *PCR* of the CCB deicer remained below 30%, indicating PNS-acceptable corrosivity levels under the specific storage conditions investigated. The DSC-derived T_c and $IMC_{30°F,\ 60min}$ of the CCB deicer samples remained very consistent within 11.2±1.2 ºF and 3.8±0.1 mL/mL (snowmelt/deicer) respectively, suggesting similar performance characteristics to FreezGard.

6. There was a significant difference in corrosion inhibitor concentration between mixed and non-mixed NaCl+GLT tanks. The average inhibitor concentration in mixed and non-mixed NaCl+GLT tanks generally remained within 3.8±0.2% and 4.3±0.4% respectively, again with the mixed tank showing lower readings and less data variability. The inhibitor-to-chloride concentration ratio in the mixed and non-mixed NaCl+GLT tanks was highly variable over the months of field storage and averaged at 1:4.0 and 1:3.4 respectively. <u>NaCl+GLT was the only liquid deicer to have non-passing PCR corrosion scores, suggesting potential shelf-life issues.</u> The DSC-derived T_c and $IMC_{30°F,\ 60min}$ of the NaCl+GLT deicer samples remained very consistent within 23.5±1.9 ºF and 3.8±0.2 mL/mL (snowmelt/deicer) respectively, suggesting higher T_c and similar $IMC_{30°F}$ relative to the $MgCl_2$- or $CaCl_2$-based liquid deicers.

7. The properties of stratified samples obtained from the top, middle and bottom of the mixed and non-mixed deicer tanks were also measured every six months or so during the field storage, which shed light on the effect of mixing on the homogeneity of each liquid deicer in the storage tanks.

8. With few exceptions, the IceSlicer samples from the covered pile generally featured slightly higher chloride concentrations and significantly lower inhibitor concentrations, relative to those from the uncovered pile. While the chloride concentration in both covered and uncovered piles remained relatively consistent over the 12 months of field storage, the inhibitor concentration in both piles tended to increase over time. The deicer corrosivity to steel (*PCR*) fluctuated between 60 and 100, regardless of the storage condition or the sieving of the deicer sample, indicating unacceptable corrosivity levels under the specific storage conditions investigated. The inhibitor-to-chloride concentration ratio in the cistern attached to the uncovered pile remained fairly consistent in the first eight months of monitoring. Yet the low inhibitor concentrations in the cistern during last four

months may be correlated with the high inhibitor concentrations in the uncovered pile, both suggesting that the leaching rate of chloride from the uncovered pile exceeded that of the corrosion inhibitor.

9. ANN has demonstrated great potential in finding meaningful, logical results from the noisy data associated with the metallic corrosion experiments. One ANN model was established to correlate the corrosion data from the electrochemical test method with those from the PNS/NACE test method (featuring a R-square of 0.84). Two additional ANN models were established to achieve better understanding of the complex correlation between the deicer composition (deicer type, chloride and inhibitor concentrations, pH, and electrical conductivity) and the deicer corrosivity (in *PCR*) and performance (in T_c) respectively. According to the ANN modeling, there are strong correlations inherent in the deicer samples (indicated by the R-square values of 0.91 and 0.98 for *PCR* and T_c respectively), whereas the trends differ as a function of the deicer type.

10. High E_{corr} values generally corresponded with low *PCR* values. The E_{corr} value higher than -562 mV (vs. SCE) generally corresponded to *PCR* values lower than 30. It should be noted, however, that an E_{corr} value lower than -562 mV_{SCE} does not necessarily indicate a *PCR* value higher than 30. As such, the electrochemical test could be used as a quality assurance tool for rapid assessment of deicer corrosivity to mild steel.

This study also investigated the longevity of corrosion inhibitors and the performance of corrosion-inhibited deicer products, by daily sampling of deicer residuals on the pavement for seven days after deicer application for a black ice event, a man-made snow event, and a natural snow event respectively. To simulate realistic climatic and logistical situations, the field operational tests were conducted at the TRANSEND facility at Lewistown, MT. Subsequently, the analytical methods established previously were used to analyze the properties of pavement-collected samples in the laboratory. The key findings are presented as follows.

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2. The samples collected from the control test lanes (with no deicer applied) seemed to contain contaminants that affect their UV-vis spectrum, pH, and corrosion data, yet their low chloride concentration and low conductivity suggested the absence of salt. The E_{corr} data of steel in control samples suggest that the natural snow event and the black ice event collected the least and the most amount of contaminants from pavement respectively, while the man-made snow event fell in between.

3. Out of the seven test days for the three events, NaCl+GLT had the greatest number of passing *PCR* values (14/21), followed by CCB (13/21) and FreezGard (11/21).

4. A number of mechanisms may have accounted for the much lower chloride recovery from the pavement during the natural snow event, relative to the man-made snow event, including warmer pavement temperature, more precipitation, loss of deicer to the leveling-off step, and more time waited before day-one sampling.

5. The longevity of the corrosion inhibitor and chlorides of liquid deicers after pavement application depended on the deicer type, storm type, and likely other field factors. In general, the fate and transport of the corrosion inhibitor differed from those of the chlorides, in which dilution by precipitation and likely wicking of the deicer into the pavement and the top snow layer contributed to the loss of inhibitor and chlorides. UV-degradation, if any, might have played a minor role.

6. The black ice event featured a total of 0.75″ of precipitation (mostly snow/ice) during day 4 to day 7. The percent of chloride recovered from the pavement by day 4 was approximately 30%, 20%, and 50% for NaCl+GLT, CCB, and FreezGard respectively. Starting on day 5, the chloride recovery for all three deicers significantly dropped, attributable to the rain precipitation on day 3 and the snow precipitation on day 3 (trace amount), day 4 (>1/2″), and day 5 (1/2″). Up to 80% of the CCB inhibitor was recovered from the pavement four days after the deicer application. The *PCR* of residuals recovered from the pavement by day 4 was approximately 40, 15 and 35 for NaCl+GLT, CCB, and FreezGard respectively. Note that the relative corrosivity of deicer solutions on the field pavement differed from that of them tested in the laboratory, where the *PCR* was 32, 21, and 16 for NaCl+GLT, CCB, and FreezGard respectively.

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8. The natural snow event featured 3.5-4″ of natural snow in the first 24 hours and about 0.75″ of blowing snow on day 2. The percent of chloride recovered from the pavement was less than 0.7% by day 6 and less than 0.5% by day 7, for all three deicers. Up to 21% and 4% of the GLT inhibitor was recovered from the pavement one day and five days after the deicer application respectively. Up to 83% of the FreezGard

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4.2 Implementation Recommendations

In light of the research findings from this project, we provide the following recommendations for implementation:

1. The three liquid deicers ($MgCl_2$-based FreezGard, $CaCl_2$-based CCB, and NaCl+GLT) investigated did not lose their quality over the 14 months of field storage, regardless of the storage condition (mixed or non-mixed). As such, it is unnecessary to implement any mixing for the liquid deicer tanks, other than immediately prior to the use of the liquid deicers to ensure uniform composition and minimize stratification.

2. It would be best to cover solid deicers during field storage to minimize leaching of active ingredients (especially corrosion inhibitor), but the solid deicer after 12 months storage under uncovered conditions can still be an effective deicer despite its reduced corrosion inhibition.

3. When determining whether the inclusion of corrosion inhibitor in deicers is economical, be aware that the investigated inhibitor packages did not show any side benefits in deicer performance and they served merely as corrosion inhibitors for the deicer products. The fate and transport of inhibitors differed from those of chlorides, once applied on the pavement.

4. Without dilution by rain or snow precipitation (e.g., the early days of black ice event), the percent of chloride recovered from the pavement by day 4 was approximately 30%, 20%, and 50% for NaCl+GLT, CCB, and FreezGard respectively. Up to 80% of the CCB inhibitor was recovered from the pavement four days after the deicer application. While such residuals could be washed away by precipitation, their presence on the pavement could potentially be measured and taken into consideration when re-applying chemicals for snow and ice control.

5. This project revealed that the relative corrosivity of deicer solutions on the field pavement differed from that of them tested in the laboratory. It merits further investigation to develop laboratory tests that can correlate better with the actual

field corrosion of metals caused by deicer exposure, taking the fate and transport of corrosion inhibitor (vs. chlorides), relative humidity, temperature cycles, etc. in the service environment into account.

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APPENDIX A: LABORATORY TESTING METHODS

The following standard operating procedures (SOPs) have been developed and followed by the Corrosion and Sustainable Infrastructure Laboratory (CSIL) at the Western Transportation Institute, Montana State University (WTI/MSU) to characterize the properties of various deicer samples investigated in the Pooled Fund Study led by the Pacific Northwest Snowfighters (PNS) Association.

In some cases, SOPs have been developed specifically within the project's scope as determined by the proposal; other SOPs are ASTM or NACE methods that have been modified by PNS for this project's scope and are references accordingly.

Please note the following definitions that may appear throughout the SOPs:

- *Storage collected* samples are those samples collected for the Inhibitor Longevity in Storage task of this research project and were collected from storage tanks on-site at the TRANSCEND facility in Lewistown, Montana. Following collection samples should be wrapped in aluminum foil and placed into cold storage in the laboratory. Samples are labeled according to deicer brand, mix strategy, and collection date.
- *Pavement* collected samples are those samples collected from each of the three storm events: Black Ice Event, Man-Made Snow Event, and Natural Snow Event, completed at the TRANSCEND facility in Lewistown, Montana. These samples were collected from pavement after a certain storm simulation occurred by adding deionized (DI) water to each respective plot, stored in 1 L sample bottles, wrapped in aluminum foil, and placed into cold storage.
- *Field-collected* sample is a general label that includes *Storage* and *Pavement* collected samples from the TRANSCEND facility, Lewistown, Montana. All *field-collected* samples are handled similarly throughout the entirety of this project.

This document consists of ten test methods aimed to characterize the pH, chloride concentration, inhibitor concentration, instantaneous corrosivity, 72-hour average corrosivity, thermal properties of the deicer solution, conductivity, total phosphorus, inhibitor degradation by ultraviolet radiation, and inductively coupled plasma mass spectrometry. The details of each test method are provided.

A1. Test Method for Determining pH of an Undiluted Deicer Solution

The purpose of this test is to determine the pH of an undiluted deicer solution. The test method follows ASTM D 1293. The field samples are removed from cold storage and allowed to reach room temperature. The pH meter, Accumet Basic AB15 (Fisher Scientific), is calibrated following manufacturer's instructions with pH buffer solutions 4, 7, and 10. The field sample is placed on a stir plate with a clean stir bar and mixed throughout the entire measurement process. The pH sensor is placed in the field sample and allowed to stabilize before accepting the pH reading (approximately two minutes). The pH meter is re-calibrated periodically throughout a series of sample measurements in order to reduce the possibility of meter drifting.

A2. Test Method for Determining pH of a Diluted Deicer Solution

The purpose of this test is to determine the pH of deicer solution diluted to a 4:1 with de-ionized (DI) water- one part liquid deicer to four parts DI water.

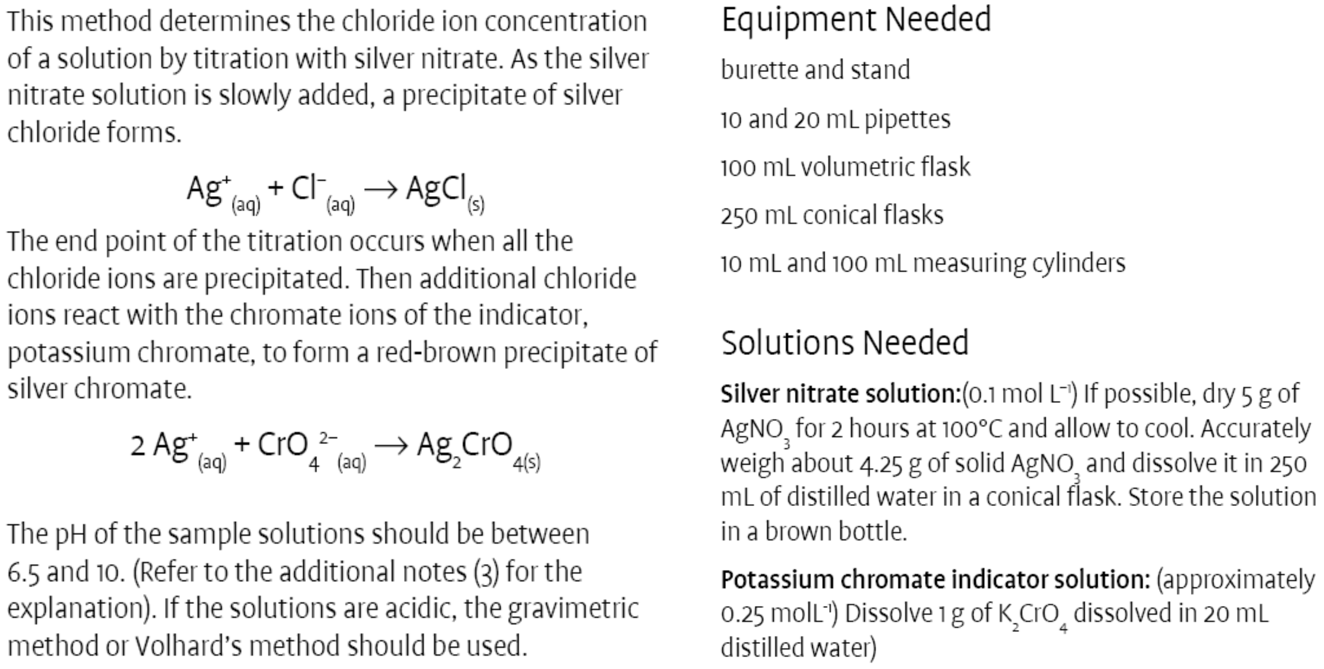
The test method follows ASTM D 1293 with the PNS-specified dilution method. The field samples are removed from cold storage and allowed to reach room temperature. The pH meter, Accumet Basic AB15 (Fisher Scientific), is calibrated following manufacturer's instructions with pH buffer solutions 4, 7, and 10. To dilute the sample, 10 milliliters (mL) of a thoroughly mixed field sample is measured and added to 40 mL of DI water in a 100 mL beaker. The diluted sample is placed on a stir plate with a clean stir bar and mixed. The pH sensor is placed in the continuously agitated field sample and allowed to stabilize before accepting the pH reading (approximately two minutes). The pH meter is rinsed with DI water and dabbed dry between sample readings and periodically re-calibrated throughout a series of sample measurements in order to reduce the possibility of meter drifting.

A3. Test Method for Rapidly Determining Chloride Concentration of a Deicer Solution

The purpose of this test is to establish methods to rapidly determine the chloride concentration of a deicer solution, which would enable the tracking of chlorides in field samples once applied onto the roadway or the monitoring of chloride concentration in deicers that are subjected to various storage conditions and mixing strategies.

Titration analysis, following the Mohr's method (detailed below and at: http://www.outreach.canterbury.ac.nz/chemistry/documents/chloride_mohr.pdf) was used to determine the initial chloride ion concentration of the liquid deicers received from the vendors. The liquid deicers were removed from cold storage, diluted by 100 times (1 part deicer solution to 99 parts DI water), and allowed to reach room temperature before titration analysis.

Mohr’s method to determine chloride ion concentration by titration:



This method determines the chloride ion concentration of a solution by titration with silver nitrate. As the silver nitrate solution is slowly added, a precipitate of silver chloride forms.

$$Ag^{+}_{(aq)} + Cl^{-}_{(aq)} \rightarrow AgCl_{(s)}$$

The end point of the titration occurs when all the chloride ions are precipitated. Then additional chloride ions react with the chromate ions of the indicator, potassium chromate, to form a red-brown precipitate of silver chromate.

$$2\ Ag^{+}_{(aq)} + CrO_{4\ (aq)}^{2-} \rightarrow Ag_2CrO_{4(s)}$$

The pH of the sample solutions should be between 6.5 and 10. (Refer to the additional notes (3) for the explanation). If the solutions are acidic, the gravimetric method or Volhard’s method should be used.

Equipment Needed

burette and stand

10 and 20 mL pipettes

100 mL volumetric flask

250 mL conical flasks

10 mL and 100 mL measuring cylinders

Solutions Needed

Silver nitrate solution:(0.1 mol L^{-1}) If possible, dry 5 g of $AgNO_3$ for 2 hours at 100°C and allow to cool. Accurately weigh about 4.25 g of solid $AgNO_3$ and dissolve it in 250 mL of distilled water in a conical flask. Store the solution in a brown bottle.

Potassium chromate indicator solution: (approximately 0.25 molL^{-1}) Dissolve 1 g of K_2CrO_4 dissolved in 20 mL distilled water)

Sample Preparation

If the diluted deicer solution contains traces of solid matter such as sand, it must be filtered before use. Otherwise they will end up weighed along with the silver chloride precipitate and interfere with the results.

Please note: GLT was titrated with 0.01 M $AgNO_3$, whereas FreezGard CI Plus and CCB were titrated with 0.1 M $AgNO_3$.

Titration

1. Further dilute the deicer solution by pipetting a 20 ml sample into a 100 ml volumetric flask and filling it up to the mark with DI water.
2. Pipette a 10 ml aliquot of diluted deicer solution into a conical flask and add about 50 ml DI water and 1 ml of chromate indicator.
3. Titrate the sample with 0.1 M silver nitrate solution (again please note that GLT was titrated with 0.01 M $AgNO_3$ instead). Although the AgCl that forms is a white precipitate, the chromate indicator initially gives the cloudy solution a faint lemon-yellow color (see Figure 1). The endpoint of the titration is identified as the first appearance of a red-brown color of silver chromate (Figure 1 & Figure 2).
4. Repeat the titration with further aliquots of diluted deicer solution until concordant results (agreeing within 0.1 ml) are obtained.

Figure 1 Before the addition of any silver nitrate the chromate indicator gives the clear solution a lemon-yellow colour.

Figure 2 Left flask: before the titration endpoint, addition of Ag^+ ions leads to formation of silver chloride precipitate, making the solution cloudy. The chromate indicator gives a faint lemon-yellow colour. Centre flask: at the endpoint, all the Cl^- ions have precipitated. The slightest excess of Ag^+ precipitates with the chromate indicator giving a slight red-brown colouration. Right flask: If addition of Ag^+ is continued past the endpoint, further silver chromate precipitate is formed and a stronger red-brown colour results. NB: The titration should be stopped when the first trace of red-brown colour is observed. Using an incompletely titrated reference flask for comparison is a helpful way to identify the first appearance of red-brown colouration.

Figure 1 Color change observed during titration.

Results Calculations

1. Determine the average volume of silver nitrate used from the concordant titres.
2. Calculate the moles of silver nitrate reacting.
3. Determine the moles of chloride ions reacting.
4. Calculate the concentration of chloride ions in the diluted deicer solution and then the original storage-collected deicer solution.

Additional Notes

1. Silver nitrate solution will stain clothes and skin. Any spills should be rinsed with water immediately.
2. Residues containing silver ions are usually saved for later recovery of silver metal. Check this with laboratory manager.
3. The Mohr titration should be carried out under conditions of pH 6.5 – 9. At higher pH silver ions may be removed by precipitation with hydroxide ions, and at low pH chromate ions may be removed by acid-base reaction to form hydrogen chromate ions or dichromate ions affecting the accuracy of the end point.
4. It is a good idea to first carry out a “rough” titration in order to become familiar with the color change at the end point.

For each deicer (GLT, CCB, and FreezGard CI Plus), once its chloride concentration is known, a less time-consuming alternative method is used to rapidly determine the chloride ion concentration in deicer solutions with unknown properties including field-collected samples.

Method

A custom-made chloride ion-selective plated sensor was used to quickly quantify the chloride concentration in deicer products and field samples. The commercial chloride sensor gives a reading in electrochemical potential (*E*), which is between a silver/silver chloride (Ag/AgCl) electrode in contact with the deicer solution and an imbedded reference electrode. The Ag/AgCl electrode functions as a redox electrode and the reaction is between the silver metal (Ag) and its salt — silver chloride (AgCl):

$$Ag^0(s) + Cl^- \rightarrow AgCl(s) + e^-$$

Step 1- Fabrication of the Chloride Sensor

The chloride sensors are plated by researchers at the Corrosion and Sustainable Infrastructure Laboratory (CSIL) using a silver wire (99.99% pure Ag) approximately 2 mm in diameter and 70 mm in length. A Princeton Applied Research Potentiostat/ Galvanostat Model 263A was used to apply the coating. Select a straight length of silver wire and uniformly clean with a fine grade emery paper. Rinse the wire with acetone followed by DI water. Prepare a 1 Molar (M) solution of KCl to include a few drops of 0.1 M HCl solution from a small bulb pipette; this is the "working fluid" for the coating process.

Measure the diameter of the silver wire using a set of Calipers and determine the length of the working portion on the wire to be coated to calculate the effective approximate surface area (SA). Example:

$$\text{For diameter, d} = 2.03 \text{ mm \& length, l} = 35\text{mm:}$$

$$SA = \pi \times d \times l$$

$$SA = 3.142 \cdot 2.03\text{mm} \cdot 35\text{mm} = 223.2391 \text{ mm}^2$$

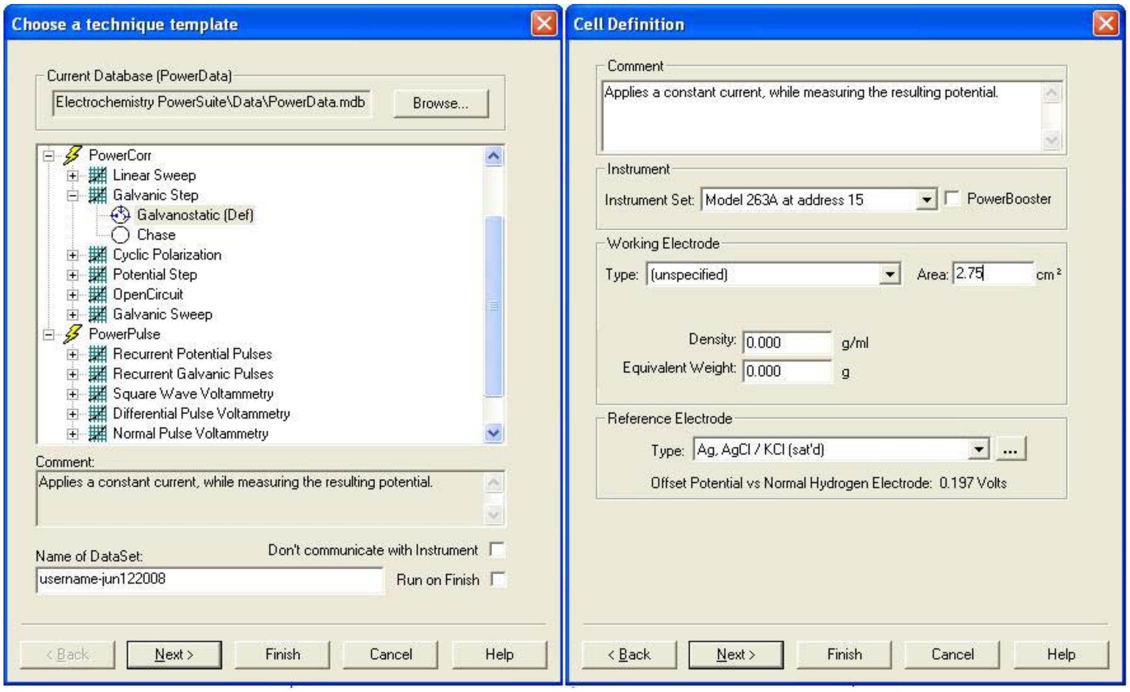
$$223.2391 \text{ mm}^2 \cdot \left(\frac{1 \text{ cm}^2}{100 \text{ mm}^2}\right) = 2.2324 \text{ cm}^2$$

Fix the portion of the wire calculated to be coated to the inside of a 250mL beaker. Fix the sacrificial silver wire to the opposite side of the beaker. Fill the beaker to the appropriate height with the working solution. Using a ring stand as support, attach the red and white lead clips from the potentiostat to the wire that will be coated and the green lead clip to the sacrificial wire. Connect the black ground clip to the base of the ring stand and power on the potentiostat.

On the computer hosting the 263A unit, open the PowerSuite® software to set up experiment. Select **Experiment** > **New**. Under **PowerCorr**, select **Galvanostatic Step** and **Galvanostatic (Def)** experiment type. A dialogue will appear requiring parameters for the experiment to be entered. On the first tab, enter in or select the following parameters under the **Cell Definition** tab; these parameters will not change throughout the four separate experiment runs (**Figure 3**):

- Instrument
    - *Instrument Set:* Original Model 263A at address xx

- Working Electrode
    - *Type:* (unspecified)
    - *Area:* Input the surface area calculated previously, SA, in units of cm^2
    - *Density:* 0.000 g/ml
    - *Equivalent Weight:* 0.000 g
- Reference Electrode
    - *Type:* Ag, AgCl / KCl (saturated)



Choose a technique template

Current Database (PowerData)

Electrochemistry PowerSuite\Data\PowerData.mdb

- PowerCorr
    - Linear Sweep
    - Galvanic Step
        - Galvanostatic (Def)
        - Chase
    - Cyclic Polarization
    - Potential Step
    - OpenCircuit
    - Galvanic Sweep
- PowerPulse
    - Recurrent Potential Pulses
    - Recurrent Galvanic Pulses
    - Square Wave Voltammetry
    - Differential Pulse Voltammetry
    - Normal Pulse Voltammetry

Comment: Applies a constant current, while measuring the resulting potential.

Name of DataSet: username-jun122008

Don't communicate with Instrument ☐

Run on Finish ☐

Cell Definition

Comment: Applies a constant current, while measuring the resulting potential.

Instrument

Instrument Set: Model 263A at address 15 ☐ PowerBooster

Working Electrode

Type: (unspecified) Area: 2.75 cm^2

Density: 0.000 g/ml

Equivalent Weight: 0.000 g

Reference Electrode

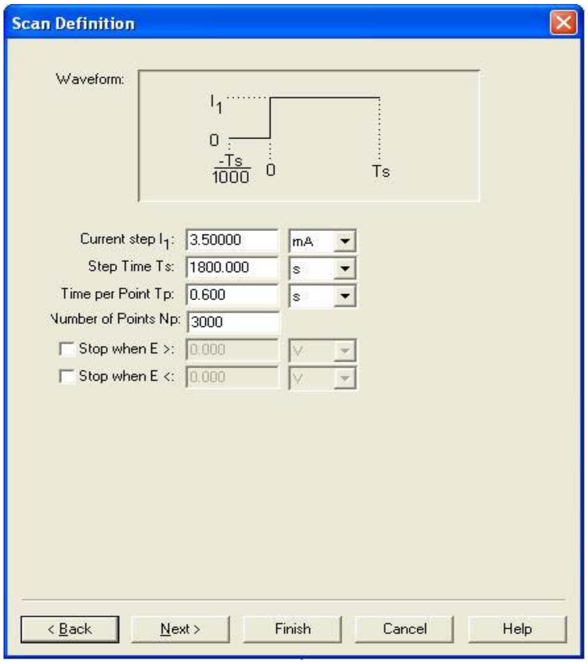
Type: Ag, AgCl / KCl (sat'd)

Offset Potential vs Normal Hydrogen Electrode: 0.197 Volts

Figure 2 Silver sire electrode plating set-up screen.

Select **NEXT** and continue entering in or selecting the following parameters under the **Scan Definition** tab (Figure 4):

- For Run 1
    - *Current step I_1:* $1 \cdot SA$ mA
    - *Step Time Ts:* 30.00 min (1800s)
    - *Time per Point Tp:* 1.2 s
    - *Number of Points Np:* This entry will be automatically calculated
- For Run 2
    - *Current step I_1:* $0.2 \cdot SA$ mA
    - *Step Time Ts:* 30.00 min (1800s)
- For Run 3
    - *Current step I_1:* $0.5 \cdot SA$ mA
    - *Step Time Ts:* 30.00 min (1800s)
- For Run 4
    - *Current step I_1:* $0.1 \cdot SA$ mA
    - *Step Time Ts:* 60.00 min (3600s)



Current step I_1: 3.50000 mA

Step Time Ts: 1800.000 s

Time per Point Tp: 0.600 s

Number of Points Np: 3000

☐ Stop when E >: 0.000 V

☐ Stop when E <: 0.000 V

Figure 3 Scan definition set-up screen.

The default values for all parameters on the next two tabs, **PreScan Definition** & **Expert Options**, are acceptable. Finally, select **OK** and the experiment plot will appear. To start the experiment, press the **Play** (▶) button and the experiment will begin. To verify that the coating process is operating normally, the potential (mV) of the system should drop to approximately -1.6 mV shortly after beginning the first run. The potential will remain fairly constant throughout each run with slight perturbation during the experiment. The final run should stabilize from -0.6 to -0.9 mV. The coated sensor should be stored in a 1 M KCl solution when not in use.

Step 2- Standard Curves and Sensor Calibration

Pair the newly coated chloride sensor with a saturated Calomel electrode (SCE), used as the reference electrode, and clean both off with DI water. Readings of open circuit potential (OCP) of the chloride sensor in each sample solution are taken with a multimeter. Clip the black cable from a multimeter to the SCE and the red wire to the coated chloride sensor. Submerge the chloride sensor and the SCE in each standard solution beginning with lowest concentration solution and finishing with the highest. Allow up to two minutes for the chloride sensor to stabilize in each solution before entering a reading in millivolts (mV). Enter the results into Microsoft Excel to construct a data chart and calibration curve (Figure 5). The charts X-axis will be log (chloride concentration); y-axis will be the sensor readings in mV. It should be a strong line fitting as y=alog(x)+b. Between readings the sensor and electrode should be rinsed at least three times with DI water followed by a rinse with the next standard NaCl solution to be measured.

For each type of chloride-based deicer ($MgCl_2$, $CaCl_2$ and NaCl), the research team will prepare standard solutions with known chloride concentration (using water as the solvent) and subject them to an Ag/AgCl electrode. The presence of the chloride will give a reading (*E*) proportional to the concentration. As such, a standard calibration curve can be established for each chloride. For any field samples with unknown chloride concentration, the electrode's response to the sample can be compared against the calibration curve to derive the chloride concentration. For example, Figure 5 shows a calibration curve for a chloride sensor prepared by the WTI CSIL researchers. This data provides the chloride sensor calibration curve established using the NaCl+GLT deicer, which shows a strong linear correlation between the natural logarithm of the chloride concentration in the deicer and the electrochemical potential reading of the chloride sensor placed in the deicer (in mV). The same correlation also held well for standard solutions made from reagent-grade NaCl (as indicated by the empty dots in the graph).

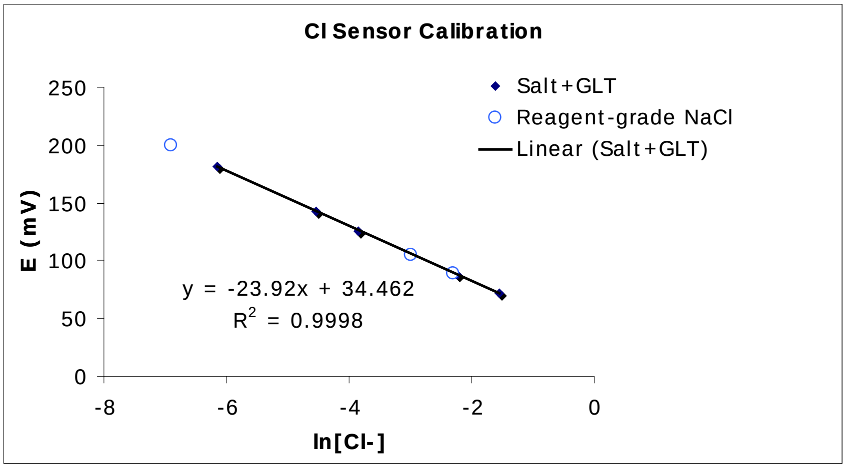


Figure 4 Calibration curve for chloride sensor in NaCl solutions.

Due to the logarithmic relationship between the Galvanostatic Coated Silver-wire and the SCE Reference Electrode, a new standard curve was required for each deicer on the day of testing. The standard curves were also re-run throughout the day of measurement to reduce risk of sensor drift. Standard solutions were made by diluting deicer brine mixed with deicer inhibitor at Vendor specifications. For a standard curve to be valid the R^2 value of 0.90 or greater yields a statistically acceptable standard curve. If R-square of the linear regression was lower than 0.9, the calibration process was repeated. If the problem continued, then the chloride sensor was re-fabricated. The resulting correlation is then used to relate the mV readings from the Sensor/Reference Electrode measurement system to dilution. Using the information from previous reagent-grade standard curves and chloride data as well as vendor supplied information the chloride concentration can then be calculated.

Step 3- Sample Preparation and Analysis

Remove the samples to be measured from cold storage and allow them to warm to room temperature; this usually requires setting out the night before measurement. Begin by ensuring that the glass beaker is clean and rinsing it with DI water. A sub-sample of the sample may not be poured into the beaker. Avoid contamination of this sub-sample as it will be returned to the original sample when measurement is completed. Place a clean and dry stir bar in the sub-sample and begin stirring at a moderate rate. Connect the ground lead of the multi-meter to the SCE Reference Electrode and place the electrode into a beaker filled with water and a paper towel for protection. Connect the active lead to the coated chloride sensor and power on the digital multi-meter set to read in mV. While the sub-sample is stirring, hold both the reference electrode and the coated chloride sensor in the solution so that they are both submerged to roughly the same depth. When the mV reading stabilizes, record the value. Remove the coated chloride sensor, rinse with DI water, dab dry with a Kim-Wipe®, and return sensor to the 1 M KCl solution. Remove the SCE reference electrode, rinse with DI water and return to beaker filled with DI water. Remove the stir bar from the sub-sample with a clean magnetic retriever. Pour the sub-sample back into the original sample.

Data Analysis

There are two methods for calculating chloride concentration from the mV results. The first involves using reagent grade salts to synthesize a standard curve that bounds the expected range of salt molarity in the storage-collected samples. This proved to be expensive and time consuming, so the second method was developed using vendor provided and mixed deicing products for the standard curve and tracking. The correlated dilution rates were then converted to molarity using results from the first method on the deicers used for the standard curve at full concentration. Regardless of the method, the molarity values obtained were then converted using a prescribed formula. The following discussion illustrates both the first and second methods in greater detail.

Molarity Method

The molarity method will be demonstrated using FreezGard CI Plus and $MgCl_2$ information and formulae.

Standard (M)	Sensor 2 (mV)
1	-23.2
2	-43.0
3	-60.2
4	-76.7
5	-81.0

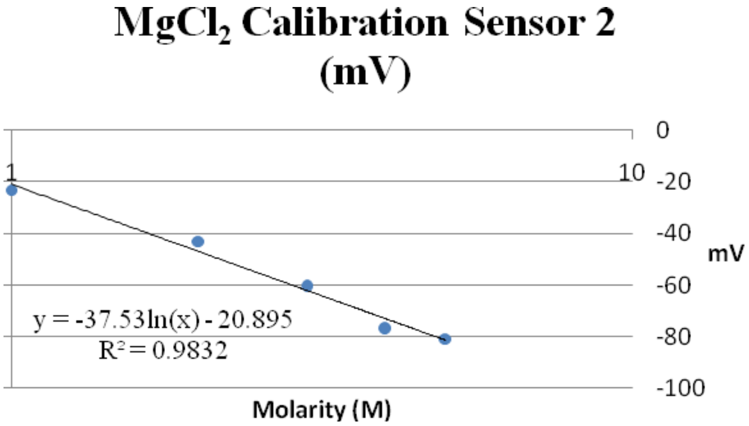


Figure 5 An example of a standard curve correlating salt molarity with sensor potential.

The standard curve (Figure 6) is used to correlate mV readings to molarity concentrations with the following re-arrangements:

$$\mathrm{mV} = -37.53 \cdot \ln(\mathrm{M}) - 20.895$$

$$\mathrm{mV} + 20.895 = -37.53 \cdot \ln(\mathrm{M})$$

$$\frac{\mathrm{mV} + 20.895}{-37.53} = \ln\ (\mathrm{M})$$

$$e^{\left(\frac{\mathrm{mV}+20.895}{-37.53}\right)} = e^{\ln(\mathrm{M})}$$

$$M = e^{\left(\frac{mV + 20.895}{-37.53}\right)}$$

The values this formula yields are then converted using a chloride concentration formula specific to the salt-brine type, in this case $MgCl_2$ with a molecular weight of 95.211.

$$\text{Chloride Level } (\%) = \left(\frac{\text{Molarity} \cdot 95.211}{1000}\right)$$

Dilution Rate Method

For the dilution rate method example numbers will be used for demonstration. Using the resulting correlation from the standard curve, the dilution rate, D, can be derived using the same re-arrangements as the molarity:

$$mV = -25.34 \cdot \ln(D) + 12.314$$

$$D = e^{\left(\frac{mV - 12.314}{-25.34}\right)}$$

The acquired dilution rate, D, can then be converted to Molarity using previously determined data for the associated deicer from the Molarity method. From the Molarity method, FreezGard CI Plus was determined to have a Molarity of 6.305 M $[MgCl_2]$ at full concentration (i.e., No Dilution). Thus, the dilution rate compared to the full concentration of FreezGard can then be calculated by comparison:

$$\text{For } D = 86.7\%$$

$$M = 0.867 \cdot 6.305 = 5.466$$

Now the Molarity of the sample can be converted to chloride concentration using the Molarity method previously discussed. CCB, NaCl+GLT, and IceSlicer Elite products undergo the same calculation process, and their key values that are listed in Table 1.

Table 1 Molarity and molecular weight values required for dilution rate method calculations of chloride concentration.

Deicing Product	Experimental Molarity	Molecular Weight of the Salt (g/mol)
NaCl+GLT	4.81	58.443
CCB	3.92	110.984
FreezGard	6.305	95.211
IceSlicer Elite	N/A	58.443

A4. Test Method for Determining Inhibitor Concentration of a Deicer Solution

The purpose of this test is to rapidly determine the concentration of corrosion inhibitor in a deicer solution by examining the signal strength of the known characteristic UV-absorption peak in its ultraviolet/visible spectrum. This would enable the tracking of inhibitors in field samples once applied onto the roadway or the monitoring of inhibitor concentration once the deicers are subjected to various storage conditions and mixing strategies.

The ultraviolet-visible spectroscopy or spectrophotometry (UV-Vis) method has been routinely used in the quantitative determination of solutions of transition metal ions and highly conjugated organic compounds. Organic compounds, especially those with a high degree of conjugation, also absorb light in the UV or visible regions of the electromagnetic spectrum. The research team will identify the *characteristic* UV-absorption peak for each of the selected corrosion inhibitors possibly without knowing their exact chemical composition. The inhibited NaCl liquid deicer (with Shield GLT^{TM}), the inhibited $CaCl_2$ liquid deicer (CCB^{TM}) and the inhibited $MgCl_2$ liquid deicer (FreezGard CI Plus^{TM}) each showed a characteristic UV-absorption peak near 275 nm, 264 nm and 260 nm respectively.

For each corrosion inhibitor of interest, the research team will then prepare standard solutions with known inhibitor concentration (using water as the solvent) and subject them to a UV/Vis spectrophotometer. The presence of the inhibitor will give a response (e.g. optical density) proportional to the concentration. As such, a standard calibration curve can be established for each inhibitor. For any field samples with unknown inhibitor concentration, the instrument's response to the sample can be compared against the calibration curve to derive the inhibitor concentration.

Method

The UV-VIS instrumentation is Spectromax 384 Plus form Molecular Devices. Data acquisition and transfer are performed via SoftMax Pro 4.3.1 software on Mac OS 9.2. Final analysis is computed using Microsoft Excel®. The spectrophotometer is set to collect the full spectrum 190 to 750 nm data of each deicer. Full-spectral data was collected for each standard and field sample. Each deicer is ran at the endpoint (peak wavelength) determined from the method development. A DI water sample is run as a reference sample for each UV-Vis analysis. Each deicer-inhibitor solution has a specific set of standard dilutions and sample dilutions as well as a specific peak adsorption wavelength. A standard curve, a correlation between the inhibitor concentration and the UV signal intensity, is generated with the endpoint data from the series of standard dilutions. For any field samples with unknown inhibitor concentration, the measured UV-Vis absorbance of the sample is compared against the calibration curve to derive the inhibitor concentration. On each testing day, an inhibitor concentration standard curve is established for each deicer type, using at least five standard solutions with known inhibitor concentration. These procedures are detailed below for each deicer/inhibitor used in this research project.

Standard concentration curves are diluted from a 1% deicer stock solution that is mixed by adding 99 mL of DI water to 1 mL of the FreezGard CI Plus, CCB, and NaCl+GLT inhibitor-only solution. Each standard is mixed well and stored in a seven dram snap-cap sample vial. All vials are labeled with the concentration (in percent) and dilution date. A TenSette© Pipette is used throughout the process for accuracy of all dilution procedures. The remaining 1% stock solution is stored in a 7-dram vial and is considered the final concentration for establishing a standard curve.

All standard solutions and field collected samples are stored in cold storage in CSIL and covered with aluminum foil to prevent photo-degradation. The equation $C_1V_1 = C_2V_2$ was used to calculate volumes for making the standard curve and also for diluting the storage-collected samples. All field-collected samples are diluted to fall in the lower range of the standard curve for each deicer because they have dark color following collection from the pavement. **Figure 7** represents the full spectral data of FreezGard CI Plus from early method development stages, where inhibitor concentrations were too high to provide reliable characteristic peak signal strength.

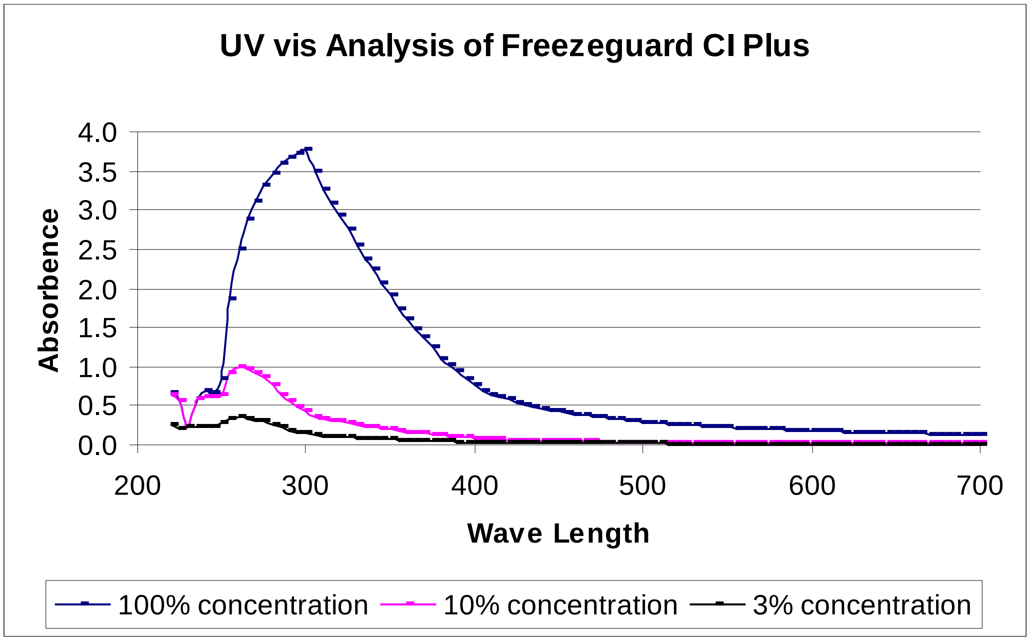


Figure 6 UV-Vis spectra of FreezGard CI Plus deicer solutions diluted to various degrees.

Please note the following definitions:

- *Storage-collected* samples are those samples collected from the storage tanks from TRANSCEND facility, Lewistown, Montana. These samples are wrapped in aluminum foil and placed into cold storage in the laboratory. Samples are labeled according to deicer brand, mix strategy, and collection date.
- *Pavement-collected* samples are those samples collected from each of three field events performed at TRANSCEND facility, Lewistown, Montana: Black Ice Event, Man-Made Snow Event, and Natural Snow Event. These samples were collected from pavement after the storm simulation occurred by adding DI water to each respective plot, stored in 1 L sample bottles, wrapped in aluminum foil, and placed into cold storage.
- *Standard solution* samples are inhibitor-only and brine-only solutions received from the manufacturer. These samples are diluted in the laboratory and used to establish standard

concentration curves (in percentage) for calculating the inhibitor concentration of all storage and pavement collected samples. A minimum of five standard solutions are used to generate each standard curve.

FreezGard CI Plus

Standard concentration curve solutions of FreezGard CI Plus inhibitor-only must be diluted to account for the high amount of suspended particles in solution and to achieve acceptable adsorption values on the UV-Vis. For the standard curve, 1% FreezGard inhibitor-only stock solution is mixed with DI water to achieve 0.1%, 0.25%, 0.5%, 0.75%, and 1.0% concentrations. Each standard solution is mixed well and stored in a seven dram snap-cap sample vial. All vials are labeled with the percent concentration and dilution date.

On the spectrophotometer, the full spectrum of each standard solution, beginning with the lowest percent concentration is analyzed. From those spectra, determine the wavelength with the highest adsorption value (endpoint or peak height), but still equal to or less than a value of one. For the endpoint analysis, the endpoint value used for FreezGard CI Plus samples is 260 nm, and the standards solutions are analyzed at this specific wavelength for concentration calculations. The full spectrum of each field-collected sample is collected followed by the endpoint analysis at 260 nm.

The storage-collected samples are thoroughly mixed prior to dilution to ensure sample homogeneity. Each storage-collected sample is diluted to a 10% solution with DI water and mixed well. Storage-collected samples are diluted to ensure absorption values less than 1.0 at the specified wavelength. Diluted storage-samples are stored in seven dram snap-cap sample vials and labeled with collection date, mix regimen, and deicer type.

Diluted samples of FreezGard CI Plus are stored for no more than 24 hours in cold storage prior to testing. Excessive handling or mixing of FreezGard CI Plus sample vials must be avoided prior to UV-Vis analysis to reduce the amount of suspended particles in solution. If the samples are mixed or aggressively handled the adsorption values on UV-Vis will be erroneous from re-suspension of particles. During the initial stages of method development, it was observed that excessive mixing just prior to analysis generated adsorption values that were greater than 1; adsorption values greater than 1 are typically considered too high to give reliable results for this test method.

Pavement-collected samples were tested without further dilution. The pavement samples are stored in seven dram snap-cap sample vials and labeled with collection date, plot number, and deicer type. Prior to test the pavement samples are inverted once to ensure analysis of a homogenous sample.

Calcium Chloride with Boost

Standard concentration curve solutions of CCB inhibitor-only must be very dilute to account for the dark color of the inhibitor and to achieve acceptable adsorption values. For the standard curve, 1% CCB inhibitor-only stock solution is mixed with DI water to achieve 0.0375%, 0.04%, 0.05%, 0.06%, 0.07%, and 0.1% solutions. Each standard solution is mixed well and stored in a seven dram snap-cap sample vial. All vials are labeled with the percent concentration and dilution date.

On the spectrophotometer, the full spectrum of each standard concentration curve is analyzed beginning with the lowest percent concentration. From those spectra, determine the wavelength with the highest adsorption value (endpoint or peak height), but still equal to or less than one. The full spectrum of each storage- and pavement-collected sample is analyzed followed by the endpoint analysis. The endpoint value used for CCB samples is 264 nm and the standards are analyzed at this specific wavelength for concentration calculations.

For storage-collected samples the sample is thoroughly mixed prior to dilution to ensure sample homogeneity. Each field sample is diluted to 0.1% with DI water and mixed well. Diluted Storage samples are stored in seven dram snap-cap sample vials and labeled with collection date, mix regimen, and deicer type. Diluted samples of CCB in the vials are stored for no more than 24 hours in cold storage. CCB samples vials are inverted once to ensure a homogenous sample.

Pavement-collected samples are not diluted further for testing. The pavement samples are stored in seven dram snap-cap sample vials and labeled with collection date, plot number, and deicer type. CCB Pavement sample vials are inverted once to ensure analysis of a homogenous sample.

NaCl+GLT

Standard concentration curve solutions of GLT inhibitor-only must be very dilute to account for the dark color of the inhibitor and to achieve acceptable adsorption values on the UV-VIS. For the standard curve, 1% GLT inhibitor-only stock solution is mixed with DI water to achieve 0.0375%, 0.04%, 0.05%, 0.06%, 0.07%, and 0.1%. Each standard is mixed well and stored in a seven dram snap-cap sample vial. All vials are labeled with the percent concentration and dilution date.

On the spectrophotometer, the full spectrum of each standard concentration curve is analyzed beginning with the lowest percent concentration. From those spectra, determine the wavelength with the highest adsorption value (endpoint or peak height), but still equal to or less than a value of one. The full spectrum of each storage- and pavement-collected sample is analyzed followed by the endpoint analysis at 275 nm and the standards are analyzed at this specific wavelength for concentration calculations.

For storage-collected samples, a 1% solution of each sample will be analyzed. The solution is thoroughly mixed prior to dilution to ensure sample homogeneity. Each storage-collected sample is diluted to 1% with DI water and mixed well. Diluted samples are stored in seven dram snap-cap sample vials with labels noting collection date, mix regimen, and deicer type. Diluted storage samples of GLT are stored for no more than 24 hours in cold storage. GLT sample vials are inverted once to ensure analysis of a homogenous sample. Because the salt brine (NaCl) in the samples is an inorganic compound, it had no effect on the adsorption values collected during the UV-Vis analysis.

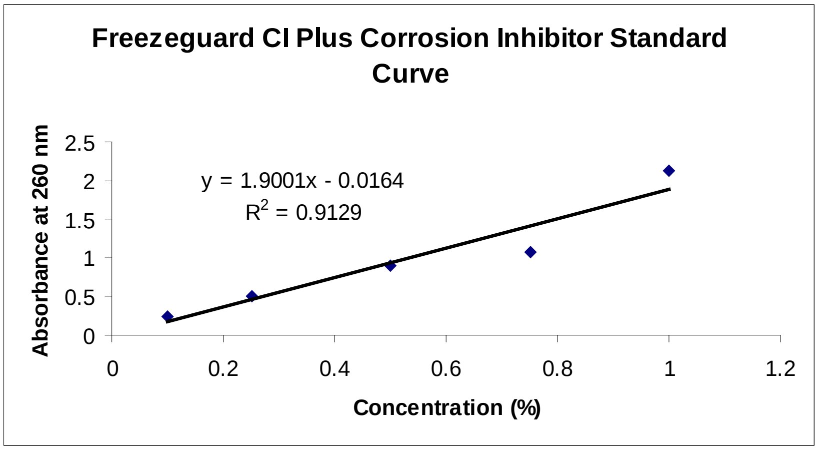
Pavement-collected samples are not diluted further for testing. The pavement samples are stored in seven dram snap-cap sample vials and labeled with collection date, plot number, and deicer type. NaCl+GLT pavement sample vials are inverted once to ensure analysis of a homogenous sample.

IceSlicer Elite

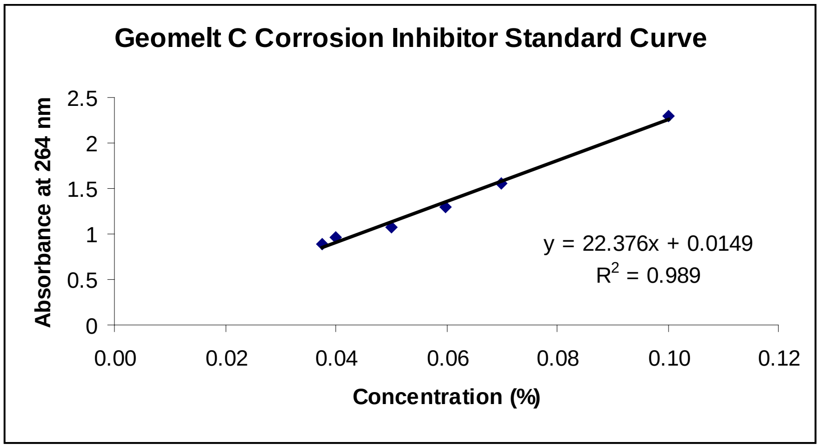
We experimented with the use of UV-Vis to quantify its inhibitor concentration once it was prepared into 23 wt% solution but failed to obtain a strong correlation with the standard curves. This may be attributable to the dark color of the deicer, the relatively high content of suspended solids in the liquid solution, and the poor solubility of its inhibitor. As such, the inhibitor concentration in IceSlicer Elite solutions was determined by measuring the total phosphorus concentration instead (as detailed in Appendix A9).

Data Analysis

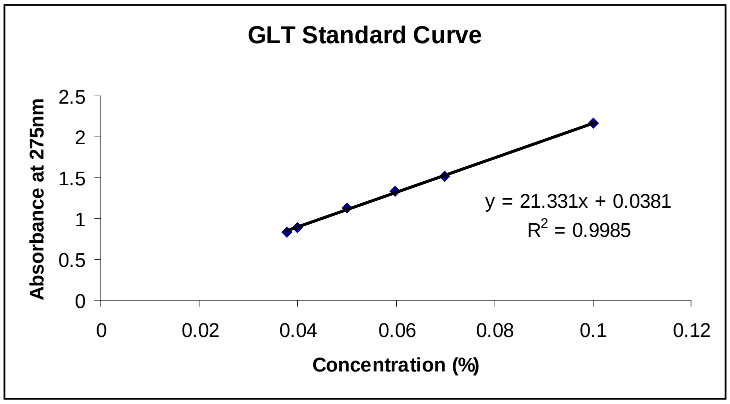
A standard curve is made for each product using the diluted standard solutions and correlates the inhibitor concentration with the UV signal intensity. The presence of the inhibitor gives a response (e.g. optical density) proportional to the concentration. **Figure 8** (a-c) shows the standard calibration curve for FreezGard CI Plus corrosion inhibitor (R^2=0.91), CCB corrosion inhibitor (R^2=0.99), and GLT corrosion inhibitor (R^2=0.99), respectively. For any field samples with unknown inhibitor concentration, the measured UV-Vis absorbance of the sample is compared against the calibration curve to derive the inhibitor concentration.



(a)



(b)



(c)

Figure 7 UV-Vis standard curves correlating the characteristic absorption strength as a function of inhibitor concentration: a) FreezGard CI Plus corrosion inhibitor, b) CCB corrosion inhibitor, and c) GLT corrosion inhibitor.

A5. Test Method for Determining Instantaneous Corrosivity of a Deicer Solution

The purpose of this test is to determine the instantaneous corrosivity of a deicer solution to steel using electrochemical techniques. Electrochemical techniques may provide an attractive alternative to the gravimetric method (PNS/NACE method) in terms of allowing rapid determination of corrosion rate of metals and revealing information pertinent to the corrosion mechanism and kinetics. For instance, **Figure 9** shows *potentiodynamic polarization curves* of a simulated deicer solution with or without corrosion inhibitors. Such polarization curves are expected to provide "signature" information pertinent to the corrosion behavior of steel in the inhibited or non-inhibited solution and to be used for quality assurance of deicer products.

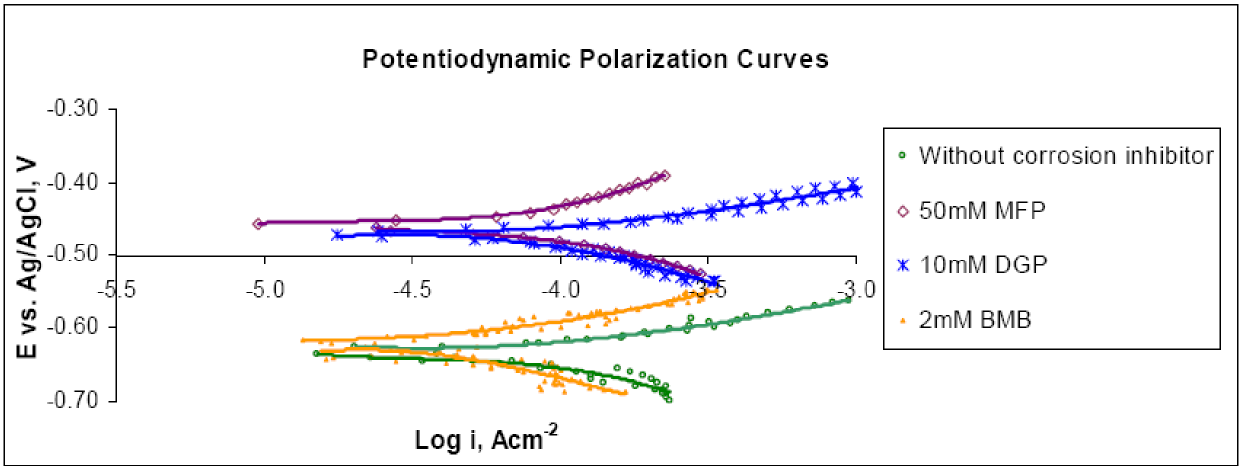


Figure 8 Potentiodynamic polarization curves of a steel sample in a simulated deicer solution, as a function of inhibitor presence.

<u>Method</u>

Please note the following definitions:

- *Working Electrodes (WE)* are the steel coupons, prepared by the WTI-CSIL research team, at which the cell reaction takes place.
- *Counter Electrode (CE)* is the platinum mesh cloth that balances the current between the sample solution and working electrode (**Figure 10**).
- *Reference Electrode (RE)* is a saturated calomel electrode of SCE used to measure and control the working electrodes potential (Figure 11).

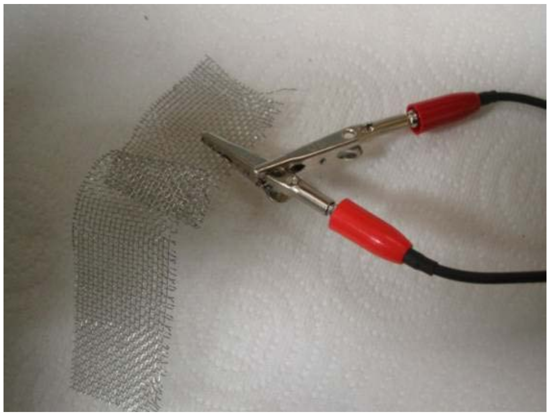


Figure 9 Counter electrode.

Figure 10 Reference electrode.

Preparation of the working electrode

A sheet of mild steel (ASTM A36) is laser cut into 1 cm square coupons. To make the working electrode, one side of a steel coupon is connected to a copper wire using silver-conductive paint and allowed to dry. The steel coupon and copper wire are encased in an epoxy resin puck in a PVC mould. After the epoxy resin has cured, the coupon is polished to provide uniform surface roughness. The coupon is wet-polished with tap water on a metallographic silicon carbide polishing disc with a grit size #1000. After polishing, the coupon is rinsed with running tap water to remove any remaining grit or residue. The final step in cleaning the coupon surface of the working electrode is sonication in DI water. The working electrode is then rinsed with acetone and dried before any electrochemical testing.

Test Procedure

The storage-collected deicer samples are diluted to 3% by weight for solid samples or by volume for liquid samples using DI water. The field-collected samples are not diluted. For each diluted deicer solution, four working electrodes are placed in the same beaker containing the deicer solution to ensure statistical reliability of corrosion test results. The counter electrode and reference electrode are also placed in the solution in such a way that no electrodes are in physical contact with each other and the reference electrode is at an equal distance from the exposed surface of each working electrode. For each solution of interest, the *open circuit potential (OCP)* of the working electrodes are monitored for **24 hours** to allow them to stabilize before *potentiodynamic polarization* measurements. The OCP monitoring of multiple working electrodes is achieved by connecting them and the reference electrode to an 8-channel Electrochemical Multiplexer ECMB.

Electrochemical measurements of each working electrode are conducted using a computer-controlled Gamry Instruments® Potentiostat and a three-electrode system (with the WE, CE, and RE connected to the Potentiostat following the manufacturer's manual). The underlying mechanism of *potentiodynamic polarization* is to apply an external electric potential (DC) signal as perturbation to polarize the working electrode from its natural state (the signal is measured against the reference electrode and intended to either provide electrons to or obtain electrons from the working electrode) and subsequently collect the corresponding electric current (DC) response between the working electrode and the counter electrode. By plotting the relationship between the applied potential signal and the corresponding current response, the Potentiostat software can be used to obtain a few critical parameters characterizing the corrosion behavior of the steel in the test solution, including: corrosion potential (E_{corr}), instantaneous corrosion rate in term of current density (i_{corr}) and two other electrochemical parameters characteristic of the anodic and cathodic half-reactions respectively (b_{a} and b_{k}). There are three major techniques in the category of *potentiodynamic polarization* measurements: Tafel polarization, linear polarization, and weak polarization, all of which can be used to characterize the corrosivity of the test solution to steel.

We chose the weak polarization technique, i.e., defining the potential scan range from OCP-30mV to OCP+30mV at a sweeping rate of 1.0 mV/S. Compared with the more popular linear polarization technique (typically OCP ±15 mV), this would enable the software to obtain b_{a} and b_{k} values from the measured polarization curves and also provide corrosion data less prone to measuring errors associated with the test instrument. Compared with the more destructive Tafel polarization (typically OCP ±200 mV), this would minimize the risk of significantly disturbing the steel/electrolyte interface being measured or altering the test solution composition or the controlling corrosion mechanism or kinetics. The weak polarization experiments use a typical sweep rate of 1mV/s for potential scan.

For weak polarization of steel in the salt solutions, the polarization due to mass transfer or ohmic drop is negligible. Therefore, the relation between current density (i) and potential (E) on the polarization curve is governed by the following equation:

$$i = i_{corr}\left\{\exp\frac{2.3(E-E_{corr})}{b_a} - \exp\frac{2.3(E-E_{corr})}{b_k}\right\}$$

As such, the Potentiostat software is used to fit the measured weak polarization curve and obtain the four key parameters, E_{corr}, i_{corr}, b_a and b_k. For any known metal, the corrosion rate can be easily converted from current density (mA/cm^2) to weight loss (MPY or milli-inches per year).

A6. Test Method for Determining 72-hour Average Corrosivity of a Deicer Solution

The purpose of this test is to determine the 72-hour average corrosivity of a deicer solution to steel using the popular gravimetric method as specified by the Pacific Northwest Snowfighters (PNS) Association. Products that are submitted to meet the Corrosion Rate Test and to have Percent Effectiveness determined should be tested according to the National Association of Corrosion Engineers (NACE) Standard TM0169-95 as modified by the PNS. The PNS has modified this procedure so that the test procedure uses 30 ml of a 3% chemical product solution as received per square inch of coupon surface area for the corrosion test.

General Method:
Test Method: NACE Standard TM0169-95 (1995 Revision) as modified by PNS.

*Note: we used DI water instead of distilled water for all tests.

Method
Step 1- Preparation of the Coupons
The coupons used are 1/2" (approximately 1.38 in. x 0.56 in. x 0.11 in.) flat steel washers with an approximate density of 7.85 grams per cubic centimeter. Three coupons are used in each chemical product solution, for the DI water and sodium chloride (NaCl) control standards. Coupons must meet ASTM F 436, Type 1, with a Rockwell Hardness of C 38-45. Each coupon used in the test procedure is subjected to the following procedures for accurate test results.

1. Wipe the coupon with a suitable solvent to remove grease and oil.
2. Examine each coupon closely and reject those that are subject to flaws or metallurgical abnormalities.
3. All coupons are tested by the vendor prior to shipment for Rockwell Hardness of C 38-45; coupons having hardness values outside of this range are rejected.
4. Coupons deemed acceptable for testing are stamped for identification.
5. Coupons are then acid-etched (cleaned) with 1+1 hydrochloric acid (HCl) for approximately 2-3 minutes.

6. The coupons are then quickly rinsed with tap water, DI water, wiped dry and placed in chloroform.
7. When removed from the chloroform, the coupons are placed on a tray lined with paper towels and are not touching each other. The coupons are air dried in a ventilated hood for a minimum of 15 minutes.
8. Coupons are measured as specified in Step 2. (Note: gloves must be worn during cleaning and measuring to prevent the transfer of oil or other residues onto the coupons. If the coupons are handled with ungloved hands, the coupons should be re-cleaned using the method above prior to weighing.)
9. Each coupon will be weighed to a constant weight. The constant weight shall be two consecutive weights of each coupon within a minimum of 0.5 milligrams of each other.

Please note that removal of incidental flash rusting prior to weighing is not necessary. Also, galvanized coupons are not allowed to be used even after removing the zinc with acid. Hot dipped galvanization creates a Fe-Zn metallurgical surface bond that changes the characteristics of the steel.

Step 2—Measuring of the Coupons

The outer diameter, inner diameter, and the thickness of each coupon are measured twice at 90 degrees from each initial reading. The average for each measurement is calculated. These averages are used to calculate the surface area of each coupon with the following formula:

$$A = (3.1416/2)\times(D2 - d2) + 3.1416t \times D + 3.1416t\times d$$

Where D = average outside diameter
d = average inside diameter
t = average thickness

Example:

$$A = 1.5708 \times (1.9044-0.3136) + 0.4768949 + 0.1935226$$
$$A = 1.5708\times1.5908 + 0.4768949 + 0.1935226$$
$$A = 2.4988286 + 0.4768949 + 0.1935226$$
$$A = 3.1692461 \text{ square inches (Total surface area of the coupon.)}$$
$$A = 3.17 \text{ square inches}$$

Step 3—Preparation of the Solutions

ASTM D 1193 Type II DI water is used to prepare each solution, blank, and control standards. Sodium chloride (NaCl) used to prepare the salt standard will be "Analyzed Reagent Grade" quality. A 3% solution of NaCl is prepared by weight, using the reagent grade salt and DI water (Weight/Volume). A 3% solution of each chemical product to be tested is prepared using DI water to dissolve and/or dilute the chemical product. For liquid chemical products, three parts liquid chemical product (as received) is mixed with 97 parts DI water to produce the test solution (Volume/Volume). If the chemical product is a dry product, then the 3% solution is made by weight (Weight/Volume). All solutions, including the DI water blank, are covered and allowed to sit for a minimum of 12 hours to stabilize and reach equilibrium, to ensure solubility, and to account for any reactivity that may occur.

Step 4—The Corrosion Test

The Corrosion Testing Machine (Ad-Tek, Inc.) is used to perform the corrosion tests. In November 2009 the machine was upgraded from an analog to a digital control system due to a failure in the analog system. Approximately 300 milliliters (actual volume is determined by the surface area of test coupons) of each solution as mixed in Step 3 is poured into a 500 milliliter Erlenmeyer flask. Each flask is equipped with a rubber stopper that has a 3-4 millimeter diameter hole drilled through it to allow a line to run through the stopper. One end of the line is attached to a rotating bar, and the other end of the line is attached to a plastic frame made to hold coupons inside the flask. Three prepared coupons are attached to each plastic frame. The rotating bar is controlled by an electric timer that lowers the bar for 10 minutes then raises the bar up for 50 minutes, but keeps the coupons inside of the flask for the duration of the test. This allows the coupons to be exposed to the test solution 10 minutes of each hour. The corrosion test is run for 72 hours. The solution is not agitated during the corrosion test.

Corrosion tests are conducted at 21-23°C. The room temperature is recorded daily during testing. A calibrated thermometer located next to the corrosion testing machine will be used to monitor room temperature. The temperature readings will be used to assist determination of varying corrosion rates; temperature readings will not be used to correct data.

Step 5—Cleaning of the Coupons after Corrosion Test

The coupons are removed from the solution after 72 hours. The coupons are rinsed and slightly agitated with gloved hands under running tap water to remove any loose corrosion products. Working under a well ventilated hood, the coupons are placed into glass beakers containing the cleaning acid: concentrated hydrochloric acid (HCl) containing 50 grams/liter $SnCl_2$ (stannous chloride) and 20 grams/liter $SbCl_3$ (antimony trichloride). The two salts are added to the HCl to stop the reaction of the HCl with the steel once the rust or corrosion is removed. The fumes given off by the acid during cleaning contain gases formed from the antimony and are extremely hazardous; this cleaning procedure *must be* conducted under a ventilated hood. After 15 minutes the coupons are removed from the cleaning acid and successively rinsed with tap water then DI water and finally wiped with a cloth to clean any deposits from the coupons. The coupons are returned to the cleaning acid, and the procedure is repeated. After the cleaning procedure, the coupons are rinsed in chloroform, air dried, and weighed. Each coupon will be weighed to a constant weight. The constant weight shall be two consecutive weights of each coupon within a minimum of 0.5 milligrams of each other.

Step 6—Evaluation of Corrosion

The weight loss of each coupon is determined by subtracting the final weight from the original weight. The corrosion rate for each coupon is expressed as milligrams of penetration per year (MPY) by the following formula where the density for steel is 7.85 g/cc:

$$\text{MPY} = (\text{weight loss (milligrams)})\,(534) \,/\, ((\text{area})\,(\text{time})\,(\text{metal density}))$$

The final MPY value for each solution is determined by calculating an average of the three individual coupons. Average MPY from this point forward will be referred to as only MPY of the solution being tested. Note: Wide variation of MPY of individual coupons inside the same flask typically indicates contamination of a coupon. If variation of individual MPY is too great to determine consistent data, the test should be conducted again. Reasonable variation within a triplicate of relative standard deviation (RSD) 3 is acceptable.

Step 6—Additional Information
The corrosion value of the DI water and the reagent grade sodium chloride is critical in determining the MPY value and are used in the calculations. The MPY corrosion values of the DI water and the reagent grade sodium chloride may vary from test to test. These are the two base lines used to determine a products relative corrosion rate.

In **Table 2** below the DI water proved to have a corrosion value of 6.00 MPY. The chart shows that the reagent grade sodium chloride has a corrected corrosion value of 45.00 M PY. This means that the original corrosion value of the reagent grade sodium chloride and the DI water (in a 3% solution) was 51.00 MPY. The 6.00 MPY value for the DI water was subtracted from the original 51.00 MPY for the reagent grade sodium chloride and DI water solution to arrive at the DI water corrected value of 45.00 MPY for the reagent grade sodium chloride.

Table 2 Chemical Products Corrosion Test Results - All Values Are DI water Corrected (NACE Standard TM0169-95 as modified by the PNS)

Product	Mils/year	Percentage	Remarks
*Super Stuff	-0.03	-0.07	Good stuff
*Ice Melter	0.035	0.08	Good
*Magic Melter	1.00	2.22	Smells good
*Magic Melter II	10.15	22.55	Ok
Acme Melter	19.99	44.42	Nice appearance
Acme Melter-1	23.71	52.69	50% @#*&^
Wondermelt	54.07	120.16	Very Corrosive
*Wondermelt-A	-5.18	-11.51	Good corrosion protection
Salt	45.00	100.00	
DI water	6.00	13.33	

*ACCEPTABLE PRODUCT NOTE: The results used in the above table are for example only, and they are not firm numbers.

The corrosion value of 6.00 MPY for the DI water is subtracted from the total MPY for each of the 3% solutions for each product tested. When this calculation is completed for each product being tested the resulting value is the corrected corrosion value. According to criteria adopted by PNS; “Only corrosion inhibited chemical products that are at least 70% less corrosive than reagent grade sodium chloride may be used.” To determine if a product is acceptable, take the corrected corrosion value of the reagent grade sodium chloride and multiply it by 30%. In this case, 45.00 MPY multiplied by 30% equals 13.5 MPY which is the highest acceptable corrected corrosion value for any product in this test. Any product in this test that produces a MPY value higher than 13.5 MPY is rejected.

Step 8—Negative Numbers

Some products actually end up with a negative number as their corrected MPY value. A negative number is exceptionally good and actually indicates that the product, when mixed with DI water in a 3% solution, is less corrosive than DI water. To show an example of a negative number note that in Table 1 the DI water in this test had a corrosion factor of 6.00 MPY. Also, note that the 3% solution of Wondermelt-A had a corrected corrosion value of -5.18 MPY. To quickly repeat the math used to arrive at this negative number the 3% solution corrosion value of 1.18 MPY, had been subtracted from it the DI water corrosion value of 6.00 MPY. This resulted in the corrected MPY value of -5.18. The larger the negative number, the better a product is in terms of corrosion inhibiting abilities.

Data Analysis
Results will be reported in Percent Effectiveness. Percent values equal to or less than 30% are passing. The DI water corrected values of the chemical product and the salt are used to make this calculation. The corrected value of the chemical product is divided by the corrected value of the salt; this value is then multiplied by 100 to give percent.

Example:

Magic Melter II has a corrected value of 10.15
Salt has a corrected value of 45.00

Therefore: (10.15 / 45.00) × 100 = 22.6% Pass

Acme Melter has a corrected value of 19.99

Therefore: (19.99 / 45.00) × 100 = 44.4% Fail

A7. Test Method for Characterizing Thermal Properties of a Deicer Solution

The purpose of this test is to rapidly and consistently characterize and quantify the thermal properties of deicer compounds using a differential scanning calorimeter (DSC) thermogram. DSC is an experimental technique that measures the energy necessary to maintain a near-zero temperature difference between the test substance and an inert reference material, with the two subjected to an identical (heating, cooling or constant) temperature program. DSC measurements typically require only a few milligrams of the sample, which is sealed in an aluminum capsule. By measuring the heat flow, DSC can detect phase transitions, quantify energy change, and measure kinetics of the transitions.

Determining the changes in the heat flow of deicing and anti-icing compounds provides insight into their freeze/thaw behavior, effective temperatures, and ice melting capacity. Method development involved testing various sample dilution rates, cooling and heating rates, and temperature regimes. The DSC method below was developed based on trials and errors which eventually led to a deicer dilution ratio and a cooling/heating rate that provide reliable, reproducible results.

Method:

Step 1- Deicer Preparation

To test liquid deicers, collect a sample of product at room temperature and shake or stir to ensure a homogenous sample. The initial concentration should be equal to the solution used in the field. To test solid deicers, a liquid can be obtained by dissolving the solid deicer in deionized water at a concentration seen in typical deicers (e.g., 23% for NaCl-based deicer). Dilute the initial sample with deionized water by three times (i.e., water : deicer = 2:1 by volume). A convenient method is to combine 10 mL of deionized water with 5 mL of deicer.

Step 2- Sample Preparation

Weigh an empty aluminum sample pan and lid designed specifically for the DSC and record the mass to the nearest 0.1 mg. Use a micropipette to collect 10 µL (microliter) of the diluted deicer and hermetically seal in the aluminum sample pan. Weigh the sealed pan with deicer sample to determine the deicer mass to the nearest 0.1 mg. An empty aluminum sample pan that is hermetically sealed is used as the reference for DSC. The same reference pan can be used for dozens of tests.

Step 3- DSC Test Parameter

Run a DSC test with a temperature range of 77 to -76°F (25 to -60°C) at a rate of 3.6°F (2°C) per minute. Run a cooling cycle first and then a heating cycle.

Step 4- Replication

Conduct the DSC test for at least three replicate samples of deicer. Additional replicates may need to be run to achieve a reasonable RSD (in analysis portion).

Step 5- Integration

Isolate and integrate the peak in the warming cycle on the thermogram to determine heat flow (J/g) and peak temperature. Depending upon the instrument model, integration is performed using the software for the DSC. If more than one peak is present, the heat flow and peak temperature associated with the *warmer* peak should be determined- for example NaCl-based deicers have two peaks in the heating cycle and the warmer peak should be used in the analysis.

Step 6- Calculations

Calculate the average and standard deviation of the integrated heat flow and peak temperature from results of at least three test runs for a single deicer. Additionally calculate the coefficient of variation for the integrated heat flow. The averages should be reported to three significant digits; the standard deviations and coefficients of variation should be reported to two significant digits.

$$H_{avg} = \frac{\sum_{i=1}^{n} H_i}{n} \qquad T_{avg} = \frac{\sum_{i=1}^{n} T_i}{n}$$

$$H_{stdev} = \sqrt{\frac{1}{n-1}\sum_{i=1}^{n}\left(H_i - H_{avg}\right)^2} \qquad T_{stdev} = \sqrt{\frac{1}{n-1}\sum_{i=1}^{n}\left(T_i - T_{avg}\right)^2}$$

$$H_{cov} = \frac{H_{stdev}}{H_{avg}} \times 100\%$$

Where

H_i is integrated heat flow (J/g) for test i

T_i is peak temperature (°F) for test i

n is number of replicate tests

Step 7- Analysis

If $H_{cov} < 10$ percent and $T_{stdev} < 0.5°F$, then report the calculated values (average, standard deviation, and coefficient of variation). If either condition is not met, additional tests should be performed until the calculations using results from at least three replicate samples meet these criteria.

Interpretation:

Step 1- Characteristic Temperature

The average peak temperature determined from the analysis is the characteristic temperature of the deicer. It should be compared to the characteristic temperature of a 23% NaCl salt brine, which was found to be 21.8°F for this project. If the characteristic temperature of the test deicer is lower than 21.8°F, the relative performance of the tested deicer is greater than 23% NaCl and it is most likely more effective in the field at lower temperatures than 23% NaCl. Likewise, if the characteristic temperature is greater than 21.8°F, then the tested deicer is likely *less effective* than 23% NaCl at colder field conditions.

Step 2- Predicted Ice Melting Performance:

If the tested deicer is a chloride-based liquid deicer[*], the integrated heat flow and characteristic temperature can be used to estimate the performance of the tested deicer under the Modified SHRP Ice Melting Test using these empirical equations:

$$IMC_{30^\circ F}(\text{mL brine}) = -4.476 - 0.0288T + 3.83\log(\Delta H) \quad (R^2 = 0.90)$$
$$IMC_{15^\circ F}(\text{mL brine}) = 9.027 - 0.1009T - 2.54\log(\Delta H) \quad (R^2 = 0.94)$$

Where:

IMC = Ice Melting Capacity (expected volume of brine that will be collected in Modified SHRP Ice Melting Test after 60 minutes (mL))

ΔH = 334 J/g minus average heat flow (H_{avg} in J/g)

T = average peak temperature (T_{avg} in °F)

A8. Test Method for Determining Conductivity of a Deicing Solution

The purpose of this test is to rapidly determine the conductivity of a deicer solution using the CON510 Bench Meter. Conductivity is used to determine the ionic content in a sample solution

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[*] Note that the equations relating the *IMC* with the T_c and ΔH were developed using chloride-based liquid deicers. As such, they may not be suitable for predicting *IMC* of pure additives or non-chloride deicers from their DSC thermogram.

specifically in the pavement collected samples collected during the field portion of this project. The CON510 Bench Meter measures the conductivity of a solution through two steel bands spaced one centimeter apart on the sensors shaft. A long plastic collar within the shaft allows for space for fluid to rest and stabilize for a measurement. The following procedure is adapted from the Instruction Manual for the Model CON 510.

Method:

The Model CON510 Bench Conductivity/TDS Meter, conductivity calibration standards, stir plates, clean stir bars and DI water in a Mouth Wash bottle will be needed for testing.

Step 1- Instrument Calibration

The Bench Meter has five measurement ranges, r1 through r5. In order to achieve optimal accuracy the instrument should be calibrated to approximately 2/3 of the total range of those predicted of the sample solution. The sensor must first be well rinsed with DI water using the Mouth Wash bottle followed a rinse with a small amount of calibration standard solution. Approximately 100 mL of the calibration standard solution is then poured into a 150 mL beaker with a stir bar and placed on a stir plate. Once the sensor is submerged into the calibration standard solution, press the **CAL/MEAS** key. The appropriate value of calibration standard is adjusted using the **MI/▲** or **MR/▼** keys. Press **ENTER** to accept calibration or **CAL/MEAS** to abort. The sensor is now calibrated to the range selected.

Step 2- Sample Measurement

After calibration, the sensor must be well rinsed with DI water followed by rinsing with a small amount of sample solution prior to sample measurement. Approximately 100 mL of the sample solution are placed into a 150 mL beaker and constantly stirred throughout the measurement. Once the meter has stabilized record the result for that sample. When measuring the conductivity of a sample, the Bench Meter automatically adjusts the range of measurement based on the conductivity as it is being read. The range can be manually selected while measuring by pressing the **RANGE** key.

Analysis:

Results are recorded in millisiemens (mS). The conductivity results are specifically used for this project to determine the ionic content of the storage- or pavement- collected field samples.

A9. Test Method for Determining Total Phosphorus in a Solid Deicer

The Total Phosphorus test method was used in this project to determine the corrosion inhibitor effectiveness in the solid deicer IceSlicer Elite when subjected to specific storage conditions. IceSlicer Elite contains a corrosion inhibitor with phosphates that are present in a condensed inorganic form. This must be converted to a reactive orthophosphate using acid and heat before analysis and determination of Total Phosphorus in the sample. A Hach® DRB 200 Reactor used in conjunction with a Hach® DR/890 Colorimeter following Hach® Method 10127 “Molybdovanadate Method with Acid Persulfate Digestion, Test ’N Tube™ Procedure” was used to determine Total Phosphorus content IceSlicer Elite samples- i.e. the concentration of the corrosion inhibitor in the sample.

Method- For Collecting Total Phosphorus Data:

Due to the phosphate characteristic of the IceSlicer Elite inhibitor and the difficulty of putting the corrosion-inhibitor into solution, two Total Phosphorous testing methods were used to determine the inhibitor concentration of each sample. The first method described below determined the total phosphate concentration following Method 10127 from the Hach® Colorimeter Testing Handbook. Essentially, a test represents one blank standard of de-ionized water and three repetitions of one sample. Prior to adding to the "Test 'N Tube^{TM}" vials, the samples are diluted to an appropriate level to ensure that their measurements fall within 10.0-100.0 mg/L PO_4^{3-}. The dilution rates were typically around 3% to achieve an acceptable reading. The vials are filled with sample, a Potassium Persulfate Pillow for Phosphonate, and run through a hydrolysis process where the vials are subjected to 150°C for 30 minutes in the DRB200 reactor unit. Once the hydrolysis process is complete and the vials are allowed to cool to room temperature, a ratio of sodium hydroxide and Molybdovanadate Reagent is added to each vial. Within 7-9 minutes the measurement must be taken and is done with the Hach® DR/890 Colorimeter.

Instrumentation required for this process are the Hach® DR/890 Colorimeter, a TenSette© Pipette, and the Test 'N Tube™ Kit containing; Total Phosphorous Vials, De-Ionized Water, Sodium Hydroxide, Molybdovanadate, Potassium Persulfate Pillow Packets, and a Bulb Pipette.

Step 1- Sample Preparation

Prepare the proper dilution of the sample so that the resulting measurement will read within the accurate range of 10-100 mg/L of the colorimeter. Through a series of trial and error experimentation it was discovered that the appropriate dilution rate of an IceSlicer Elite sample was from 3%-5% depending on the method used (Total Phosphorus method vs. Phosphate differentiation).

First pre-heat the hydrolyser to 150 °C. Add 5 mL of DI water to the first clean vial labeled "blank". Then add 5 mL of sample to each of three clean and labeled vials. Carefully add a "Pillow" packet to each vial. Replace cap the tightly and shake to thoroughly mix the sample. Run all vials through the pre-heated hydrolyser for 30 minutes. Remove vials from the hydrolyser and let the vials cool to room temperature.

Step 2—Processing the Samples

Following the cooling process of the vials, add 2 mL of sodium hydroxide to each vial including the standard using a TenSette© Pipette. Add 0.5 mL of Molybdovanadate to each vial including the standard using a Bulb Pipette. Replace each vials cap and invert to mix. Then allow the mixed vials to rest for seven to nine minutes before taking a measurement. Remove the cover from the colorimeter to insert the vial labeled "blank". Replace colorimeter cover securely and press "Zero" to calibrate the measurements. Repeat this process with the remaining sample vials pressing "Read" instead of "Zero.

Step 3—Standardization and Measurement

Ensure the proper insert adapter is intact in the colorimeter. Power on the colorimeter and select Program 87 for measurement collection. Place the "blank" vial into the insert adapter and replace the cover. Allow the instrument to stabilize before taking a measurement.

Method- For Differentiating Orthophosphate and Pyrophosphates:

The second method, as described below, was used to determine the pyrophosphate concentration of the sample by measuring the initial orthophosphate concentration. Prior to adding to the "Test 'N Tube$^{\text{TM}}$" vials, the samples are diluted to an appropriate level to ensure that their measurements fall within 10.0-100.0 mg/L PO_4^{3-}. The dilution rates for this method were typically around 4%- 5% to achieve an acceptable reading. The vials are filled with sample and a Potassium Persulfate Pillow for Phosphonate. Immediately following the addition of the Pillow the measurement must be taken using the Hach® DR/890 Colorimeter. For this method the hydrolysis process and subsequent methods are not done.

Step 1—Sample Preparation

Prepare the proper dilution using the same methods outlined above. Differentiating Orthophosphates and Pyrophosphates will require the use of six vials for six repetitions instead of three vials for each sample. The first three vials for each sample will undergo the exact process as outlined in the methods above and in the Test Methods Booklet. The remaining three vials are also subjected to the same process, but do not go through the hydrolysis step. The result of the first three vials reveals the total phosphate, while the result of the last three vials reveals the initial orthophosphate. Thus, the difference of the results is the initial pyrophosphate in solution.

Analysis:

Results are reported in mg/L PO_4^{3-}. Once the measurement is finished, the diluted results can then be back-calculated a full-sample result. This is done by taking into account the dilution rate and the approximate lack of phosphate in the de-ionized water. For example, if a 3% sample yielded 65, 70, and 75 mg/L PO_4^{3-}, the average of 70 mg/L PO_4^{3-} would then be converted to full-sample result by:

$$\left(70\,\frac{mg}{L}\,PO_4^{3-}\right) * \left(\frac{100\%}{3\%}\right) = 2333.3\overline{33}\,\frac{mg}{L}\,PO_4^{3-}$$

A10. Test Method for Determining Inhibitor Degradation by Ultraviolet Radiation

Organic-based corrosion inhibitors may be subject to ultraviolet (UV) radiation degradation that could potentially decrease the effectiveness of the inhibitor. The purpose of this standard operating procedure addresses the use of UV-a and UV-b wavelengths in a temperature controlled environment to determine the effects ultraviolet radiation has on the corrosion inhibitor found in liquid and solid deicers. Results from this experiment will be used in conjunction with an ultraviolet-visible spectroscopy (UV/Vis) test and total phosphorus calorimetry (for phosphorus-containing corrosion inhibitors) to determine the impacts of UV-a/-b on corrosion inhibitor effectiveness.

Method:

UV degradation testing is conducted at the Montana State University Subzero Cold Lab facility. For each experiment within the study, the cold lab is set to a specific temperature, based on prescribed experimental design schedule, and allowed to equilibrate at each temperature regime for 12 hours. An experimental design schedule was generated to incorporate random combinations of experiments using parameters such as; inhibitor type (FreezGard CI Plus, CCB, NaCl+GLT, and IceSlicer Elite), temperature, UV intensity (UV-a, UV-b, and UV-a + UV-b, no UV exposure), and UV exposure time (24 to 96 hours). Temperature regimes of 42°C, 28°C, 18°C, and -9.4°C were chosen for this study to include a wide spectrum of temperatures that mimic storage conditions in the field. A four-tiered shelving unit is used to set up each experiment where each shelf represents a UV radiation wavelength. The top shelf is for control samples with no UV exposure. The second shelf is for samples that are exposed both UV-a + UV-b wavelengths. The third and fourth shelves are the UV-a and UV-b exposures, respectively.

Step 1- Sample Preparation

Liquid deicer samples are prepared from undiluted deicer sample solutions. If the deicer is a solid, the solid deicer is put into a solution by adding 100mL of DI water to 23 grams of solid deicer and stirred over low heat for five minutes. From the randomized experimental design schedule (Attachment 1) nine samples are run for each temperature regime. Each of those nine samples is replicated five times. Each sample is measured placed in a clean, non-UV-resistant Petri dish with a lid. The Petric dishes are weighed empty with a lid and this weight is recorded (Attachment 2). The samples are labeled on the side of the Petri dish to avoid influencing UV penetration to the deicers. The deicer sample is added to the Petri dish in 5mL aliquots of liquid deicer sample and 15mL aliquots of solid deicer solution sample for temperature regimes of 18°C and -9.4°C. At temperature regimes of 40°C and 28°C the volume of deicer solution is doubled per Petri dish to reduce the loss of sample through evaporation. The lid is then placed on the Petri dish and the final weight of Petri dish plus deicer is recorded.

Step 2- Sample Testing

Testing will begin when the cold lab has equilibrated to the specified temperature regime. The UVP® Compact Handheld Ultraviolet lamps are affixed to the shelving unit and turned on and the Petri dishes with deicers are placed on the specified UV wavelength shelf according to the experimental design schedule. The dishes are adjusted under the lamps so each dish is equally exposed to the UV light from above. The inside of the cold lab is darkened at the start of the experiment. The cold lab windows are covered to avoid contamination from any external light sources.

<u>Analysis:</u>

Once the samples are removed from the cold lab they are immediately weighted. The initial weight is then subtracted from the final weight and recorded on the weights data sheet to determine evaporative losses. At this point the Petri dish lid and base are sealed together with Parafilm to avoid sample loss through evaporation or handling. Samples are organized by exposure time per experiment and are wrapped with aluminum foil to avoid further light exposure.

These samples will be analyzed to determine the inhibitor degradation (Test Method for Determining Inhibitor Concentration of a Deicer Solution and Test Method for Determining Total Phosphorus in a Solid Deicer). Inevitably, the deicer solutions lost mass through evaporation during the photo degradation experiment. For experimental analysis samples were rehydrated to the original aliquot of deicer solution using the weight loss calculations. After rehydration, the five replicates of each deicer were combined in a seven dram vial to obtain enough volume for analysis. For liquid deicers the final volume for analysis was 25mL and for solid deicers 75 mL.

APPENDIX B. MIXING AND SAMPLING METHODS FOR LIQUID AND SOLID DEICERS

B1. Liquid Deicer Mixing and Sampling Methods

The purpose of this method protocol is to standardize the mixing and sampling of the deicer tanks for the deicer and inhibitor longevity in storage portion of the project. The three liquid deicers; FreezGard CI Plus, Calcium Chloride with Boost (CCB), and salt brine plus Shield GLT (NaCl+GLT) are contained in six 3000-gallon Norwesco® above-ground tanks located outside, and stored in a containment basin at the TRANSEND cold regions test-bed in Lewistown, MT. Each of the three deicers was stored in designated “mixed” and “non-mixed” tanks.

Tank Mixing

The three “mixed” tanks will be mixed once a week for one hour for the first month of testing and twice monthly for one hour thereafter. Equipment needed for the mixing includes; a flat-head screw driver, robber boots, 220-volt extension cord, chemical resistant gloves, cordless power drill with Torx25 drill bit, and paper towels.

The deicer tanks are equipped with a 2” ball valve at the top and bottom of every tank. The three “mixed” tanks will be mixed using designated pump boxes each containing a 2” pump with power/power switch and two-2” hoses. Each pump and “mixed” tank has a permanently attached 2” hose connecting the bottom valve of the tank to the inlet of the pump. The second hose connects from the outlet of the pump to the top valve on the “mixed” tank creating a vortex to ensure uniform mixing. The hose and the tank both have protective end caps that need to be removed before connecting.

The 2” ball valves are opened once the “mixed” tank is properly connected to the pump. Use a power drill and a Torx25 screw tip to open all the pump boxes prior to use so the pumps can vent during operation. Plug the male end of the 220-volt extension cord into the power box outside of the containment area and the female end into the switch on the pump box. Turn the pump on from the switch on the side of the pump box and let each of the three tanks mix for 1 hour. Only one tank will mix at once due to power limitations at the site.

Turn the pump off after one hour of mixing using the switch. Unplug the extension cord from power pole before unplugging from pump. Move extension cord to the next pump and plug in the pump first followed by plugging back into the power pole. Shut both 2” ball valves (upper and lower) on the previously mixed. Disconnect the hose from the upper connection on the tank, and replace the hose and valve protective caps. Begin connecting the second tank after ensuring proper closure and shutdown of the previous mixed tank. When all three tanks have been mixed, closed and each pump box secured, ensure all valves are closed as well, and all protective end caps are replaced. Coil up and properly store the 220-volt extension cord in the on-site shop facility.

Tank Sampling

Tanks will be sampled immediately following the second tank mixing of the month. One-liter deicer samples will be collected from each tank once a week for the first month and once monthly thereafter for a total of 12 months. Samples will be collected by opening the bottom valve of the “mixed” and “non-mixed” tanks immediately following mixing of the “mixed” tanks at which point the liquid deicer is collected into the sterilized 1 L plastic bottle, sealed and labeled with mixing strategy, deicer type, date, time and personal.

Stratified samples of the mixed and non-mixed tanks will be collected once every six months to determine if the deicer solutions in the tanks remained homogenous over time. Using an eight foot ladder to access the top of the deicer tank, use a Van Dorn Bottle® to collect a representative sample at three levels; top, middle, and bottom beginning with the top. Collect each sampled in a sterilized 1 L plastic bottle sealed and labeled with mixing strategy, deicer type, date, time, depth of sample and personal. Wash and rinse the Van Dorn Bottle® between each deicer type and mixing strategy.

B2. Solid Deicer Sampling Methods

The sampling method for the solid NaCl deicer (IceSlicer Elite) includes collecting samples from both the storage enclosure and the pile left outside following the ASTM D 632 method, which requires at least three sub-samples to be selected at random from the top, middle and bottom profiles of each storage pile. This is to ensure a representative cross-section of the material being collected. A sub-sample will be obtained from a randomly chosen area within the top third, at the midpoint, and at the bottom third of the total volume of material. Following the specifications provided by the Washington State DOT, we will use a sampling tube for sub-sample collection to ensure a cross sectional representation of the materials. The sample tube will be constructed of thick-walled PVC pipe 1 ½″ in diameter and no less than 48″ long with a tapered 45-degree edge on one end to obtain desired sample depths and quantities. Each sub-sample will be collected by scraping aside the top layer of material to a depth of at least one inch then driving the sampling tube into the material to a depth of no less than six inches to collect a total target sample of at least five pounds. The collected sub-samples of the solid deicer will be thoroughly mixed in the 5-gallon bucket to make up one composite sample representative of the storage pile.

APPENDIX C. STORM EVENTS AND FIELD SAMPLING METHODS

C1. Black Ice Field Sampling Event Field Anti-Icer Application and Sampling Standard Operating Procedure

The following standard operating procedure (SOP) has been developed by the Corrosion and Sustainable Infrastructure Laboratory (CSIL) at the Western Transportation Institute, Montana State University (WTI/MSU) to apply and sample deicers or anti-icers in a field situation for deicer samples investigated in the Pooled Fund Study led by the Pacific Northwest Snowfighters (PNS) Association. This SOP was developed through pilot field and laboratory efforts within this project's scope.

The purpose of this procedure is to apply and sample liquid anti-icers on a roadway. Samples collected through this SOP will be tested according to the SOPs detailed in the Laboratory Standard Operating Procedures.

A test section within the drive surface area has been chosen to accommodate four test lanes with dimensions of 12 feet by 100 feet and six 18 foot buffer zones. The 18 foot wide buffer zone will provide the requisite separation needed to minimize contamination between test lanes. This buffer zone will also provide a staging area for the sampling activities. Prior to test section set-up and application of the liquid anti-icers, the test sections will be cleared and washed with water to reduce the potential contamination of collected samples from the drive surface (**Figure 12**).

Figure 11 Clearing and washing test sections on the driving surface area using a plow truck and high pressure hose.

Once the washing is complete and the drive surface is dry, the four test section lanes will be demarcated using orange and blue safety cones. Three of the test section lanes are designated for the three anti-icing liquid products and the fourth will serve as a control section. Once the test section has been prepared, the anti-icing liquids (CCB, FreezGard CI Plus, and NaCl+GLT) will be applied to delineated test lanes using the anti-icing applicator trailer at a rate of 30 gallons per lane mile. No anti-icers will be applied over the control lane. The anti-icer application trailer uses nozzles with a flow rate of 5 gallons per minute at 25 pounds per square inch of pressure. Vehicle speed was calculated at 10.0 miles per hour (mph), 9.1 mph, and 8.1 mph to apply 30 g/l-m of CCB, FreezGard Cl Plus, and NaCl+GLT, respectively. Each anti-icer will be mixed in its storage container using air agitation techniques prior to filling application tanks on the application trailer.

To calculate more precisely the actual amount of liquid deicer applied to each test section three sets of five Petri-dishes will be used to collect anti-icer during application. The dishes will be labeled and pre-weighed using a scale measuring out to one one-hundredth of a gram. The Petri dishes will then be placed within the test sections between test plots and driven over with the anti-icer application trailer. The dishes will be collected in Ziploc storage bags and reweighed following anti-icer application. Based on weight measurements and the specific gravity of the anti-icers we can more accurately quantify the application rate in each sample plot. Results will be recorded for each anti-icer immediately following application and photographs will be taken during and after anti-icer application.

Between each anti-icer application the entire application system will be flushed with warm well water from a raised tank for three to four minutes (**Figure 13**a). Following the warm water flush all nozzles will be removed and cleaned separately. The system will be flushed a second time with the nozzles off and the trailer boom will be rinsed using warm well water. After flushing, rinsing, and nozzle replacement the next anti-icer will be flushed through the system to remove any remaining water and to prevent the system from freezing for the next application (**Figure 13**b).

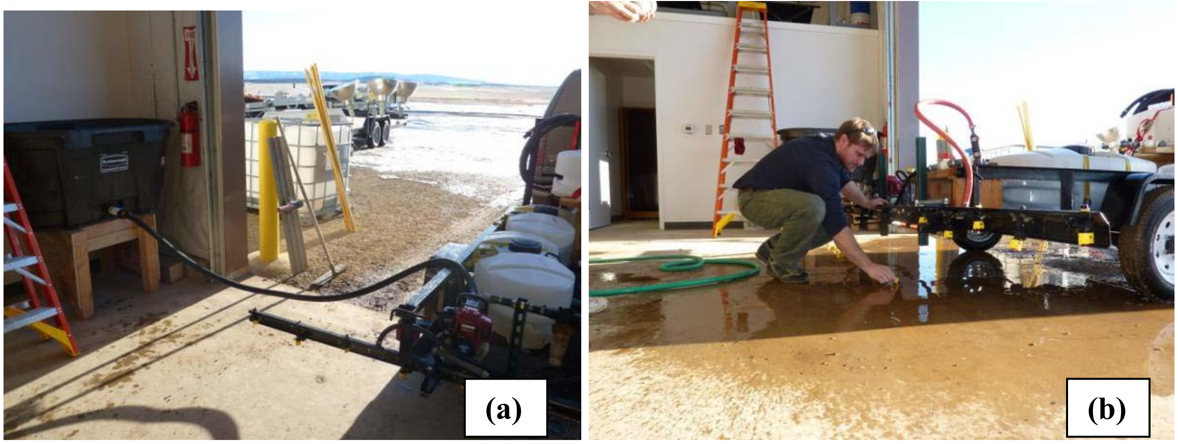


Figure 12 Raised tank filled with warm well water connected to the trailer to flush the system (a) and replacing clean nozzles for final flush with the next anti-icer (b).

Each test lane will contain seven sets of sample plots. The sample plots will be spaced twelve and a half feet from each other and the upper and lower edge of the test lane (**Figure 14**). Each test box will measure 32”x 32” and will be constructed using a High Tech© silicone sealant. The sealant will serve as a dike; it will extend above the drive surface a minimum of 0.375 inches to prevent the anti-icer and free liquids from flowing out of the sample box. The silicone sealant needs to fully cure before the anti-icer application activities begin (**Figure 15**).

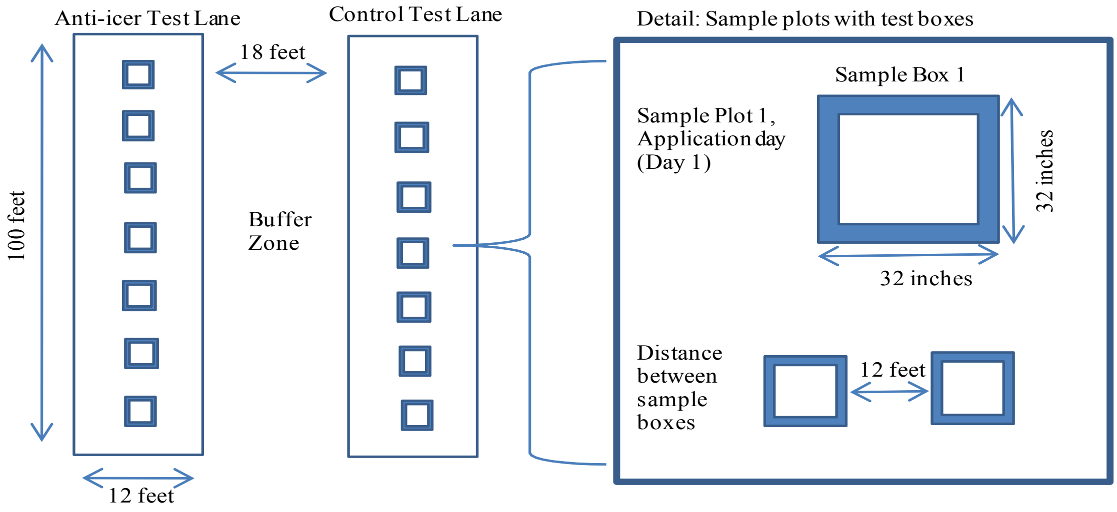


Figure 13 Diagram of test lanes and sample plot layout

Figure 14 Example of sample boxes (32”x32”) laid out on the asphalt surface using silicone sealant in test sections.

Each sample plot represents one of seven timed sample events. For the black-ice storm event the first timed sample will be collected immediately following anti-icer application and labeled “Sample-day 1” with plot number, date, time, and anti-icer type. The second timed event, associated with the second sample plot, must occur the day following anti-icer application and labeled “Sample-day 2” again with plot number, date, time, and anti-icer type. Sampling will continue following this schedule and labeling style up to seven days following anti-icer application or until environmental factors and/or other adequate data shows that no more deicer and inhibitor is present in the test section.

No snow making activities will occur for the black-ice event. The black-ice event will take place within a reasonably predicted 7-day time period of dry weather after anti-icers have been applied to each test section. Photographs will be taken of weather and pavement conditions at the time of sample collection. Detailed notes including air temperature, pavement temperature and cover (if any from blowing snow), wind speed, cloud cover, and precipitation (if any) will be collected daily during the seven day sampling period to record natural weather occurrences and anti-icer performance.

The sample collection process will begin by first adding 1 liter (L) of DI water to each sample box. The de-ionized water will aid in anti-icer recovery and vacuum collection (**Figure 16**a).

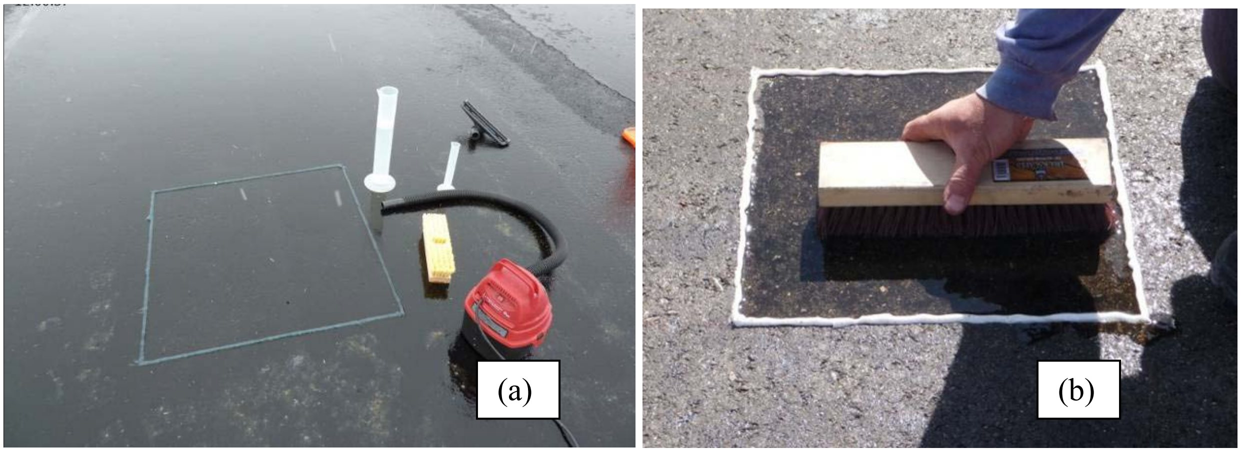


Figure 15 Sample test boxes shown after addition of 1 L of DI water (a) and sample test box agitation technique (b).

Figure 16 Sample collection using a vacuum with squeegee attachment.

Before the DI water is vacuum collected from the surface, it will be agitated with a clean 14" coarse bristle brush for a period of two minutes (**Figure 16**b). After the two minute agitation period, the liquid will then be vacuumed from the test surface using a small vacuum with a squeegee attachment (Figure 17). The sample is then poured from the vacuum cylinder into a labeled 1 L plastic bottle. After sampling of test box is complete the vacuum hose, squeegee attachment, cylinder, and agitation brush will be thoroughly washed and rinsed with de-ionized water. For operational efficiency and prompt sample collection a crew of two personnel will assist with test section preparation, anti-icer application, and sample collection procedures.

C2. Man-made Snow Sampling Event Field Anti-Icer Application and Sampling Standard Operating Procedure

The following standard operating procedure (SOP) has been developed by the Corrosion and Sustainable Infrastructure Laboratory (CSIL) at the Western Transportation Institute, Montana State University (WTI/MSU) to apply and sample deicers or anti-icers in a field situation for deicer samples investigated in the Pooled Fund Study led by the Pacific Northwest Snowfighters (PNS) Association. This SOP was developed through pilot field and laboratory efforts within this projects scope.

The purpose of this procedure is to apply and sample liquid anti-icers on a roadway. Samples collected through this SOP will be tested according to the SOPs detailed in the Laboratory Standard Operating Procedures.

A test section within the drive surface area has been chosen to accommodate four test lanes with dimensions of 12 feet by 100 feet and six 18 foot buffer zones. The 18 foot wide buffer zones will provide the requisite separation needed to minimize contamination between test lanes. This buffer zone will also provide a staging area for the sampling activities. Prior to test section set-up and application of the liquid anti-icers, the test section will be cleared and washed with water to reduce the potential of contaminants being collected with the samples from the drive surface (see Figure 12).

Once the washing is complete and the drive surface is dry, four test lanes within the test section will be demarcated with orange and blue safety cones. Three of the test lanes are designated for the three anti-icing liquid products and the fourth will serve as a control lane. Once the test lanes have been prepared and demarcated, the anti-icing liquids (CCB, FreezGard CI Plus, and NaCl+GLT) will be applied using the anti-icing applicator trailer at a rate of 60 gallons per lane mile. No anti-icers will be applied over the control lane. The anti-icer application trailer is equipped with a boom suspending 13 stainless steel XR TeeJet Extended Range Flat Spray nozzle tips. The nozzle tips are spaced 11.5 inches on-center and are raised approximately 11 inches from the drive surface. The anti-icer application trailer nozzles have a flow rate of 5 gallons per minute at 25 pounds per square inch of pressure. Driving at a speed of 5 miles per hour will yield an application rate of 60 gallons per lane mile for CCB for example. Each anti-icer will be mixed in its storage container using air agitation techniques prior to filling application tanks on the application trailer.

To validate the application rate of the liquid anti-icers applied and to account for inconsistencies due to moderate nozzle overlap (drilling) each test lane will accommodate four sets of five Petri-dishes to collect anti-icer during application. The dishes will be labeled and pre-weighed using a scale measuring out to one one-hundredth of a gram. The Petri dishes will be placed within the test lanes between sample plots and driven over with the anti-icer application trailer. Following application of anti-icers the dishes will be collected; the outside surface wiped clean, and then placed in Ziploc storage bags and reweighed immediately following anti-icer application. Drill marks from nozzle overlap will be counted in each sample plot and compared with the corresponding Petri-dish sample set. Based on weight and specific gravity measurements of the anti-icers we can more accurately quantify the application rate in each sample plot. Results will be recorded for each anti-icer immediately following application and photographs will be taken during and after anti-icer application, in addition to notes on product performance and drill mark patterns.

Between each anti-icer application the entire application system will be flushed and rinsed with warm well water from a raised tank for three to four minutes (see Figure 13a). After flushing and rinsing, the next anti-icer will be flushed through the system to remove any remaining water and to prevent the system from freezing prior to the next application (see Figure 13b).

Immediately following anti-icer application, snowmaking activities will commence. Three Turbocrystal© snow guns will be located around the test sections based on current wind speed and direction. Once the equipment is in place and air temperatures are in range, snowmaking over the test section will begin. Snowmaking will continue until a minimum depth of 1 inch of snow has been achieved over each test lane.

The manmade snow event will take place within a reasonably predicted 7-day time period of dry weather after anti-icers have been applied and snow has been made over each test lane. Snowmaking for the event will occur with ambient air temperatures ranging from 15-25 degrees Fahrenheit, pavement temperature readings below freezing, and wind speeds below 6 miles per hour to maximize accurate and timely snow depth accumulations.

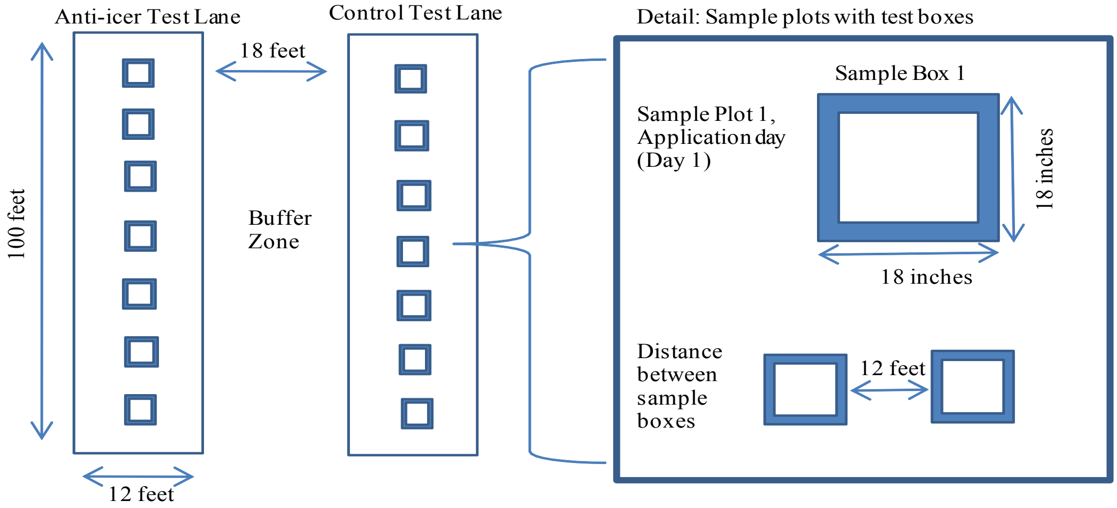


Figure 17 Diagram of test lanes and sample plot layout.

Each test lane will contain seven sets of sample plots. The sample plots will be spaced 12 feet from each other and the upper and lower edge of the test lane (Figure 18). Each sample plot will measure 18 by 18 inches and will be constructed using a High Tech© silicone sealant prior to anti-icer application and snowmaking activities. The sealant will serve as a dike; extending above the drive surface a minimum of 0.375 inches to prevent the anti-icer and free liquids from flowing out of the sample box. The silicone sealant needs to cure for approximately one hour before the anti-icer application activities begin (Figure 19).

Figure 18 Example of a sample box (18 by 18 inches) laid out on the asphalt surface within a test lane using silicone sealant.

Each sample plot represents one of seven timed sample events. Immediately following the snowmaking activities each sample plot will be leveled off to a known depth of ½ inches using a metal frame with dimensions 18 ¼ by 18 ¼ by ½ inches. The frame will be placed on the sample plot cutting through the manmade snow. A flat metal bar 20 by ½ by 1/8 inches will be used to uniformly skim the excess snow off the top to attain a uniform snow depth for each sample plot of ½ inches. All sample boxes will be leveled off immediately following snow making activities. For the manmade storm event the first sample will be collected immediately following leveling of the "Sample-day 1" sample plot and labeled "Sample-day 1" with plot number, date, time, and anti-icer type. The second sample will be collected the following day and labeled "Sample-day 2" with plot number, date, time, and anti-icer type. Sampling will continue following this schedule and labeling style up to seven days following anti-icer application or until environmental factors and/or other adequate data shows that no more deicer and inhibitor is present in the test plots.

The sample collection process will begin by first collecting and melting the snow remaining in the sample plot. Based on data collected from previous projects, manmade snow typically has a snow water density between 35 and 40% with a weight of 24 lbs/ft^3. With sample plot dimensions of 18 by 18 by ½ inches the volume of water from the snow melt will range between 929 mL and 1061 mL of water with a weight of approximately 2.25 lbs per sample plot. The melted snow will be measured in a graduated cylinder and then placed in a labeled 1 L plastic bottle. The volume of water collected in the form of snow melt on sample day one will replace the addition of DI water to the sample plot. Subsequently, 0 to 1000 mL of de-ionized water was added to the 18x18 inch sampling box (see Figure 16a), depending on the amount of snowmelt water in the sampling box. In all cases, each sampling day would yield typically 1000 mL of liquids collected from the pavement, providing adequate volumes for laboratory testing.

Before the snow melt and/or de-ionized water is vacuum collected from the surface, it will be agitated with a clean 14 inch coarse bristle brush for a period of two minutes (see Figure 16b).

After the two minute agitation period, the liquid will then be vacuumed from the test surface using a small vacuum with a squeegee attachment (see Figure 17). The sample will then be poured from the vacuum cylinder back into a graduated cylinder to record the volume of the sample recovered then collected in a labeled 1 L plastic bottle. After sampling of each test box is complete the vacuum hose, squeegee attachment, cylinder, and agitation brush will be thoroughly washed and rinsed with DI water. One test box for each sample day will yield approximately 1 L of sample providing an adequate volume for laboratory testing. For operational efficiency a crew of three personnel will assist with test section set-up and washing, sample plot layout, anti-icer application, and snowmaking activities. A crew of two personnel will carry out sample collection procedures throughout the seven day period.

Photographs will be taken of weather and pavement conditions at the time of anti-icer application, snowmaking, and sample collection. Detailed notes including air temperature, pavement temperature and snow cover remaining, wind speed, cloud cover, and natural precipitation (if any) will be collected daily during the seven-day sampling period.

C3. Natural Snow Event Field Anti-Icer Application and Sampling Standard Operating Procedure

The following standard operating procedure (SOP) has been developed by the Corrosion and Sustainable Infrastructure Laboratory (CSIL) at the Western Transportation Institute, Montana State University (WTI/MSU) to apply and sample deicers or anti-icers in a field situation for deicer samples investigated in the Pooled Fund Study led by the Pacific Northwest Snowfighters (PNS) Association. This SOP was developed through pilot field and laboratory efforts within this project's scope.

The purpose of this procedure is to apply and sample liquid anti-icers on a roadway. Samples collected through this SOP will be tested according to the SOPs detailed in the Laboratory Standard Operating Procedures.

A test section within the drive surface area has been chosen to accommodate four test lanes with dimensions of 12 feet by 100 feet and six 18 foot buffer zones. The 18 foot wide buffer zones will provide the requisite separation needed to minimize contamination between test lanes. This buffer zone will also provide a staging area for the sampling activities. Prior to test section set-up and application of the liquid anti-icers, the test section will be cleared and washed with water to reduce the potential of contaminants being collected with the samples from the drive surface (see Figure 12).

Once the washing is complete and the drive surface is dry, four test lanes within the test section will be demarcated with orange and blue safety cones. Three of the test lanes are designated for the three anti-icing liquid products and the fourth will serve as a control lane. Once the test lanes have been prepared and demarcated, the anti-icing liquids (CCB, FreezGard CI Plus, and NaCl+GLT) will be applied using the anti-icing applicator trailer at a rate of 60 gallons per lane mile. No anti-icers will be applied over the control lane. The anti-icer application trailer is equipped with a boom suspending 13 stainless steel XR TeeJet Extended Range Flat Spray nozzle tips. The nozzle tips are spaced 11.5 inches on-center and are raised approximately 11 inches from the drive surface. The anti-icer application trailer nozzles have a flow rate of 5 gallons per minute at 25 pounds per square inch of pressure. Driving at a speed of 5 miles per hour will yield an application rate of 60 gallons per lane mile for CCB for example. Each anti-icer will be mixed in its storage container using air agitation techniques prior to filling application tanks on the application trailer.

To validate the application rate of the liquid anti-icers applied and to account for inconsistencies due to moderate nozzle overlap (drilling) each test lane will accommodate four sets of five Petri-dishes to collect anti-icer during application. The dishes will be labeled and pre-weighed using a scale measuring out to one one-hundredth of a gram. The Petri dishes will then be placed within the test lanes between sample plots and driven over with the anti-icer application trailer. The dishes will be collected; the outside surface wiped clean, and then placed in Ziploc storage bags and reweighed immediately following anti-icer application. Drill marks from nozzle overlap will be counted in each sample plot and compared with the corresponding Petri-dish sample set. Based on weight and specific gravity measurements of the anti-icers we can more accurately quantify the application rate in each sample plot. Results will be recorded for each anti-icer immediately following application and photographs will be taken during and after anti-icer application, in addition to notes on product performance and drill mark patterns.

Between each anti-icer application the entire application system will be flushed and rinsed with warm well water from a raised tank for three to four minutes (see Figure 13a). After flushing and rinsing, the next anti-icer will be flushed through the system to remove any remaining water and to prevent the system from freezing prior to the next application (see Figure 13b).

The natural snow event will take place within a reasonably predicted 7-day time period of precipitation with an estimated snowfall of 1-4 inches over the first 24 hours. Anti-icers will be applied over each test lane prior (within 5 hrs) of the predicted start of the natural snow event. Ambient air temperature, pavement temperature, and wind speed will be recorded throughout the test event.

Each test lane will contain seven sets of sample plots. The sample plots will be spaced 12 feet from each other and the upper and lower edge of the test lane (Figure 20). Each sample plot will measure 18 by 18 inches and will be constructed using a High Tech© silicone sealant prior to anti-icer application and snowmaking activities. The sealant will serve as a dike; extending above the drive surface a minimum of 0.375 inches to prevent the anti-icer and free liquids from flowing out of the sample box. The silicone sealant needs to cure for approximately one hour before the anti-icer application activities begin.

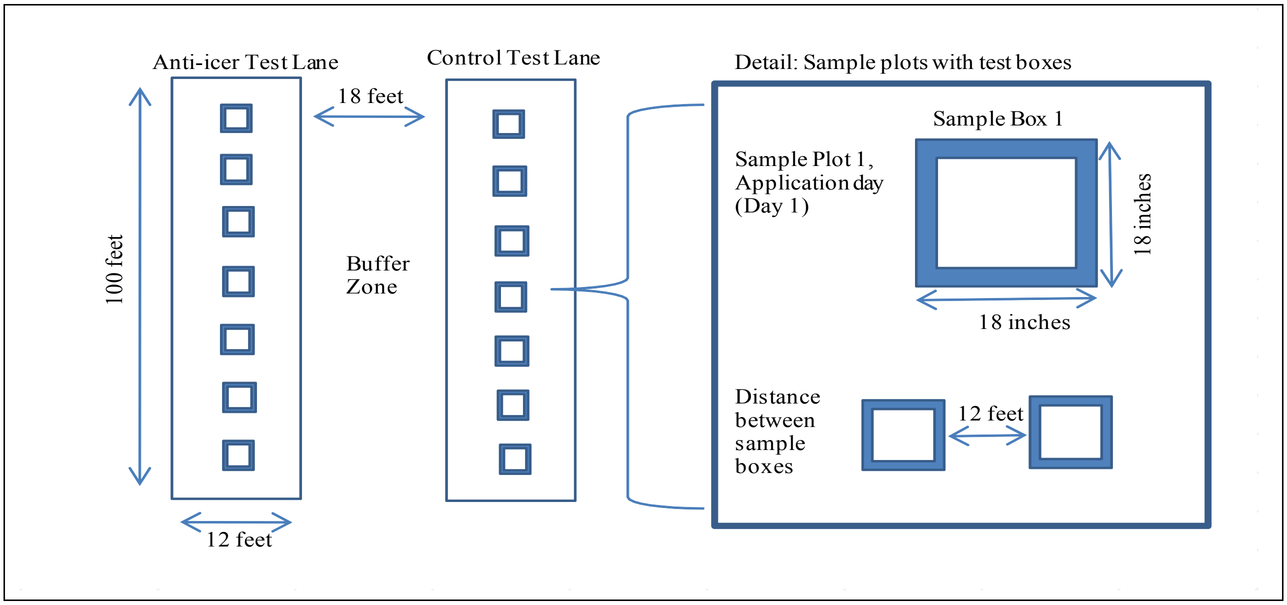


Figure 19 Diagram of test lanes and sample plot layout.

Each sample plot represents one of seven timed sample events. Following the 24hr precipitation each sample plot will be leveled off to a known depth of ½ inches using a metal frame with dimensions 18 ¼ by 18 ¼ by ½ inches. The frame will be placed on the sample plot cutting through the natural snow. A flat metal bar 20 by ½ by 1/8 inches will be used to uniformly skim the excess snow off the top to attain a uniform snow depth for each sample plot of ½ inches. All sample boxes will be leveled off on Day 1 of the experiment.

For the natural storm event the first sample will be collected immediately following leveling of the "Sample-day 1" sample plot and labeled "Sample-day 1" with plot number, date, time, and anti-icer type. The second sample will be collected the following day and labeled "Sample-day 2" with plot number, date, time, and anti-icer type. Sampling will continue following this schedule and labeling style up to seven days following anti-icer application or until environmental factors and/or other adequate data shows that no more deicer and inhibitor is present in the test plots.

The sample collection process will begin by first collecting and melting the snow remaining in the sample plot. Based on typical snow water equivalent values, natural spring snow typically has a snow water density between 20 and 40%. With sample plot dimensions of 18 by 18 by ½ inches the volume of water from the snow melt will range between 550 mL and 1061 mL of water. The melted snow will be measured in a graduated cylinder and then placed in a labeled 1 L plastic bottle. The volume of water collected in the form of snow melt on sample day one will replace the addition of DI water to the sample plot unless the snow melt is less than 1 L at which point the difference will be added as DI water. Dilution rates for the remaining six day sample period will be based on the addition of 1 L of DI water. Depending on the weather following "day one" sampling, if the measured amount of snow melt does not equal 1 L it will be subtracted from 1 L of DI water, and this amount of DI water will be added to the sample plot and vacuum collected (see Figure 16a).

Before the snow melt and/or DI water is vacuum collected from the surface, it will be agitated with a clean 14 inch coarse bristle brush for a period of two minutes (see Figure 16b). After the two minute agitation period, the liquid will then be vacuumed from the test surface using a small vacuum with a squeegee attachment (see Figure 17). The sample will then be poured from the vacuum cylinder back into a graduated cylinder to record the volume of the sample recovered then collected in a labeled 1 L plastic bottle. After sampling of each test box is complete the vacuum hose, squeegee attachment, cylinder, and agitation brush will be thoroughly washed and rinsed with DI water. One test box for each sample day will yield approximately 1 L of sample providing an adequate volume for laboratory testing. For operational efficiency a crew of three personnel will assist with test section set-up and washing, sample plot layout, and anti-icer application. A crew of two personnel will carry out sample collection procedures throughout the seven day period.

Photographs will be taken of weather and pavement conditions at the time of anti-icer application, snowfall, and sample collection. Detailed notes including air temperature, pavement temperature and snow cover remaining, wind speed, cloud cover, and natural precipitation (if any) will be collected daily during the seven-day sampling period.

APPENDIX D. FIELD OPERATION TEST REPORTS

D1. Black Ice Event Field Report (February 9-16, 2010)

The following field report has been prepared by the Corrosion and Sustainable Infrastructure Laboratory (CSIL) at the Western Transportation Institute, Montana State University (WTI/MSU) and is based on the application and sampling of anti-icers in a field situation using products investigated in the Pooled Fund Study led by the Pacific Northwest Snowfighters (PNS) Association. The field investigation and following report was based on the Black-Ice Event Standard Operating Procedure (SOP) developed through pilot field and laboratory efforts within this project's scope. Samples collected from this field test will be analyzed according to the SOPs detailed in the Laboratory Standard Operating Procedure.

Test Section Preparation

On February 9, 2010 W TI researchers traveled to the TRANSCEND Winter Testing facility in Lewistown, MT to begin the black-ice storm event. Ambient air temperatures upon arrival were 3°F. There was little wind no blowing snow and the sky was clear. In advance of the event a test section within the drive surface area on the monster pad was chosen to accommodate four test lanes with dimensions of 12 ft by 100 ft. Two 18 Ft buffer zones and two 50 ft buffer zones divided the test lanes providing the separation needed to minimize contamination between test lanes and offer a staging area for anti-icer application and sampling activities. The test lanes and buffer zones were washed with water and a high pressure nozzle to reduce the potential of contaminants being collected with the samples from the drive surface (Figure 21a). After the test section was washed and allowed to dry the four test lanes representing three anti-icer lanes and one control lane were demarcated with orange and blue safety cones (Figure 21b).

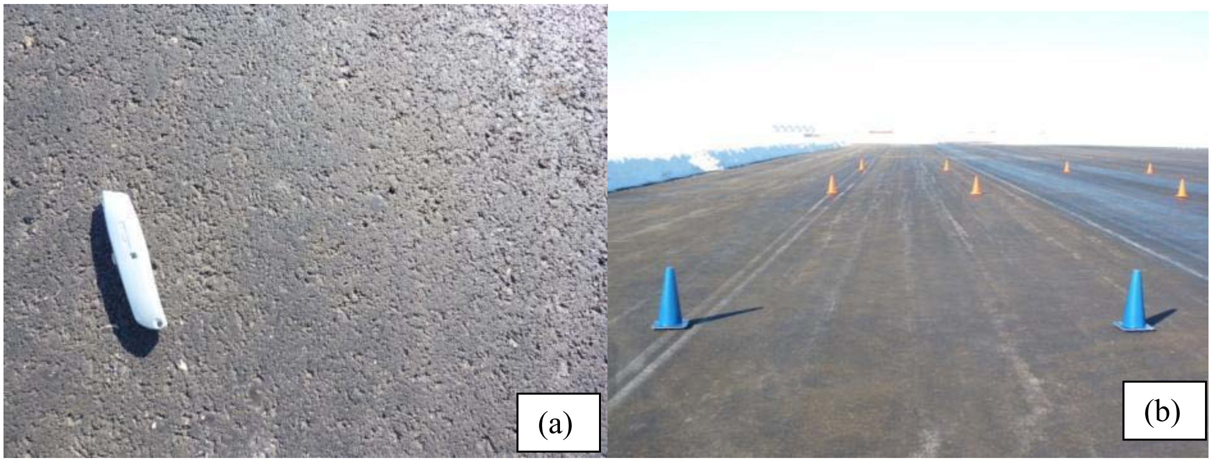


Figure 20 Condition of pavement after washing (a) and test lane layout using safety cones (b)

Seven sets of sample plots were constructed in each test lane using a clear High Tech™ silicone sealant (Figure 22a). Pavement temperatures for sample plot construction were 25° F. The sample plots were spaced twelve and a half feet from each other and the upper and lower edge of the test lane. Each sample plot was 32 x 32 inches with the sealant extending .375 inches from the pavement surface. Once the sample plots were completed they were allowed to cure overnight before anti-icing activities (Figure 22b).

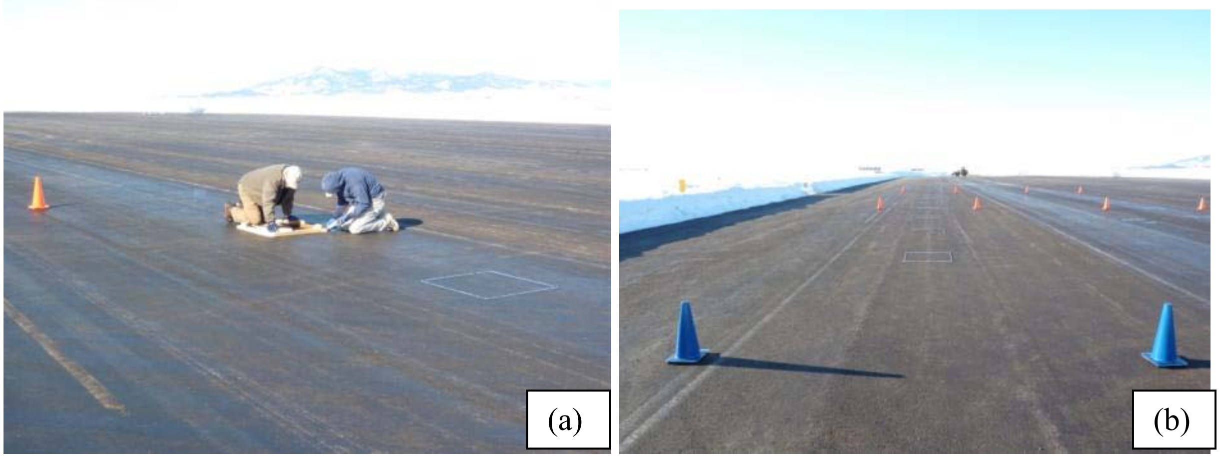


Figure 21 Silicone sample plot construction (a) and test section layout with sample plot completion (b)

Anti-Icer Application

Anti-icer application began at 8:00 a.m. on February 10, 2010 with the placement of Petri-dishes in the anti-icer FreezGard CI Plus test lane. Nine sets of five new Petri-dishes (three sets for each deicer) were weighed and recorded out to one one-hundredths of a gram. Each set was then placed in a clean Ziploc storage bag for transportation to and from the sample lanes to minimize evaporative loss during transport. Ambient air temperature was 27°F; pavement temperature was 20°F, winds up to 8 mph and no blowing snow. Cloud cover was 50%. The dishes were situated throughout the test lanes at the same width of the sample plot to capture specific application rates for correlation to each sample plot (Figure 23a). Once the Petri-dishes were in place, the anti-icing liquids (CCB, FreezGard CI Plus, and NaCl+GLT) were applied to delineated test lanes at a rate of 30 gallons per lane mile (g/l-m) using the anti-icing applicator trailer. No anti-icers were applied over the control test lane. The anti-icer application trailer used nozzles with a flow rate of 5 gallons per minute at 25 pounds per square inch of pressure. Vehicle speed was calculated at 10.0 mph, 9.1 mph, and 8.1 mph to apply 30 g/l-m of CCB, FreezGard Cl Plus, and NaCl+GLT, respectively. Each anti-icer was mixed in its storage container using air agitation techniques prior to filling the anti-icer tanks on the application trailer.

Between each anti-icer application the Petri-dishes were collected and their exteriors wiped clean and replaced into Ziploc storage bags to avoid evaporative losses of the sample. While the collected Petri-dishes were being re-weighed, the application system was flushed with warm well water from a raised tank for three to four minutes and the application boom was rinsed using a spray nozzle on a garden hose. After flushing and rinsing the next anti-icer was flushed through the system to remove any remaining water and to prevent the system from freezing for the next application. Following the system flush the next set of Petri dishes were laid out for the next anti-icer to be applied.

After application of the deicer FreezGard it was noted that the application system technique left “drill mark” patterns throughout the test lane and sample plots (Figure 23b). Drill mark patterns were also obvious in the CCB test lane after application. Due to the difference in viscosity of the anti-icer chemicals drill mark patterns were not as evident in the NaCl+GLT test lane. This was an obvious concern due the possibility that the amount of product applied to each sample plot was inconsistent. However, after weighing the collected Petri-dishes and noting precisely the location of the dishes corresponding to each sample plot, the data gives us an actual application rate for each test plot. Drill marks associated with each test plot were noted to have the same pattern in the corresponding Petri dish sample set. Since we have the capability of quantifying the application rate for each test plot we can us the Petri dish data to determine an actual applied rate in mL for each test plot taking the drill marks into account in the final calculations.

Figure 22 Petri-dish set placement near sample plot prior to application of the anti-icer NaCl+GLT (a) and drill mark patterns of the anti-icer FreezGard obvious in the sunlight (b).

To accomplish the desired application rate, each anti-icer required a specific flow rate and application speed based on application trailer calibrations. NaCl+GLT was applied at a rate of 4.05 gallons per minute at a speed of 8.1 mph. FreezGard CI Plus and CCB were applied at a rate of 4.55 gpm and 5.00 gpm respectively while maintaining speeds of 9.1 mph and 10.0 mph respectively. Actual speeds were 8.0, 9.0 and 10.0 respectively due to limitations associated with the speed control of the vehicle used to tow the application trailer.

Actual application rates were based on weight measurements and the specific gravity of each anti-icer. Results were used to determined sample dilution rates, actual application rates per sample plot, and difference in desired application rate vs. actual application rate (Table 3). Using mL of deicer in each test plot and the total amount of water added we are able to calculate a dilution rate for each sample plot for use in laboratory calculations. Photographs were taken during and after anti-icer application.

Table 3 Petri dish data collected for the Black Ice Event for FreezGard CI Plus, CCB, and NaCl+GLT.

FreezGard Calcs (Set 1)	***Results***	***Units***
Deicer weight in 5 dishes	0.92	grams
Deicer density	10.79	lb/gallon
Deicer specific gravity	1.30	
Desired applied rate	30	gplm
Actual applied rate	17.82	gplm
Actual applied rate/box	7.57	mL
Dilution rate	0.75	%

FreezGard Calcs (Set 2)	***Results***	***Units***
Deicer weight in 5 dishes	1.69	grams
Deicer density	10.79	lb/gallon
Deicer specific gravity	1.30	
Desired applied rate	30	gplm
Actual applied rate	32.74	gplm
Actual applied rate/box	13.91	mL
Dilution rate	1.37	%

FreezGard Calcs (Set 3)	***Results***	***Units***
Deicer weight in 5 dishes	1.79	grams
Deicer density	10.79	lb/gallon
Deicer specific gravity	1.30	
Desired applied rate	30	gplm
Actual applied rate	34.68	gplm
Actual applied rate/box	14.73	mL
Dilution rate	1.45	%

CCB Calcs (Set 1)	*Results*	*Units*
Deicer weight in 5 dishes	1.60	grams
Deicer density	11.12	lb/gallon
Deicer specific gravity	1.34	
Desired applied rate	30	gplm
Actual applied rate	30.06	gplm
Actual applied rate/box	12.77	mL
Dilution rate	1.26	%

CCB Calcs (Set 2)	*Results*	*Units*
Deicer weight in 5 dishes	1.69	grams
Deicer density	11.12	lb/gallon
Deicer specific gravity	1.34	
Desired applied rate	30	gplm
Actual applied rate	31.75	gplm
Actual applied rate/box	13.49	mL
Dilution rate	1.33	%

CCB Calcs (Set 3)	*Results*	*Units*
Deicer weight in 5 dishes	1.70	grams
Deicer density	11.12	lb/gallon
Deicer specific gravity	1.34	
Desired applied rate	30	gplm
Actual applied rate	31.94	gplm
Actual applied rate/box	13.57	mL
Dilution rate	1.34	%

GLT Calcs (Set 1)	*Results*	*Units*
Deicer weight in 5 dishes	1.70	grams
Deicer density	9.86	lb/gallon
Deicer specific gravity	1.19	
Desired applied rate	30	gplm
Actual applied rate	36.02	gplm
Actual applied rate/box	15.30	mL
Dilution rate	1.51	%

GLT Calcs (Set 2)	*Results*	*Units*
Deicer weight in 5 dishes	1.81	grams
Deicer density	9.86	lb/gallon
Deicer specific gravity	1.19	
Desired applied rate	30	gplm
Actual applied rate	38.35	gplm
Actual applied rate/box	16.29	mL
Dilution rate	1.60	%

GLT Calcs (Set 3)	*Results*	*Units*
Deicer weight in 5 dishes	1.69	grams
Deicer density	9.86	lb/gallon
Deicer specific gravity	1.19	
Desired applied rate	30	gplm
Actual applied rate	35.80	gplm
Actual applied rate/box	15.21	mL
Dilution rate	1.50	%

Field Sampling

Collection of the first set of samples, “Sample day 1” from plot 1 of each test lane began approximately one hour following anti-icer application at 11:23 a.m. on February 10, 2010. Sample collection began by first adding 1 L of DI water to the sample plot and agitating for a period of two minutes with a clean 14” coarse bristle deck brush. Following agitation the sample was collected using a small vacuum with a squeegee attachment. The sample was then poured from the vacuum cylinder to a 1000 mL graduated cylinder to record recovery levels in milliliters then poured into a clean and labeled 1 L plastic bottle. Sample collection was completed from all four test lanes approximately forty-five minutes later. Each sample was labeled “Sample-day 1” with plot number, date, time, collector’s initials, anti-icer type, and volume recovery. Sample collection equipment was thoroughly washed and rinsed with DI water prior to use for the next sample plot. DI water for sampling activities was provided daily by the Corrosion and Sustainable Infrastructure Laboratory in Bozeman, MT.

Anti-icer was noticeable in all boxes and test lanes prior to sampling (Figure 24a). After sample collection from plot 1 from the FreezGard CI Plus test lane it was noted that no anti-icer was visible when compared the surrounding test lane (Figure 24b). Ambient air temperature on “Sample day 1” was 27°F with 50% relative humidity. Wind speeds were 6-8 mph from the south; pavement conditions were clean and dry, there was no evidence of blowing snow, no precipitation was recorded in the sample plots or collection pans, and cloud cover was approximately 50%.

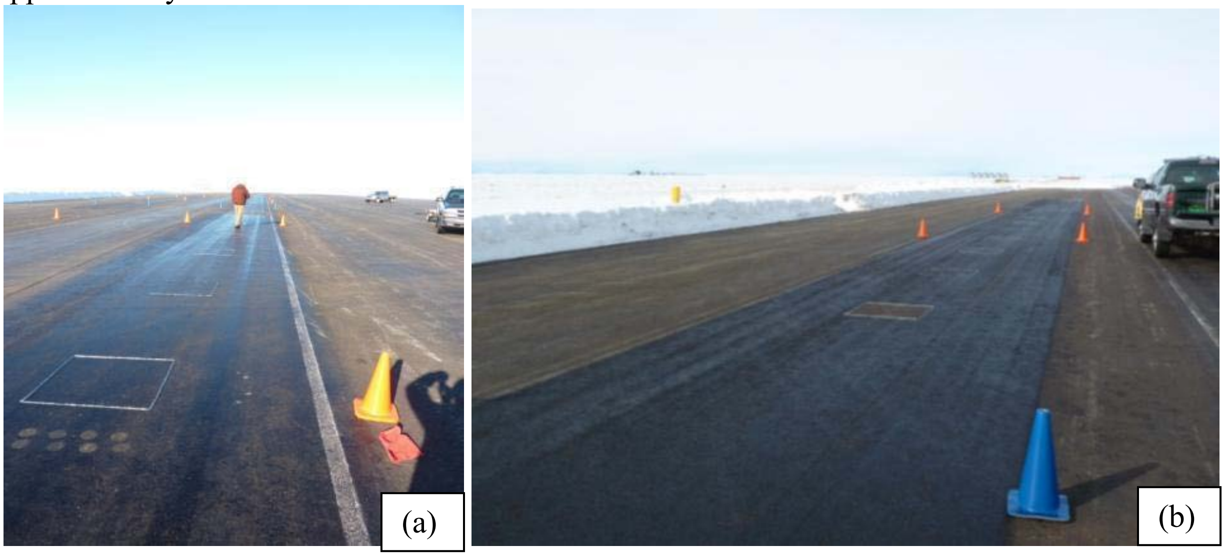


Figure 23 The anti-icer NaCl+GLT after application obvious in plots and test lanes (a) No anti-icer FreezGard CI Plus is visible after collection of “Sample day 1”, plot #1 (b).

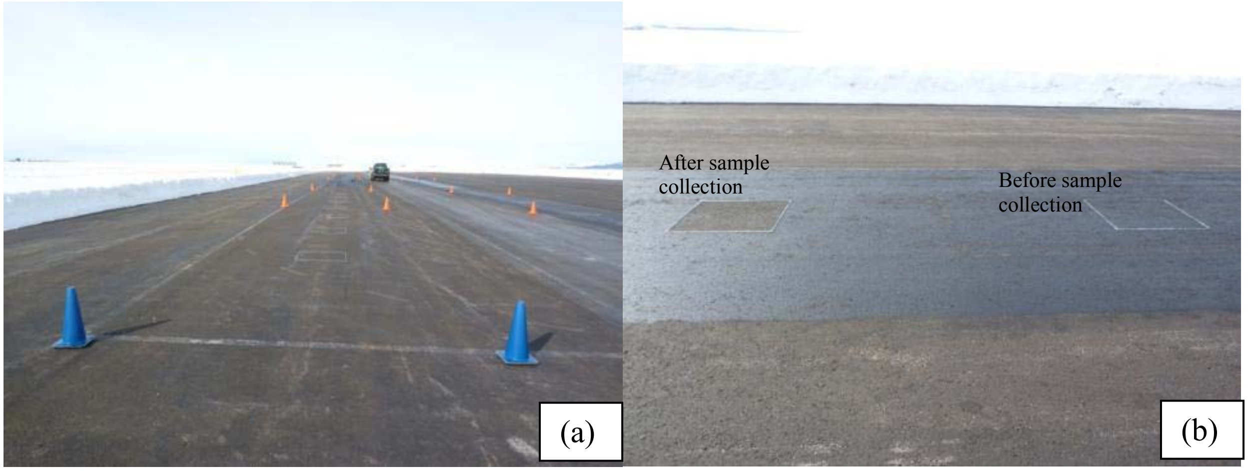


Figure 24 Sample day 2 test section conditions (a) and the FreezGard test section sample day one and day two (b).

“Sample day 2”was clear and sunny with an ambient air temperature of 48°F. The test sections were clean and dry with no overnight precipitation observed (Figure 25a). Evidence of deicers remaining on the test lanes was still visible (Figure 25b). Figure 25 (b) shows the difference in the amount of deicer present on the pavement when comparing a sampled and a non-sampled test plot. Wind speeds were 6-8 mph from the southwest; pavement conditions were clear and dry, there was no evidence of blowing snow, no precipitation was recorded in the plots or pans, and cloud cover was approximately 20%. Sampling began at 11:39 a.m. and was completed by 12:45 p.m. A rain gauge was installed on sample day 2 in addition to the 4-precip collection pans in anticipation of predicted storm event. The weather forecast predicted 50% chance of snow on the evening of day 2 and the morning of day 3.

"Sample day 3," February 12, 2010, test section conditions upon arrival were dry and clear with an ambient air temperature of 42°F. Applied liquid deicer remained visibly present in all test lanes. Wind speeds were 10 mph from the west, pavement conditions were clear and dry, there was no evidence of blowing snow, no precipitation was recorded in the plots or gauges, and cloud cover was 100%. Sampling began at 11:20 a.m. and was completed at 12:33 p.m.

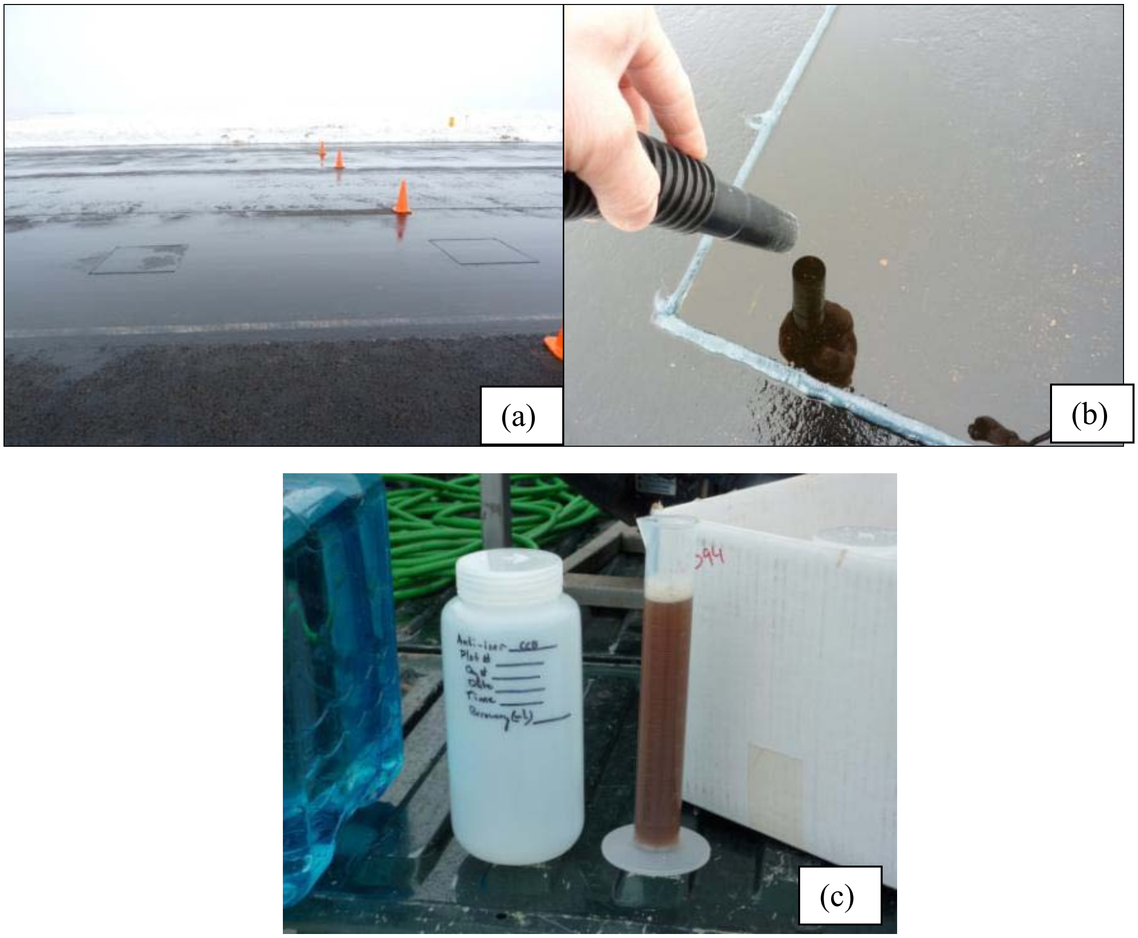


Figure 25 Test section conditions upon arrival with free water in the sample plots (a) collection of free water prior to addition of DI water (b) and measuring volume of free water for DI water addition (c).

"Sample day 4," February 13, 2010, test sections upon arrival were wet with obvious precipitation accumulation in the sample plots (Figure 26a). The test lanes were visibly wet and with no indication of applied liquid deicer. Close observation of the test plots indicated deicer suspended in the free standing water within the CCB test plot (Figure 26b). Wind speeds were 7 mph from the north northwest, pavement conditions were wet with light snow falling. There was no evidence of blowing snow, approximately ¼" of precipitation in the form of snow was recorded in the precipitation collection pans from the overnight and early morning precipitation event, and cloud cover was 100%. Sampling began at 11:00 a.m. with the removal of free water from the test plot prior to the addition of DI water (Figure 26b). Collected free water was poured into a graduated cylinder to get a total volume of free water already present in the plot (Figure

26c). The collected free water was then poured into a 1 L labeled plastic bottle. To reach a total sample volume of 1000 mL, the volume of free water collected was subtracted from a total target sample volume of 1000 mL. The remainder of sample volume needed to obtain a total of 1000 mL was measured out as DI water then poured onto the sample plot to proceed with the two minute agitation process. The DI sample was vacuum collected and added to the one liter plastic bottle containing the previously collected free water.

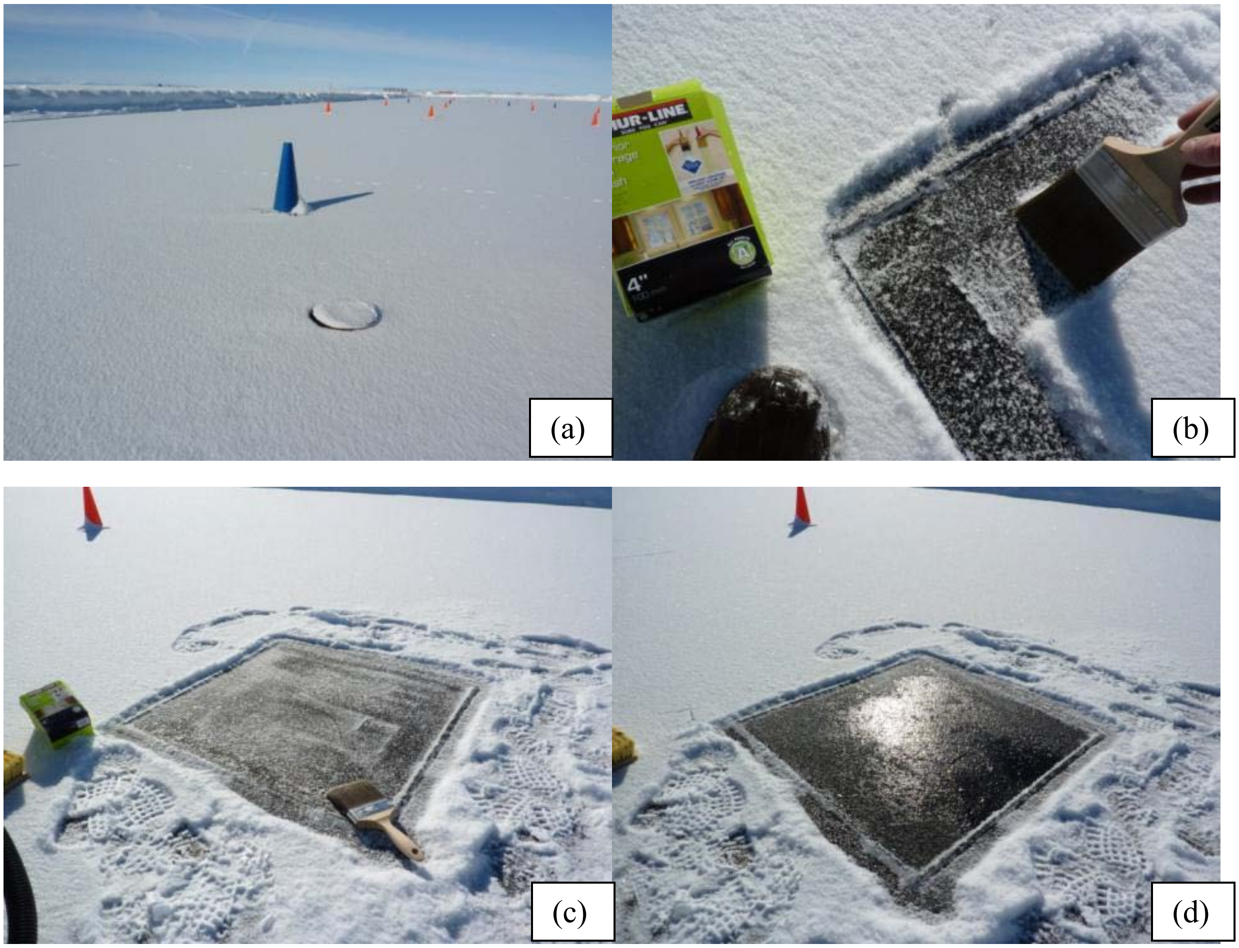


Figure 26 Sample day 5 (a) snow accumulation, (b) clearing of snow from sample boxes, (c) a cleared sample box, (d) a cleared sample box with melted ice on pavement surface.

“Sample day 5” February 14, 2010, test sections were covered with ½” of snow upon arrival. The ambient air temperature was 16°F with 62% relative humidity. Wind speeds were approximately 3 mph from the south, pavement was 100% covered with new snow, there was no evidence of blowing snow, ½” of precipitation was recorded in the plots and collection pans, and cloud cover was 5% (Figure 27a). Sampling began at 11:40 a.m. and was completed at 1:30 p.m. Beneath the layer of fresh snow was a thin layer of ice. Because of the layer of ice beneath the new snow each test plot was cleared of the new snow prior to sampling by gently brushing with a clean 4” paint brush limiting the removal of any anti-icer from box (Figure 27(b and c)). The ice melted in each sample plot prior to the addition of DI water but no free liquid was present in the plots after ice melt (Figure 27d). DI water was added and agitated as usual.

“Sample day 6” February 15, 2010, test sections were damp with free water visible in sample plots upon arrival. The ambient air temperature was 28°F and 63% relative humidity. Winds were calm, pavement was damp, there was no evidence of blowing snow, there was no evidence of 24 hr precipitation, and cloud cover was 60%. No liquid deicers were visibly present in the test lanes. Sampling began at 11:55 a.m. and was completed at 12:45 p.m.

On the final sample day “Sample day 7,” February 16, 2010, approximately ¼” inch of new snow was recorded from collection pans. The ambient air temperature was 26°F and 96% relative humidity. Wind speeds were approximately 6 mph from the east-south-east, pavement was damp, there was no evidence of blowing snow, and cloud cover was 0%. Sampling began at 9:45 a.m. and was completed at 10:45 p.m. Sampling began with the removal of free water from each test plot prior to the addition of DI water. Collected free water was poured into a graduated cylinder to get a total volume of free water already present in the plot (Figure 26c). The collected free water was then poured into a 1 L labeled plastic bottle. To reach a total sample volume of 1000 mL, the volume of free water collected was subtracted from a total target sample volume of 1000 mL. The remainder of sample volume needed to reach 1000 mL was measured as DI water then poured onto the sample plot to proceed with the two minute agitation period. The DI sample was vacuum collected and added to the one liter plastic bottle containing the previously collected free water.

D2. Man-made Snow Event Field Report (March 19-26, 2010)

The following field report has been prepared by the Corrosion and Sustainable Infrastructure Laboratory (CSIL) at the Western Transportation Institute, Montana State University (WTI/MSU) and is based on the application and sampling of deicers or anti-icers in a field situation using deicers investigated in the Pooled Fund Study led by the Pacific Northwest Snowfighters (PNS) Association. The field investigation and following report was based on the Man-Made Snow Event Standard Operating Procedure (SOP) developed through pilot field and laboratory efforts within this project's scope. Samples collected from this field test will be analyzed according to the SOPs detailed in the Laboratory Standard Operating Procedures.

Test Section Preparation

Based on predicted air temperatures, on March 19, 2010 WTI researchers traveled to the Transcend Winter Testing facility in Lewistown, MT to begin the man-made storm event. The air temperature upon arrival was 23° Fahrenheit. There was little wind no blowing snow and the sky was clear. In advance of the event a test section within the drive surface area on the monster pad was chosen to accommodate four test lanes with dimensions of 12 feet by 100 feet. Two 18 foot buffer zones and two 50 foot buffer zones divided the test lanes providing the separation needed to minimize contamination between test lanes and offer a staging area for anti-icer application and sampling activities. The test lanes and buffer zones were washed with water and a high pressure nozzle to reduce the potential of contaminants being collected with the samples from the drive surface (Figure 28(a)). After the test section was washed and allowed to dry the four test lanes representing three anti-icer lanes and one control lane were demarcated with orange and blue safety cones (Figure 28(b)).

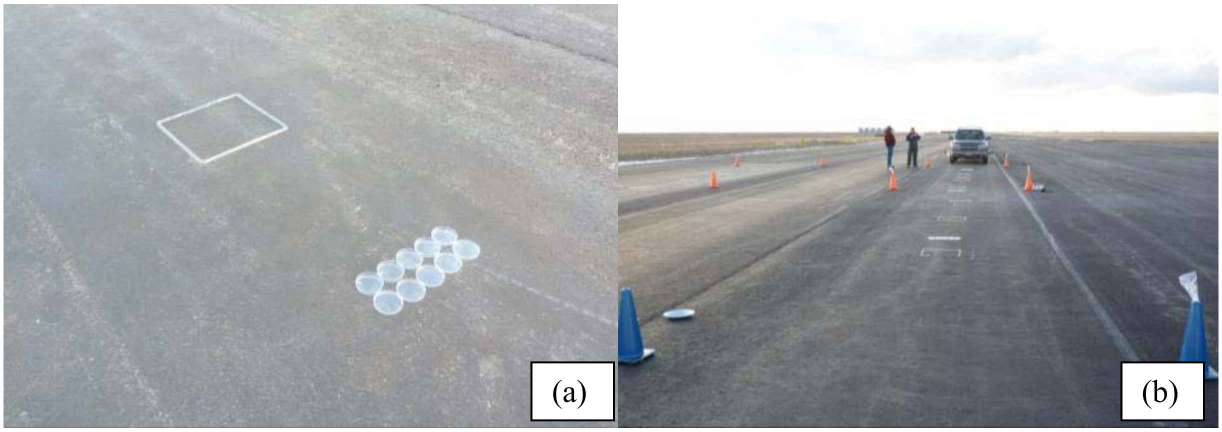


Figure 27 Condition of pavement after washing (a) and test lane layout using safety cones (b).

Seven sets of sample plots were constructed in each test lane using a clear High Tech™ silicone sealant (Figure 28(a)). The sample plots were spaced twelve and a half feet from each other and the upper and lower edge of the test lane. Each sample plot was 18 x 18 inches with the sealant extending .375 inches from the pavement surface. Once the sample plots were completed they were allowed to cure before anti-icing activities.

Anti-Icer Application

Anti-icer application began at 4:37 p.m. on March 19, 2010 with the placement of Petri-dishes in the anti-icer FreezGard test lane. To validate the application rate of the liquid anti-icers applied and to account for inconsistencies due to moderate nozzle overlap (drilling) each test lane received four sets of five Petri-dishes to collect anti-icer during application. 12 sets of five new Petri-dishes (four sets for each deicer) were weighed and recorded out to one one-hundredths of a gram. Each set was then placed in a clean Ziploc storage bag for transportation to and from the sample lanes to minimize evaporative loss during transport. Ambient air temperature was 40° F; winds up to 8 miles per hour (mph) and no blowing snow. Cloud cover was 20%. The dishes were situated throughout the test lanes at the same width of the sample plot to capture specific application rates for correlation to each sample plot (Figure 28(a)). Once the Petri-dishes were in place, the anti-icing liquids (CCB, FreezGard CI Plus, and NaCl+GLT) were applied to delineated test lanes at a rate of 60 gallons per lane mile (g/ln-m) using the anti-icing applicator trailer. No anti-icers were applied over the control test lane. The anti-icer application trailer used nozzles with a flow rate of 5 gallons per minute at 25 pounds per square inch of pressure. Vehicle speed was calculated at 5.0 mph, 4.6 mph, and 4.1 mph to apply 60 g/ln-m of CCB, FreezGard Cl Plus, and NaCl+GLT, respectively. Actual speeds were 5.0, 5.0 and 4.0 mph respectively due to limitations associated with the speed control of the Suburban used to tow the application trailer. Each anti-icer was mixed in its storage container using air agitation techniques prior to filling the anti-icer tanks on the application trailer.

Between each anti-icer application the Petri-dishes were collected and their exteriors wiped clean and replaced into Ziploc storage bags to avoid evaporative losses of the sample. While the collected Petri-dishes were being reweighed, the application system was flushed with warm well water from a raised tank for three to four minutes and the application boom was rinsed using a spray nozzle on a garden hose (Figure 29(a)). After flushing and rinsing the next anti-icer was flushed through the system to remove any remaining water and to prevent the system from freezing for the next application (Figure 29(b)). Following the system flush the next set of Petri dishes were laid out for the next anti-icer to be applied. Anti-icer application was completed on March 19, 2010 at 5:31 p.m.

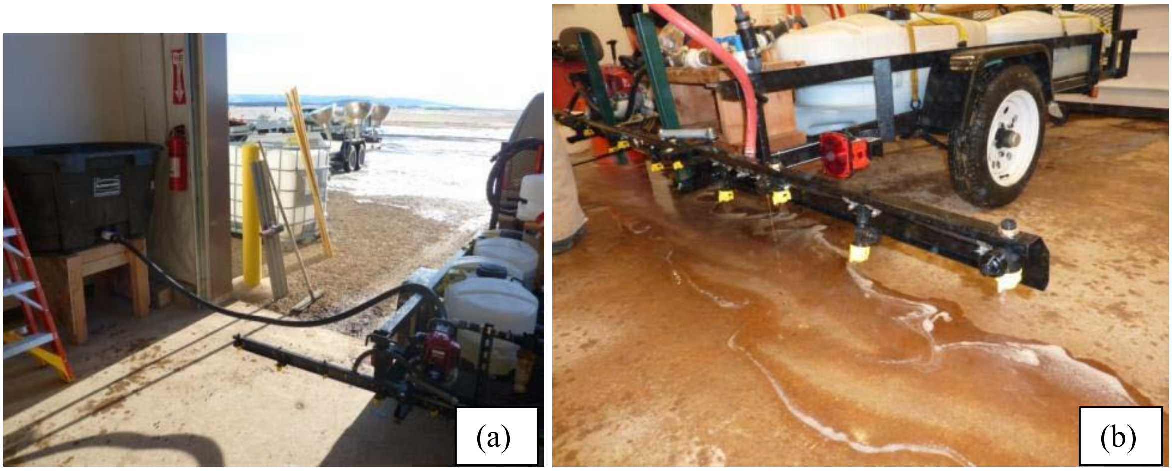


Figure 28 Raised tank filled with warm well water connected to the trailer to flush the system (a) and final flush with the next anti-icer (b).

Actual application rates were based on weight measurements and the specific gravity of each anti-icer. Results were used to determined sample dilution rates, actual application rates per sample plot, and difference in desired application rate vs. actual application rate (Table 4). Using mL of deicer in each test plot and the total amount of water added we are able to calculate a dilution rate for each sample plot for use in laboratory calculations. Photographs were taken of weather and pavement conditions at the time of anti-icer application, snowmaking, and daily sample collection. Detailed notes including air temperature, pavement temperature, snow cover remaining, wind speed, cloud cover, and natural precipitation (if any) will be collected daily during the seven day sampling period to record natural weather occurrences, anti-icer performance and man-made snow cover.

Table 4 Petri dish data collected for the Man-made Snow Event for FreezGard CI Plus, CCB, and NaCl+GLT.

FreezGard Calcs (Set 1)	*Results*	*Unit*	**FreezGard Calcs (Set 2)**	*Results*	*Unit*	**FreezGard Calcs (Set 3)**	*Results*	*Unit*	**FreezGard Calcs (Set 4)**	*Results*	*Unit*
Deicer weight in 5 dishes	2.88	grams	Deicer weight in 5 dishes	2.87	grams	Deicer weight in 5 dishes	2.93	grams	Deicer weight in 5 dishes	2.95	grams
Deicer density	10.79	lb/gallon	Deicer density	10.79	lb/gallon	Deicer density	10.79	lb/gallon	Deicer density	10.79	lb/gallon
Deicer specific gravity	1.30		Deicer specific gravity	1.30		Deicer specific gravity	1.30		Deicer specific gravity	1.30	
Desired applied rate	60	gplm	Desired applied rate	60	gplm	Desired applied rate	60	gplm	Desired applied rate	60	gplm
Actual applied rate	56	gplm	Actual applied rate	56	gplm	Actual applied rate	57	gplm	Actual applied rate	57	gplm
Actual applied rate/box	7.50	mL	Actual applied rate	7.47	mL	Actual applied rate	7.63	mL	Actual applied rate	7.68	mL
Dilution rate	0.74	%	Dilution rate	0.74	%	Dilution rate	0.76	%	Dilution rate	0.76	%

CCB Calcs (Set 1)	*Results*	*Units*	**CCB Calcs (Set 2)**	*Results*	*Units*	**CCB Calcs (Set 3)**	*Results*	*Units*	**CCB Calcs (Set 4)**	*Results*	*Units*
Deicer weight in 5 dishes	2.45	grams	Deicer weight in 5 dishes	2.63	grams	Deicer weight in 5 dishes	2.66	grams	Deicer weight in 5 dishes	2.46	grams
Deicer density	11.12	lb/gallon	Deicer density	11.12	lb/gallon	Deicer density	11.12	lb/gallon	Deicer density	11.12	lb/gallon
Deicer specific gravity	1.34		Deicer specific gravity	1.34		Deicer specific gravity	1.34		Deicer specific gravity	1.34	
Desired applied rate	60	gplm	Desired applied rate	60	gplm	Desired applied rate	60	gplm	Desired applied rate	60	gplm
Actual applied rate	46	gplm	Actual applied rate	49	gplm	Actual applied rate	50	gplm	Actual applied rate	46	gplm
Actual applied rate/box	6.19	mL	Actual applied rate/box	6.64	mL	Actual applied rate/box	6.72	mL	Actual applied rate/box	6.21	mL
Dilution rate	0.62	%	Dilution rate	0.66	%	Dilution rate	0.67	%	Dilution rate	0.62	%

GLT Calcs (Set 1)	*Results*	*Units*	**GLT Calcs (Set 2)**	*Results*	*Units*	**GLT Calcs (Set 3)**	*Results*	*Units*	**GLT Calcs (Set 4)**	*Results*	*Units*
Deicer weight in 5 dishes	2.54	grams	Deicer weight in 5 dishes	2.61	grams	Deicer weight in 5 dishes	2.58	grams	Deicer weight in 5 dishes	2.46	grams
Deicer density	9.86	lb/gallon	Deicer density	9.86	lb/gallon	Deicer density	9.86	lb/gallon	Deicer density	9.86	lb/gallon
Deicer specific gravity	1.19		Deicer specific gravity	1.19		Deicer specific gravity	1.19		Deicer specific gravity	1.19	
Desired applied rate	60	gplm	Desired applied rate	60	gplm	Desired applied rate	60	gplm	Desired applied rate	60	gplm

Actual applied rate	54	gplm	Actual applied rate	55	gplm	Actual applied rate	55	gplm	Actual applied rate	52	gplm
Actual applied rate/box	7.23	mL	Actual applied rate/box	7.43	mL	Actual applied rate/box	7.35	mL	Actual applied rate/box	7.01	mL
Dilution rate	0.72	%	Dilution rate	0.74	%	Dilution rate	0.73	%	Dilution rate	0.70	%

<u>Snow Making</u>

Snowmaking activities began immediately following anti-icer application by setting out the three Turbocrystal© snow guns and two portable light trailers. Snow making equipment was located around the test sections based on current wind speed and direction. Once the equipment was in place the research team waited for air temperatures to be within range for snowmaking. Temperatures did not drop to acceptable levels until 9:30 p.m. on March 19, 2010. Two snow guns were turned on and producing snow by 10:30 p.m. (Figure 30). Ambient air temperature was 23° F and pavement temperatures averaged 32° F. Wind speeds were 6-8 mph from the south. Snowmaking continued until 1:30 a.m. on March 20, 2010 when a consistent minimum depth of 1 inch of snow was achieved over the test area.

Figure 29 Snow guns making snow over test sections.

<u>Field Sampling</u>

Leveling of the sample plots following snowmaking activities began at 1:30 a.m. on March 19, 2010. Each sample plot was leveled off to a known depth of ½ inches using a metal frame with dimensions 18 ¼ by 18 ¼ by ½ inches. The frame was placed on the sample plot cutting through the man-made snow along the outer dimensions of the silicone test box. A flat metal bar 20 by ½ by 1/8 inches was used to uniformly skim the excess snow off the top to attain a uniform snow depth for each sample plot of ½ inches (Figure 31(a)). The artificial snow broke away from the pavement easily and in larger "sheets" (see Figure 31(a)) while removing it from around the sample plots suggesting successful elimination of the snow to pavement bond. Leveling of all sample boxes was completed at 2:45 a.m.

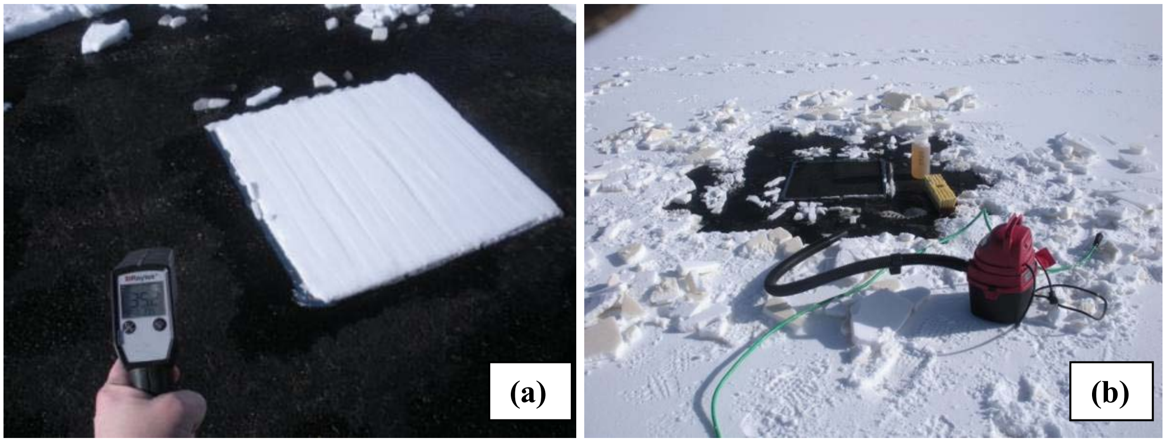


Figure 30 Example of sample box with snow leveled off to ½ inches (a) example of snow sheets around the sample box and visible coloring from the deicer on the upturned snow column (b).

Collection of the first set of samples, "Sample-day 1", began at 7:53 a.m. on March 20, 2010 approximately 14 hours after anti-icer application. The sample collection process began by first collecting and melting the ½ inches of snow remaining in the sample plots. Snow in the sample plots was visually clean on the top of the snow column; however, when the snow was collected the bottom of the snow column demonstrated coloring by the deicer suggesting slight upward migration of the deicer into the snow column (Figure 31(b)). The melted snow, collected from the test plot, was measured in a graduated cylinder. The volume of water from snow melt equaled 1420 mL, 1050 mL, 1325 mL, and 1325 mL in the FreezGard, NaCl+GLT, CCB, and Control test plots respectively. After the snow was melted and a volume recorded, it was replaced back into the appropriate test plot for agitation and vacuum recovery processes (Figure 32(a)). Total sample volumes following vacuum recovery were 935 mL, 950 mL, 1010 mL, and 940 mL of FreezGard, CCB, NaCl+GLT, and Control samples respectively. Samples were collected in a labeled 1 L plastic bottle. Sample collection was completed from all four test lanes at 10:30 a.m. Each sample was labeled "Sample-day 1" with plot number, date, time, collector's initials, anti-icer type, and volume recovery. Sample collection equipment was thoroughly washed and rinsed with DI water prior to use with the next sample plot. DI water for sampling activities was provided daily by the Corrosion and Sustainable Infrastructure Laboratory in Bozeman, MT. Ambient air temperature on "Sample day 1" was 28-35° F. Wind speeds were negligible; pavement conditions were snow covered early in the morning and clear and dry by late morning, there was no evidence of blowing snow, and cloud cover was approximately 20%.

"Sample day 2" was cloudy with an ambient air temperature of 51° F. Figure 32(b) shows snow from the event had melted off the test sections from the snow making event on March 20, 2010. Figure 32(b) also demonstrates the deicers pattern of migration outside of the test plot during the snow melt. Anti-icers were visible in all test lanes and sample boxes on day two.

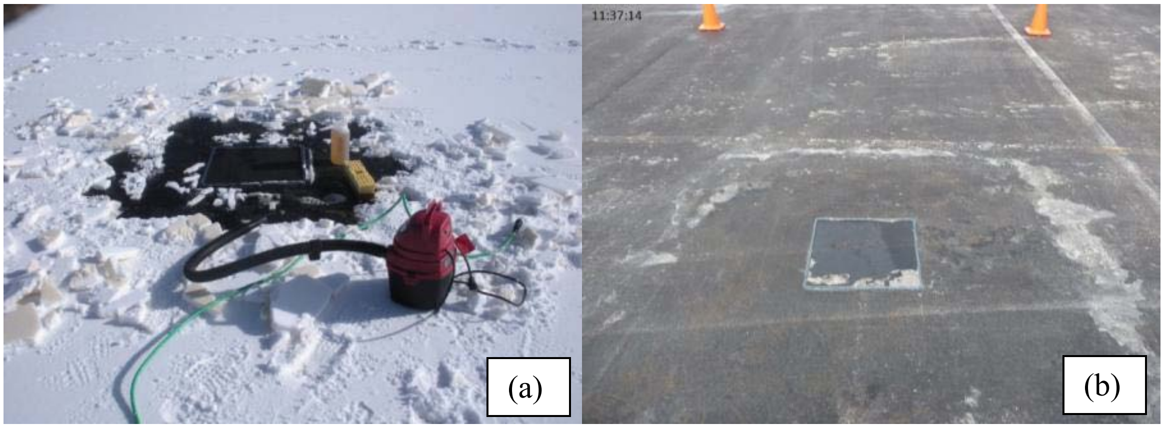


Figure 31 Sample test box shown after melting snow accumulation, replacement, agitation, and vacuum sample collection (a) and a test section with no snow and deicer visible in the un-sampled test plot (b).

Day-2 wind speeds were 21 mph from the east; pavement conditions were clear and dry, there was no evidence of blowing snow, no precipitation was recorded in the plots or pans, and cloud cover was approximately 100%. Sampling began at 12:00 p.m. and was completed by 1:15 p.m.

“Sample day 3,” March 22, 2010, test section conditions upon arrival were damp with free water standing in the test plots. Rain gauges and collection pans were noted to contain less than 1/8 inches of new precipitation. By the time sampling began at 11:39 a.m. free water in the test plots noted upon arrival had evaporated off. The ambient air temperature was 42° F. The test lanes had dried before departure showing the continued visible presence of applied liquid deicers throughout the test area. Wind speeds were 25-30 mph from the east, and cloud cover was 100%. Sampling began at 11:39 a.m. and was completed at 1:15 p.m.

“Sample day 4,” March 23, 2010, test sections upon arrival were wet with free water standing in the sample plots (Figure 33). Damp pavement conditions obscured the visibility of applied deicers within the test area. Approximately 1/8” of precipitation in the form of snow was recorded in the precipitation collection pans from the overnight and early morning precipitation event. Calm winds were from the south and cloud cover was 100%. Sampling began at 11:21 a.m. with the removal of free water from the test plot prior to the addition of DI water. Collected free water was poured into a graduated cylinder to get a total volume of free water already present in the plot. Subsequently, 0 to 1000 mL of de-ionized water was added to the 18x18 inch sampling box depending on the amount of precipitation in the sampling box. In all cases, each sampling day would yield typically 1000 mL of liquids collected from the pavement, providing adequate volumes for laboratory testing. The DI sample was agitated, vacuum collected, and added to the one liter plastic bottle containing the collected free water. Day 4 sampling was completed at 12:30 p.m.

Figure 32 Sample test box containing free standing water in the day 4 FreezGard test lane.

“Sample day 5” March 24, 2010, test section conditions upon arrival were dry and clear with an ambient air temperature of 42° F. Evidence of applied liquid deicer was visibly present in patches throughout the test lanes and within the NaCl+GLT sample box (Figure 34). Wind speeds were 5 mph from the south, pavement conditions were clear and dry, there was no evidence of blowing snow, no precipitation was recorded in the collection pans or gauges, and cloud cover was 40%. Sampling began at 10:56 a.m. and was completed at 12:10 p.m.

Figure 33 Evidence of the applied liquid deicer NaCl+GLT remains in the test box

“Sample day 6” March 25, 2010, test section conditions upon arrival were dry and clear with an ambient air temperature of 50° F. There was no visible evidence of applied liquid deicers remaining on the test sections. Wind speeds were 6-10 mph from the northeast, pavement conditions were clear and dry, there was no evidence of blowing snow, no precipitation was recorded in the plots or gauges, and cloud cover was 25%. Sampling began at 11:29 a.m. and was completed at 12:46 p.m.

On the final sample day “Sample day 7,” March 26, 2010, conditions demonstrated a trace amount of precipitation from the previous sample day of less than 1/8 inches. Sampling began with the removal of free water from each test plot prior to the addition of DI water. Winds were calm east, pavement was damp, there was no evidence of blowing snow, and cloud cover was 0%. Sampling began at 8:05 a.m. and was completed at 10:45 p.m.

D3. Natural Snow Event Field Report (April 12-19, 2010)

The following field report has been prepared by the Corrosion and Sustainable Infrastructure Laboratory (CSIL) at the Western Transportation Institute, Montana State University (WTI/MSU) and is based on the application and sampling of deicers or anti-icers in a field situation using deicers investigated in the Pooled Fund Study led by the Pacific Northwest Snowfighters (PNS) Association. The field investigation and following report was based on the Man-Made Snow Event Standard Operating Procedure (SOP) developed through pilot field and laboratory efforts within this project's scope. Samples collected from this field test will be analyzed according to the SOPs detailed in the Laboratory Standard Operating Procedures.

Test Section Preparation

Based on predicted weather forecasts, on April 12, 2010 WTI researchers traveled to the Transcend Winter Testing facility in Lewistown, MT to begin preparing for the natural storm event. Predicted forecasts indicated a 90% chance of snow accumulation on the night of April 12, 2010. The air temperature upon arrival was 40° Fahrenheit. There was little wind and cloud cover was 100%. In advance of the event a test section within the drive surface area on the monster pad was chosen to accommodate four test lanes with dimensions of 12 feet by 100 feet. Two 18 foot buffer zones and two 50 foot buffer zones divided the test lanes providing the separation needed to minimize contamination between test lanes and offer a staging area for anti-icer application and sampling activities. The test lanes and buffer zones were washed with water and a high pressure nozzle to reduce the potential of contaminants being collected with the samples from the drive surface. After the test section was washed and allowed to dry the four test lanes representing three anti-icer lanes and one control lane were demarcated with orange and blue safety cones (Figure 35(b)).

Figure 34 Clearing and washing chosen test section within the driving surface area using a plow truck and high pressure hose.

Seven sets of sample plots were constructed for use during the man-made snow event and will be used for natural storm event testing. The boxes remain sound with a strong bond to the pavement. The boxes in each test lane were constructed using a clear High Tech™ silicone sealant (Figure 35(a)). The sample plots were spaced twelve and a half feet from each other and the upper and lower edge of the test lane. Each sample plot was 18 x 18 inches with the sealant extending .375 inches from the pavement surface. Once the sample plots were completed they were allowed to cure before anti-icing activities.

Anti-Icer Application

Anti-icer application began at 4:45 p.m. on April 12, 2010 with the placement of Petri-dishes in the anti-icer FreezGard test lane. To validate the application rate of the liquid anti-icers applied and to account for inconsistencies due to moderate nozzle overlap (drilling) each test lane received four sets of five Petri-dishes to collect anti-icer during application. 12 sets of five new Petri-dishes (four sets for each deicer) were weighed and recorded out to one one-hundredths of a gram. Each set was then placed in a clean Ziploc storage bag for transportation to and from the sample lanes to minimize evaporative loss during transport. The dishes were situated throughout the test lanes at the same width of the sample plot to capture specific application rates for correlation to each sample plot (Figure 35(a)). Once the Petri-dishes were in place, the anti-icing liquids (CCB, FreezGard CI Plus, and NaCl+GLT) were applied to delineated test lanes at a rate of 60 gallons per lane mile (g/ln-m) using the anti-icing applicator trailer. No anti-icers were applied over the control test lane. The anti-icer application trailer used nozzles with a flow rate of 5 gallons per minute at 25 pounds per square inch of pressure. Vehicle speed was calculated at 5.0 mph, 4.6 mph, and 4.1 mph to apply 60 g/ln-m of CCB, FreezGard Cl Plus, and NaCl+GLT, respectively. Actual speeds were 5.0, 5.0 and 4.0 mph respectively due to limitations associated with the speed control of the Suburban used to tow the application trailer. Each anti-icer was mixed in its storage container using air agitation techniques prior to filling the anti-icer tanks on the application trailer.

Between each anti-icer application the Petri-dishes were collected and their exteriors wiped clean and replaced into Ziploc storage bags to avoid evaporative losses of the sample. While the collected Petri-dishes were being reweighed, the application system was flushed with warm well water from a raised tank for three to four minutes and the application boom was rinsed using a spray nozzle on a garden hose (Figure 36(a)). After flushing and rinsing the next anti-icer was flushed through the system to remove any remaining water and to prevent the system from freezing for the next application (Figure 36(b)). Following the system flush the next set of Petri dishes were laid out for the next anti-icer to be applied. Anti-icer application was completed on April 12, 2010 at 5:50 p.m.

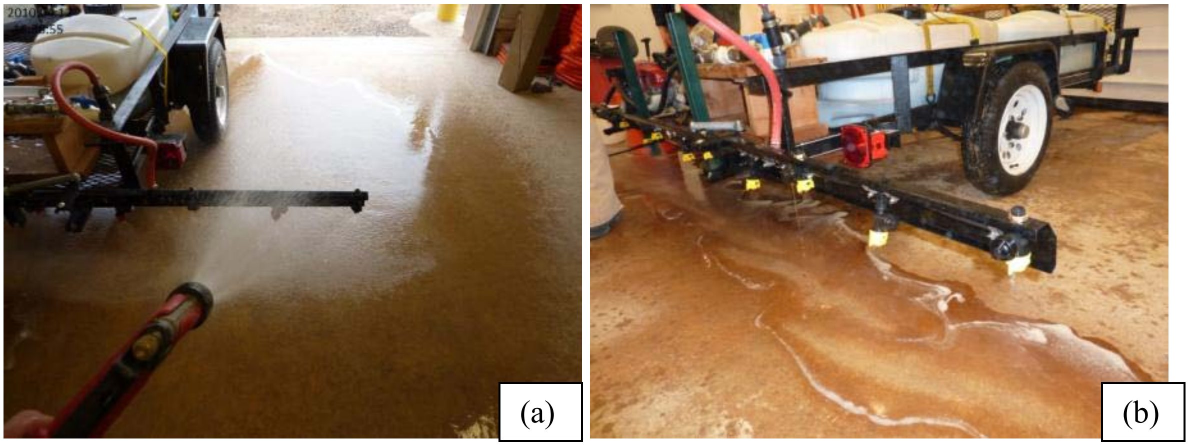


Figure 35 Garden hose with spray nozzle used for rinsing (a) and final flush with the next anti-icer (b).

Actual application rates were based on weight measurements and the specific gravity of each anti-icer. Results were used to determined sample dilution rates, actual application rates per sample plot, and difference in desired application rate vs. actual application rate (Table 5). Using mL of deicer in each test plot and the total amount of water added we are able to calculate a dilution rate for each sample plot for use in laboratory calculations. Photographs were taken of weather and pavement conditions at the time of anti-icer application, snow fall, and daily sample collection. Detailed notes including air temperature, pavement temperature, snow cover remaining, wind speed, cloud cover, and natural precipitation (if any) will be collected daily during the seven day sampling period to record natural weather occurrences, and anti-icer performance.

Table 5 Petri dish data collected for the Natural Snow Event for FreezGard CI Plus, CCB, and NaCl+GLT.

FreezGard Calcs (Set 1)	*Results*	*Unit*
Deicer weight in 5 dishes	2.84	grams
Deicer density	10.79	lb/gallon
Deicer specific gravity	1.30	
Desired applied rate	60	gplm
Actual applied rate	55	gplm
Actual applied rate/box	7.40	mL
Dillution rate	0.73	%

FreezGard Calcs (Set 2)	*Results*	*Unit*
Deicer weight in 5 dishes	3.05	grams
Deicer density	10.79	lb/gallon
Deicer specific gravity	1.30	
Desired applied rate	60	gplm
Actual applied rate	59	gplm
Actual applied rate	7.94	mL
Dillution rate	0.79	%

FreezGard Calcs (Set 3)	*Results*	*Unit*
Deicer weight in 5 dishes	3.21	grams
Deicer density	10.79	lb/gallon
Deicer specific gravity	1.30	
Desired applied rate	60	gplm
Actual applied rate	62	gplm
Actual applied rate	8.36	mL
Dillution rate	0.83	%

FreezGard Calcs (Set 4)	*Results*	*Unit*
Deicer weight in 5 dishes	2.9	grams
Deicer density	10.79	lb/gallon
Deicer specific gravity	1.30	
Desired applied rate	60	gplm
Actual applied rate	56	gplm
Actual applied rate	7.55	mL
Dillution rate	0.75	%

CCB Calcs (Set 1)	*Results*	*Units*
Deicer weight in 5 dishes	2.63	grams
Deicer density	11.12	lb/gallon
Deicer specific	1.34	

CCB Calcs (Set 2)	*Results*	*Units*
Deicer weight in 5 dishes	2.18	grams
Deicer density	11.12	lb/gallon
Deicer specific	1.34	

CCB Calcs (Set 3)	*Results*	*Units*
Deicer weight in 5 dishes	2.83	grams
Deicer density	11.12	lb/gallon
Deicer specific	1.34	

CCB Calcs (Set 4)	*Results*	*Units*
Deicer weight in 5 dishes	2.69	grams
Deicer density	11.12	lb/gallon
Deicer specific	1.34	

gravity		
Desired applied rate	60	gplm
Actual applied rate	49	gplm
Actual applied rate/box	6.64	mL
Dillution rate	0.66	%

gravity		
Desired applied rate	60	gplm
Actual applied rate	41	gplm
Actual applied rate/box	5.51	mL
Dillution rate	0.55	%

gravity		
Desired applied rate	60	gplm
Actual applied rate	53	gplm
Actual applied rate/box	7.15	mL
Dillution rate	0.71	%

gravity		
Desired applied rate	60	gplm
Actual applied rate	51	gplm
Actual applied rate/box	6.79	mL
Dillution rate	0.67	%

GLT Calcs (Set 1)	*Results*	*Units*
Deicer weight in 5 dishes	2.56	grams
Deicer density	9.86	lb/gallon
Deicer specific gravity	1.19	
Desired applied rate	60	gplm
Actual applied rate	54	gplm
Actual applied rate/box	7.29	mL
Dillution rate	0.72	%

GLT Calcs (Set 2)	*Results*	*Units*
Deicer weight in 5 dishes	2.76	grams
Deicer density	9.86	lb/gallon
Deicer specific gravity	1.19	
Desired applied rate	60	gplm
Actual applied rate	58	gplm
Actual applied rate/box	7.86	mL
Dillution rate	0.78	%

GLT Calcs (Set 3)	*Results*	*Units*
Deicer weight in 5 dishes	2.86	grams
Deicer density	9.86	lb/gallon
Deicer specific gravity	1.19	
Desired applied rate	60	gplm
Actual applied rate	61	gplm
Actual applied rate/box	8.15	mL
Dillution rate	0.81	%

GLT Calcs (Set 4)	*Results*	*Units*
Deicer weight in 5 dishes	2.88	grams
Deicer density	9.86	lb/gallon
Deicer specific gravity	1.19	
Desired applied rate	60	gplm
Actual applied rate	61	gplm
Actual applied rate/box	8.20	mL
Dillution rate	0.81	%

The Natural Storm Event

Once anti-icing was complete the research team waited until 2:00 a.m. before the snow storm began, approximately 8.75 hours after anti-icer application. The snow falling was heavy, wet, and accumulating quickly by 4:55 a.m. (Figure 37(a)). Snow accumulation reached 3.5" by 5:47 a.m. in the test area (Figure 37(b)). Snow continued to fall through 10:30 a.m. when the research team began sampling procedures.

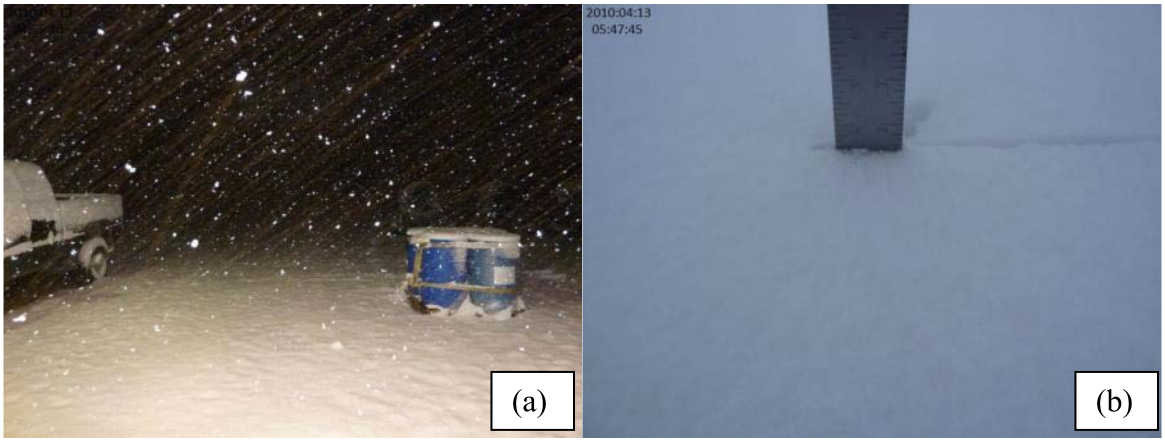


Figure 36 Snow falling outside of the shop area (a) snow depth measurement from the test area (b).

Field Sampling

Leveling of the sample plots following the natural storm event began at 10:30 a.m. on April 13, 2010. Each sample plot was leveled off to a known depth of ½ inches using a metal frame with dimensions 18 ¼ by 18 ¼ by ½ inches. The research team had to locate each sample test plot within each test section prior to applying the metal frame used in the leveling process (Figure

38(a)). Once all the test plots had been located the frame was placed on the sample plot cutting through the heavy wet snow along the outer dimensions of the silicone test box. A flat metal bar 20 by ½ by 1/8 inches was used skim the excess snow off the top to attain a uniform snow depth for each sample plot of ½ inches (Figure 38(b)). Uniform leveling of this type of snow proved to be very difficult. Snow leveling of all sample boxes was completed at 12:45 p.m.

Deicer migration into the natural snow column was observed while locating the sample test plots. Figure 38(c) shows the deicer FreezGard visibly extending into the snow column by nearly 2 inches. Figure 38(d) demonstrates the extent to which the deicer CCB was noticed in the snow column during removal around the test plots.

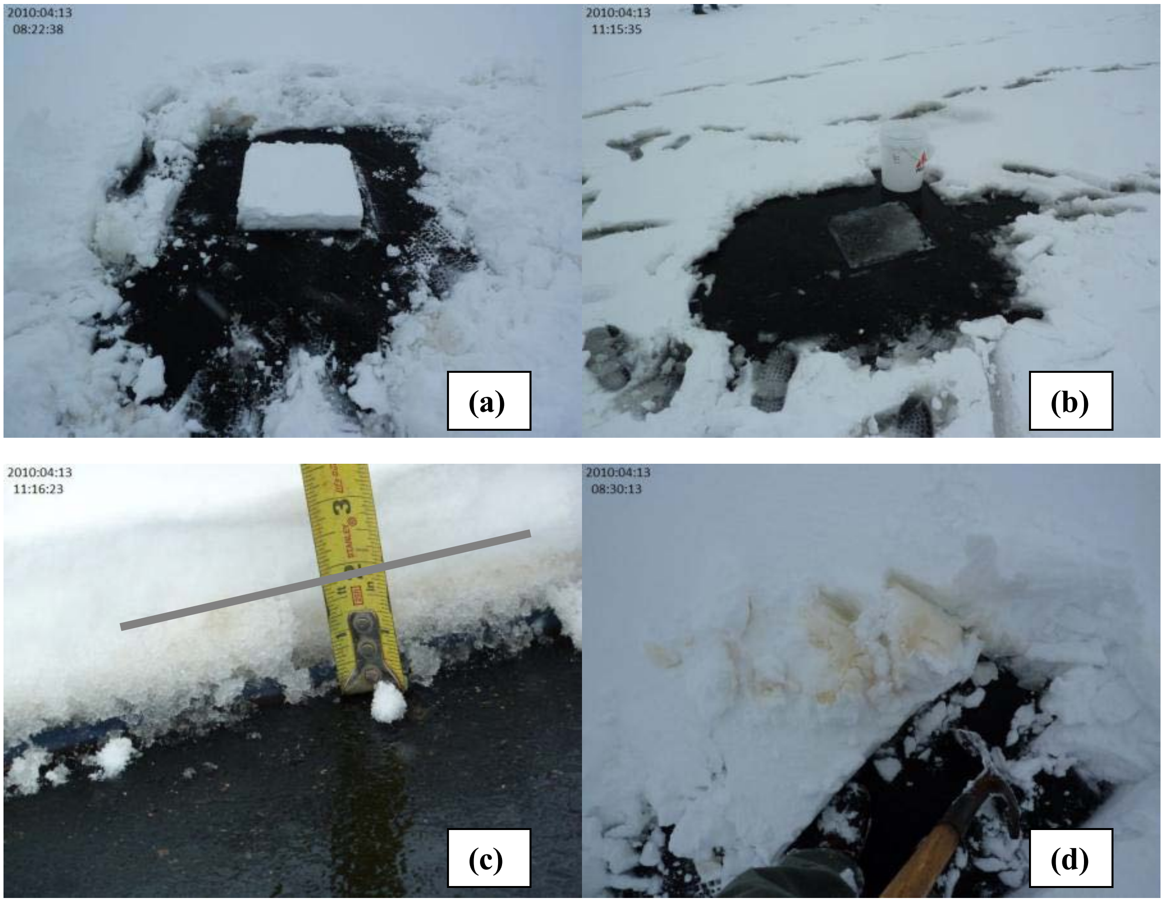


Figure 37 Removing snow surround sample test plots (a), example of test plot after leveling (note how wet the snow appears) (b), height of visible deicer in snow column denoted by gray line (c), detail of deicer discovered in snow column (d).

Collection of the first set of samples, "Sample-day 1", began at 12:45 a.m. on April 13, 2010 approximately 19.5 hours after anti-icer application. The ½ inches of snow remaining in the sample plots after leveling existed as a snow/slush mixture. The mixture maintained enough free water for agitation without removal or the addition of DI water (Figure 39(a)). Each sample plot was immediately agitated for two minutes then vacuum collected (Figure 39(b)). The mixture was allowed to melt before recovery volumes were measured and recorded. Total sample volumes following vacuum recovery were 5730 mL, 1970 mL, 2680 mL, and 3540 mL of

FreezGard, CCB, NaCl+GLT, and Control samples respectively. The discrepancy in sample volumes collected could be from the varying amount of snow/slush mixture within each sample plot from the difficulty associated with uniform leveling of heavy wet snow. Samples were collected and labeled in new 2.5-gallon plastic buckets with lids. Sample collection was completed from all four test lanes at 2:00 p.m. Each sample was labeled "Sample-day 1" with plot number, date, time, collector's initials, anti-icer type, and volume recovery. Sample collection equipment was thoroughly washed and rinsed with DI water prior to use with the next sample plot. DI water for sampling activities was provided daily by the Corrosion and Sustainable Infrastructure Laboratory in Bozeman, MT.

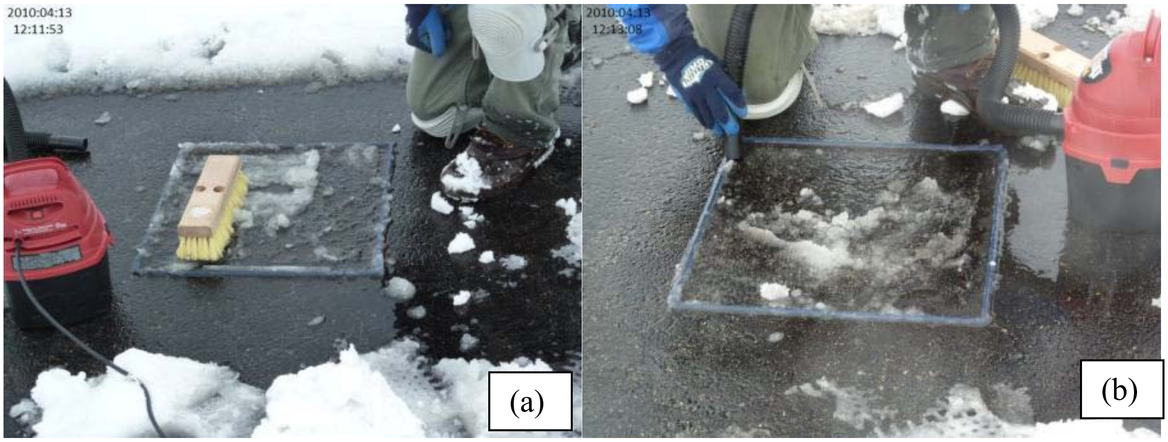


Figure 38 Sample plot after agitation (a) collection of snow/slush mixture (b).

The natural storm consisted of a heavy wet snow type typical to spring storms. Visible observation of the test area after the storm revealed heavy dilution of the applied deicer areas and significant upward migration into the snow column indicating the potential for less deicer to be collected within each sample plot. Ambient air temperature on "Sample day 1" was 30-35° F. Wind speeds began to increase throughout the day; pavement conditions were snow covered and very wet below the snow. The storm continued until 6:30 p.m. At 7:30 p.m. the wind picked up and it began to snow again.

"Sample day 2" was cloudy with an ambient air temperature of 40° F. Figure 40 shows new snow accumulation on the test area from blowing snow the previous night. Samples plots were not leveled off prior to sample collection. All of the newly accumulated windblown snow was collected from the sample plots. Anti-icers were no longer visible in all test lanes on day two.

Figure 39 Test area with new windblown snow accumulation.

Day 2 wind speeds were 21 mph from the south; pavement conditions were snow covered and wet, and cloud cover was approximately 100%. Sampling began at 10:30 a.m. and was completed by 1:15 p.m.

“Sample day 3,” April 15, 2010, test section conditions upon arrival were damp and patches of snow remained from the wind storm event the previous day. Free water was noted in the test plots. Sampling began at 10:55 a.m. with the removal of free water from the test plot prior to the addition of DI water. Collected free water was poured into a graduated cylinder to get a total volume of free water already present in the plot. Subsequently, 0 to 1000 mL of de-ionized water was added to the 18x18 inch sampling box depending on the amount of precipitation in the sampling box. In all cases, each sampling day would yield typically 1000 mL of liquids collected from the pavement, providing adequate volumes for laboratory testing. The DI sample was agitated, vacuum collected, and added to the one liter plastic bottle containing the collected free water. Day 3 sampling was completed at 12:30 p.m. No new precipitation was recorded from rain gauges or collection pans. The ambient air temperature was 52° F. Wind speeds were 10 mph from the north, and cloud cover was 0%.

“Sample day 4,” April 16, 2010, test sections upon arrival were dry and clear with an ambient air temperature of 45° F. Observation of the test area revealed little visible evidence of applied deices remaining within the test sections (Figure 41). No precipitation was recorded. Calm winds were from the south and cloud cover was 0%. Sampling began at 11:45 a.m. and was completed at 1:30 p.m.

Figure 40 Sample test lane with little visible deicer remaining.

“Sample day 5” April 17, 2010 test section conditions upon arrival were still dry and clear with an ambient air temperature of 40-45° F. There was no visible evidence of applied liquid deicers remaining on the test sections. Winds were calm, there was no evidence of blowing snow, no precipitation was recorded in the plots or gauges, and cloud cover was 50%. Sampling began at 6:50 a.m. and was completed at 8:00 a.m.

“Sample day 6” April 18, 2010 test section conditions upon arrival were dry and clear with an ambient air temperature of 60° F. There was no visible evidence of applied liquid deicers remaining on the test sections. Winds were calm, there was no evidence of blowing snow, no precipitation was recorded in the plots or gauges, and cloud cover was 0%. Sampling began at 12:30 p.m. and was completed at 1:30 p.m.

On the final sample day “Sample day 7,” April 19, 2010, test section conditions upon arrival were dry and clear with an ambient air temperature of 55° F. There was no visible evidence of applied liquid deicers remaining on the test sections. Winds were calm, there was no evidence of blowing snow, no precipitation was recorded in the plots or gauges, and cloud cover was 20%. Sampling began at 10:45 a.m. and was completed at 12:00 p.m.

APPENDIX E. DEICER PERFORMANCE – FOT PHOTOS

E1. Black Ice Event Photo Sheet – FreezGard CI Plus

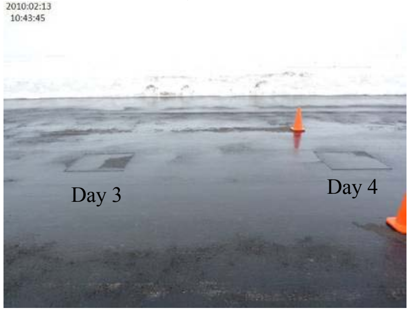
Deicer Application

FreezGard Day 1: After sample collection

FreezGard Day 2: Before sample collection

FreezGard Day 3: Conditions for sample collection

FreezGard Day 4: Before sample collection



FreezGard Day 5: Before sample collection

FreezGard Day 6: Before sample collection

FreezGard Day 7: Before sample collection

E2. Black Ice Event Photo Sheet – Calcium Chloride with Boost

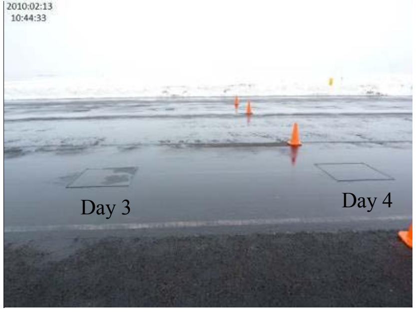
Deicer Application showing Petri dish location

CCB Day 1: After sample collection

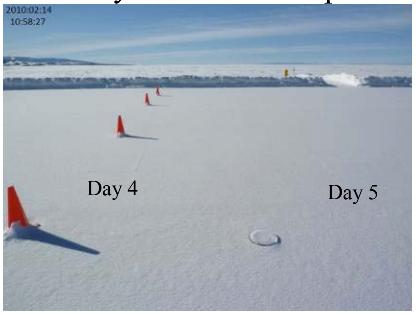
CCB Day 2: Before sample collection

CCB Day 3: Conditions for sample collection

CCB Day 4: Before sample collection



CCB Day 5: Before sample collection



CCB Day 6: Before sample collection

CCB Day 7: After sample collection

E3. Black Ice Event Photo Sheet – NaCl+GLT

Deicer Application showing Petri dish location

GLT Day 1: Before sample collection

GLT Day 2: Before sample collection

GLT Day 3: After sample collection

GLT Day 4: Before sample collection

GLT Day 5: After sample collection

GLT Day 6: Before sample collection

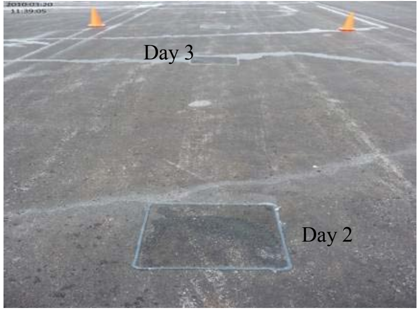
GLT Day 7: Before sample collection

E4. Man Made Snow Event Photo Sheet – FreezGard CI Plus

Snow making over test section

FreezGard Day 1: Before sample collection

FreezGard Day 2: Before sample collection

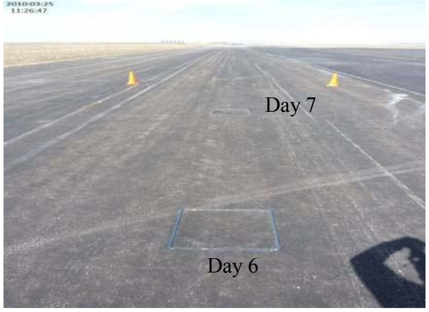


FreezGard Day 3: Before sample collection

FreezGard Day 4: Before sample collection

FreezGard Day 5: Before sample collection

FreezGard Day 6: Before sample collection



FreezGard Day 7: Before sample collection

E5. Man Made Snow Event Photo Sheet – Calcium Chloride with Boost

Snow making over test section

CCB Day 1: After sample collection

CCB Day 2: Conditions before sample collection

CCB Day 3: Before sample collection

CCB Day 4: Before sample collection

CCB Day 5: Before sample collection

CCB Day 6: Before sample collection

CCB Day 7: Before sample collection

E6. Man Made Snow Event Photo Sheet – NaCl+GLT

Snow making over test sections

GLT Day 1: Before sample collection

GLT Day 2: Before sample collection

GLT Day 3: Before sample collection

GLT Day 4: Before sample collection

GLT Day 5: Before sample collection

GLT Day 6: Before sample collection

GLT Day 7: Before sample collection

E7. Natural Storm Event Photo Sheet – FreezGard CI Plus

Deicer Application

FreezGard Day 1: Before sample collection

FreezGard Day 2: Before sample collection

FreezGard Day 3: Before sample collection

FreezGard Day 4: Conditions for sample collection

FreezGard Day 5: After sample collection

FreezGard Day 6: Before sample collection

FreezGard Day 7: Before sample collection

E8. Natural Snow Event Photo Sheet – Calcium Chloride with Boost

Deicer Application showing Petri dish location

CCB Day 1: During sample collection

CCB Day 2: During sample collection

CCB Day 3: Before sample collection

CCB Day 4: Before sample collection

CCB Day 5: Before sample collection

CCB Day 6: After sample collection

CCB Day 7: After sample collection

E9. Natural Snow Event Photo Sheet – NaCl+GLT

Deicer Application showing Petri dish location

GLT Day 1: Before sample collection

GLT Day 2: During sample collection

GLT Day 3: Before sample collection

GLT Day 4: Before sample collection

GLT Day 5: Before sample collection

GLT Day 6: Before sample collection

GLT Day 7: Before sample collection

APPENDIX F. ETHANOL FOR SAMPLE RECOVERY

The following side experiment was suggested at the November 2009 meeting of the Steering Committee, Chemistry Sub-Committee and Researchers. The procedure was developed by the Corrosion and Sustainable Infrastructure Laboratory (CSIL) at the Western Transportation Institute, Montana State University (WTI/MSU) to use ethanol as the solvent for the recovery of the anti-icer samples during field event testing. Procedures followed the objectives of the field event Standard Operating Procedure (SOP).

<u>Ethanol Recovery of Anti-Icer Application in Laboratory Testing</u>

The procedure was tested on a small scale in the laboratory prior to field implementation to further quantify product recovery rates from the pavement and test the hypothesis that inhibitors will bond more tightly to the pavement preventing acceptable recovery rates using DI water as the solvent.

Approximately 30 gallons per lane mile of the liquid deicer NaCl+GLT was applied to a 6"x 12" strip of asphalt in the lab using a hand held spray bottle. Immediately following application, 72 mL of ethanol was added to the pavement strip to mimic the amount of DI water per square inch of sample in a sample box that is 16"x16" with the addition of 250 mL. The sample was vacuum collected immediately following the addition of ethanol. Recovery of the ethanol sample was approximately 6.5 mL or 9% of the original 72 mL. Based on these results the research team attempted the experiment on a slightly larger scale.

<u>Ethanol Recovery of Anti-Icer Application in Field Testing</u>

On January, 22 2010 two 16 x 16 inch boxes were constructed using colored silicone sealant on a clean section of the monster pad at the TRANSCEND Winter Testing facility in Lewistown, MT. The liquid deicer NaCl+GLT was added to the box at a rate of approximately 30 gallons per lane mile. The second box served as the control. The "monster pad" was chosen for the experiment to represent the pavement type and exposure to contaminants of the pavement that will be used in future storm event field testing. Immediately following application, 250 mL of ethanol was added to each test plot and agitated using a 14" deck brush for a period of two minutes. The liquid was then vacuumed from the test surface using a small vacuum (Figure 42). The sample was then poured from the vacuum cylinder into a labeled 250 mL plastic bottle.

Sample recovery from each plot was less than 50%. To obtain enough sample for laboratory testing, the test plot would need to be significantly larger using a greater amount of ethanol. Visual observation of the recovered sample indicated a significant presence of dissolved pavement binder in the ethanol solution based on the dark brown color and apparent suspended solids in the sample. New laboratory experimental design techniques would need to be established to identify the inhibitor in a highly contaminated ethanol solution.

Based on the sample recovery volume and the apparent increase of contaminates recovered with the ethanol, the research team concluded using ethanol as a solvent for sample collection would significantly increase field application and laboratory processing costs.

Figure 41 Sample test box shown after addition of 250 mL of ethanol.

APPENDIX G. EFFECT OF DILUTION AND SALT CONCENTRATION ON THE PH READING OF DEICERS

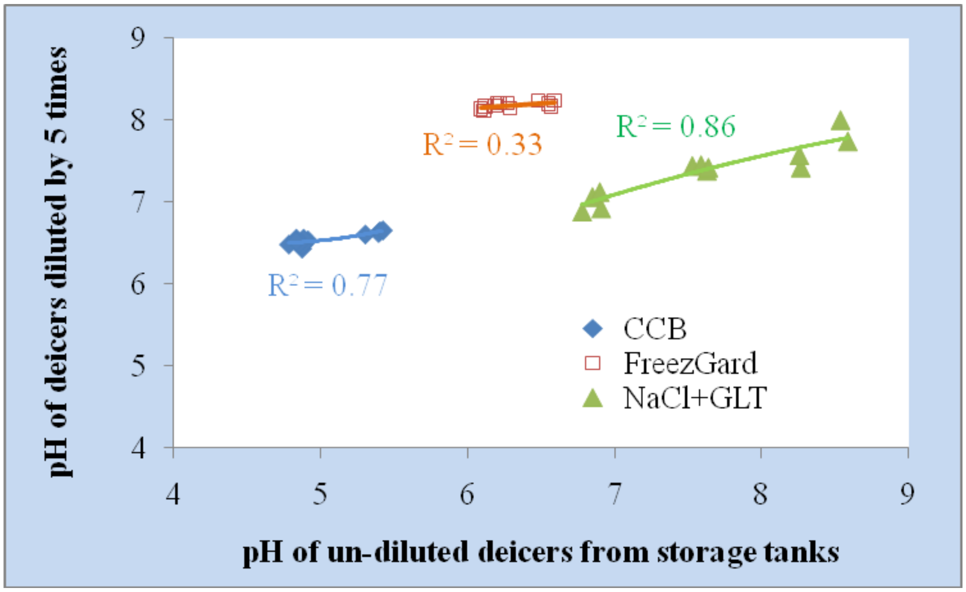
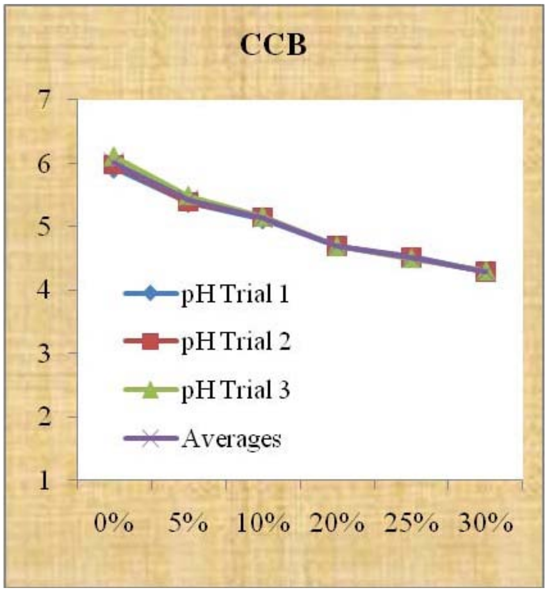
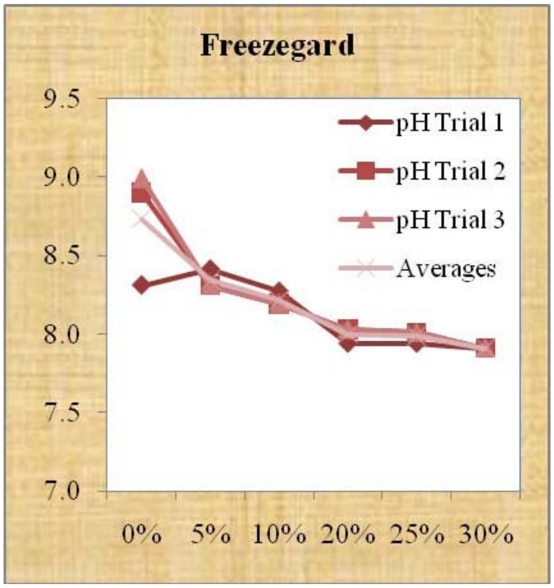


Figure 42 Effect of dilution on the pH reading of deicer samples, showing generally higher pH reading of FreezGard and CCB after dilution and lower pH reading of NaCl+GLT after dilution.



(a)



(b)

Figure 43 Effect of salt concentration on the pH reading of the aqueous solution containing 12% and 2% inhibitor for: (a) CCB, and (b) FreezGard respectively, showing generally lower pH reading at higher salt concentrations.

APPENDIX H. ADDITIONAL PHOTOS FROM THE FOTS

Snowmaking/controlled snowstorm at the TRANSEND facility

Leveling the snow content in the squares prior to the sample collection

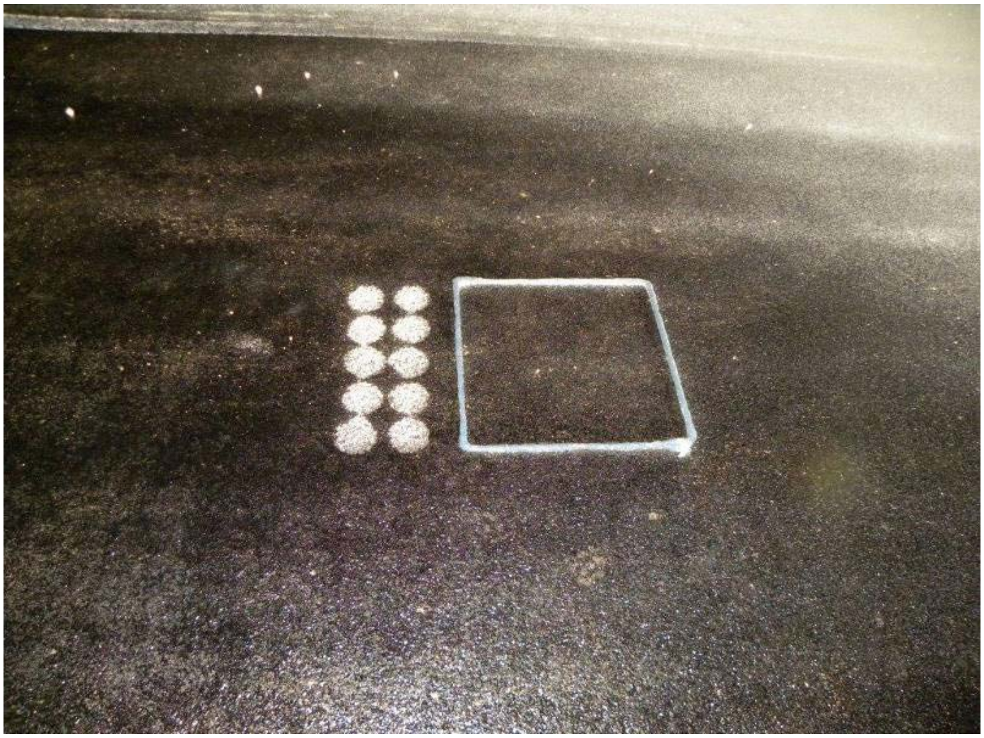
Application method of liquid chemicals

Chemical absorbed to the bottom layer of snow

Sunrise after the all-night snow event

Collect the samples from the collection squares

Illustrate how the anti-icing works: The white circles are where the petri-dishes captured the anti-icing agent and prevented it from reaching the pavement. All else is wet from chemical.



Look at the actual application rate: great performance from a small amount of chemical.

Anti-icer clearly prevented the bonding of packed snow to pavement.