

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

Final Report

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the Transportation Pooled Fund led by
the Pacific Northwest Snowfighters Association

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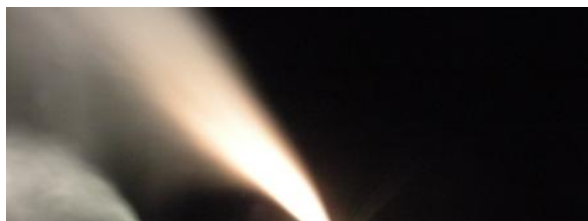




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Abbreviations and Acronyms

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

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 (MgCl₂-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 $IMC_{30°F, 60min}$). 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. 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.
- 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
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<i>Target Precipitation</i>	No precipitation	Minimum 1 inch of snow	1-4 inches in the first 24 hours
<i>Actual Precipitation</i>	Total of 0.75 ² of precipitation (mostly snow/ice) during day 4 to day 7.	1 ² of man-made snow; a total of 0.26 ² of natural snow during day 3 and day 4.	3.5-4 ² in the first 24 hours; about 0.75 ² of blowing snow on day 2.
<i>Target Air Temperature</i>	25-32 °F	15-25 °F	25-32 °F
<i>Target Pavement Temperature</i>	Less than 32 °F	Less than 25 °F	25-32 °F
<i>Moisture Content in Snow (Average Density)</i>	Not applicable	30-40% (24 lb/ft ³)	20-40% (19 lb/ft ³)
<i>Target Deicer Application Rate</i>	30 gallons/lane-mile	60 gallons/lane-mile	60 gallons/lane-mile
<i>Actual Application Rate</i>	33±5 gallons/l-m	53±4 gallons/l-m *	55±6 gallons/l-m *
<i>Target Wind Speed</i>	Not specified	Less than 6 mph	Not specified
<i>Average Wind Speed</i>	6 mph	9 mph	9 mph
<i>Average Wind Direction</i>	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.

- 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.
- 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 0.75² 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

and day 5 (12%). Up to 66% 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 1² of artificial snow and a total of 0.26² 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 3.5-4² of natural snow in the first 24 hours and about 0.75² 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.

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 (MgCl₂-based FreezGard, CaCl₂-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

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) as well as abrasives are applied onto highways to keep them clear of ice and snow. Deicers (mainly sodium chloride [NaCl], magnesium chloride [MgCl₂], and calcium chloride [CaCl₂]) 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 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 Kjeldahl 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 (SHRP 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, MgCl₂, and CaCl₂, 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 MgCl₂, agro-based products, CaCl₂, 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). MgCl₂ brines feature better performance at lower temperatures [14, 25]. Field studies have shown CaCl₂ to be more effective than NaCl, owing to its ability to attract moisture and stay on the roads [26]. The use of MgCl₂ or CaCl₂ 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, 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 [20, 21]. Recently, glucose/fructose and unrefined sugar have been mixed in and to

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 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, MgCl₂, 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 CaCl₂ liquid deicer (Calcium Chloride with Boost or CCB™), the inhibited MgCl₂ liquid deicer (FreezeGard CI Plus™), and the inhibited

with 100% of CaCl_2), the inhibited MgCl_2 liquid deicer (FreezGard or Plus[™]), and the inhibited NaCl-based solid deicer (IceSlicer Elite[™]). 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[™] 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.

Product	% CaCl_2 (Ca)	% MgCl_2 (Mg)	%KCl (K)	%NaCl (Na)	%Chloride	%NaCl (Cl)	% CaCl_2 (Cl)	% MgCl_2 (Cl)	FCR
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

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

* 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

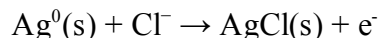
All the deicer samples from field storage were stored in the refrigerator. Prior to laboratory testing, they were removed from cold storage and allowed to reach room temperature (21 to 23°C). For each deicer property, at least three duplicate samples were tested or at least three readings were taken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



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, CaCl₂, and MgCl₂). 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 CaCl₂ liquid deicer (CCB™) and the inhibited MgCl₂ 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

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™, 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 .

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 $^\circ\text{F}$) 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]:

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

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 ($^\circ\text{F}$)

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 buried on all sides and sloping at a 3 to 5% angle to a water collection cistern buried in the ground.



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 1/2" 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

and performance of inhibitors. In this study, we focused on the factors highlighted in light blue in the diagram.

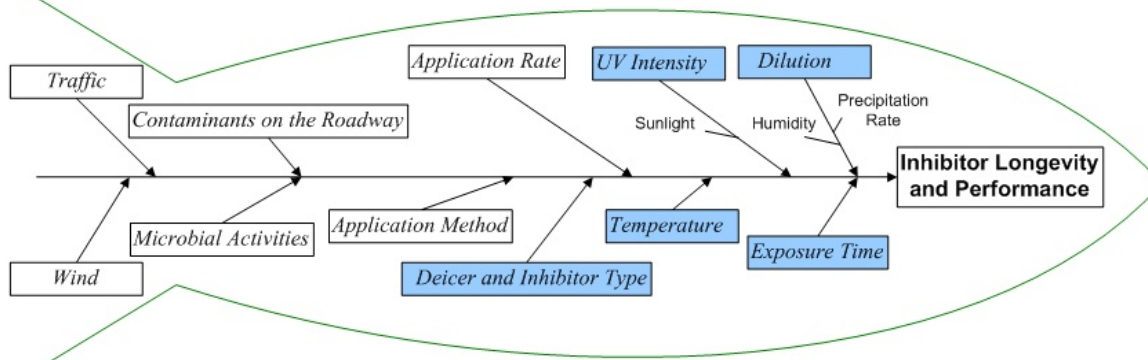


FIGURE 3 Fish diagram illustrating the influential factors in inhibitor longevity and performance.

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 °C), 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 0°F and 70°F) 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.

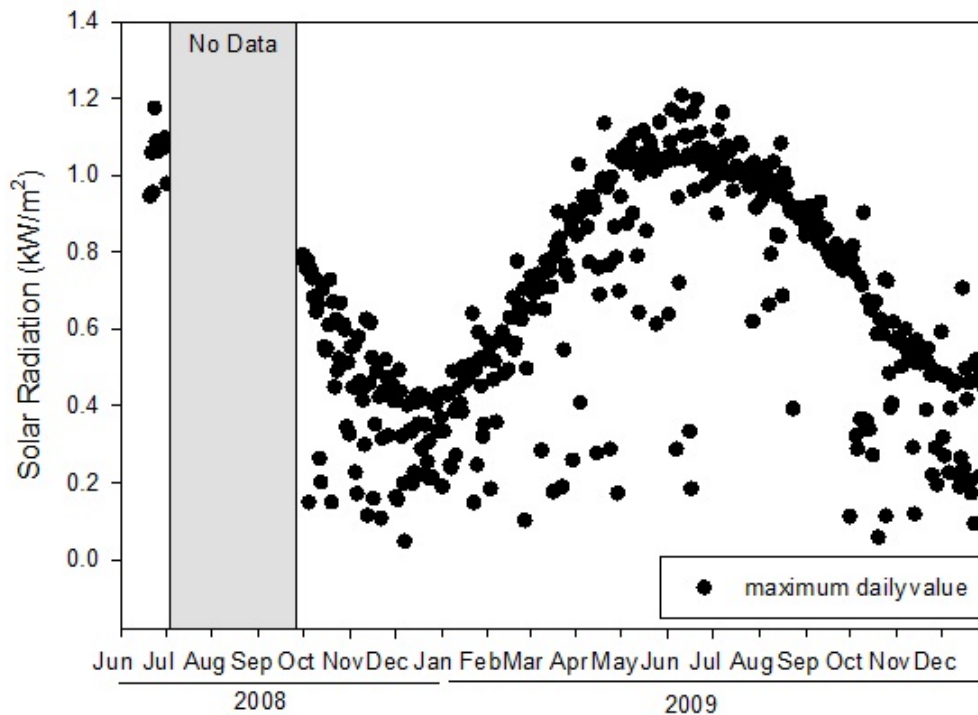


FIGURE 6
Temporal evolution
of maximum daily
solar radiation at
the storage site.

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/m². 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 MgCl₂-based FreezGard under Storage

This section presents the temporal evolution of properties of the MgCl₂-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 $IMC_{30^\circ\text{F}}$). The data are often presented in the form of average value \pm 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.

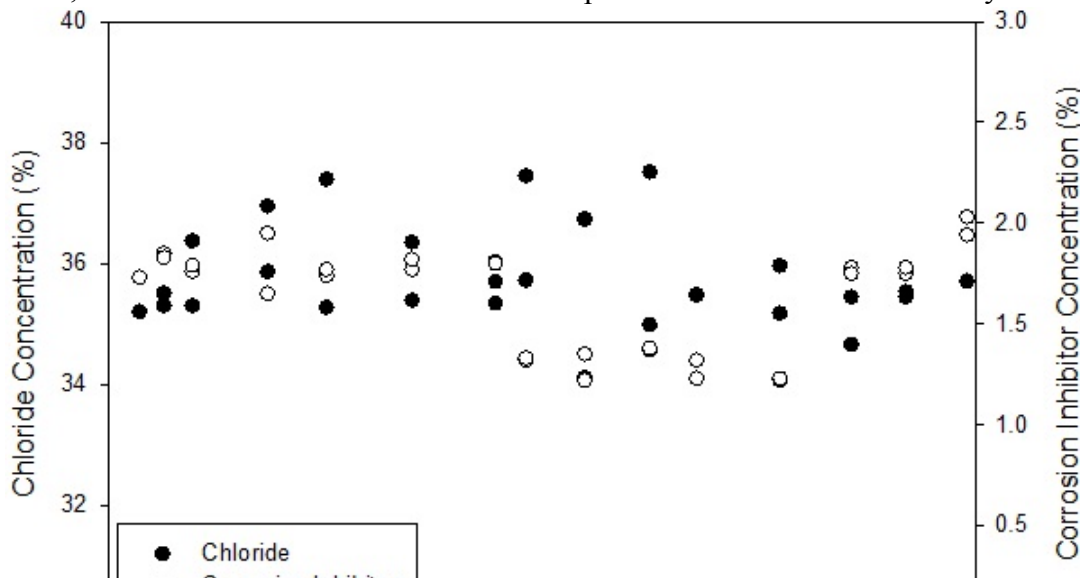
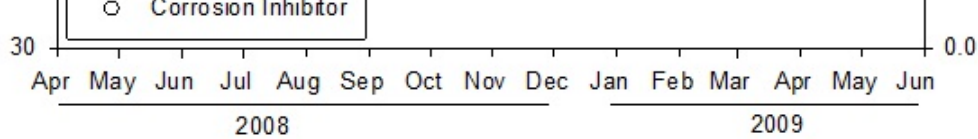


FIGURE 7
Temporal
evolution of
chloride and
inhibitor



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 $35.6 \pm 0.8\%$ and $1.7 \pm 0.3\%$ 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.

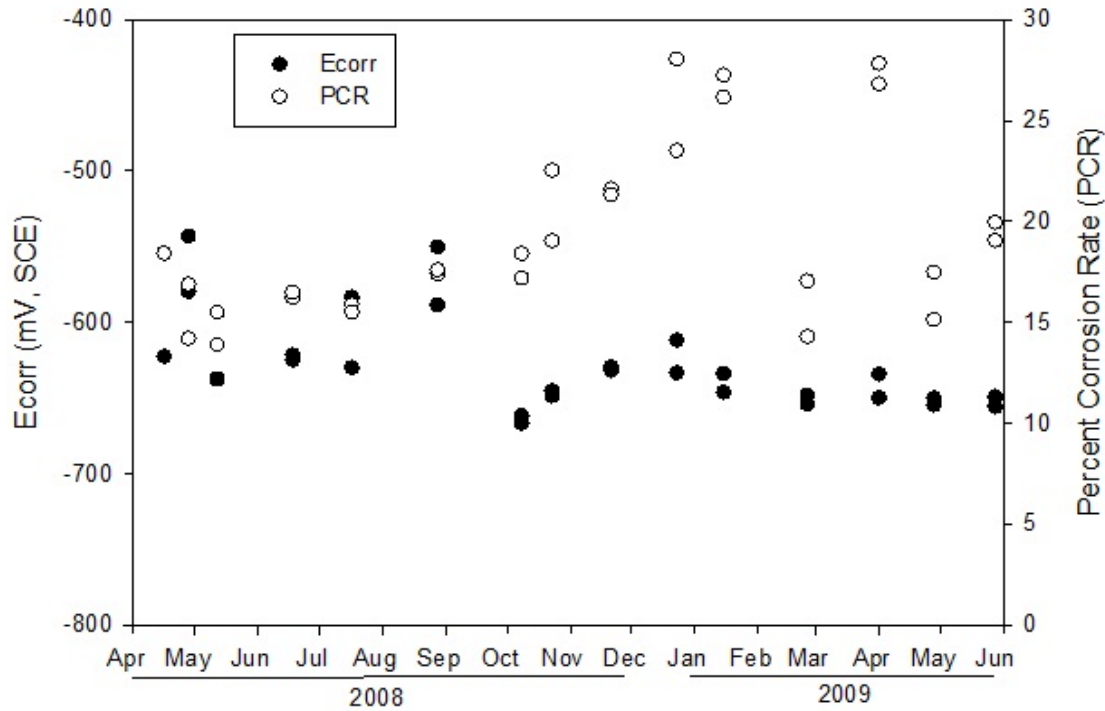


FIGURE 8 Temporal evolution of deicer corrosivity to steel (indicated by E_{corr} and PCR) in the FreezGard deicer tanks.

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 $19.7 \pm 3.9\%$. 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 ($IMC_{30^\circ\text{F}, 60\text{min}}$) of the FreezGard deicer samples remained very consistent within 10.2 ± 1.2 °F and 3.7 ± 1.1 mL/mL (snowmelt/deicer) respectively. 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 CaCl₂-based CCB under Storage

This section presents the temporal evolution of properties of the CaCl₂-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 $37.0 \pm 3.0\%$.

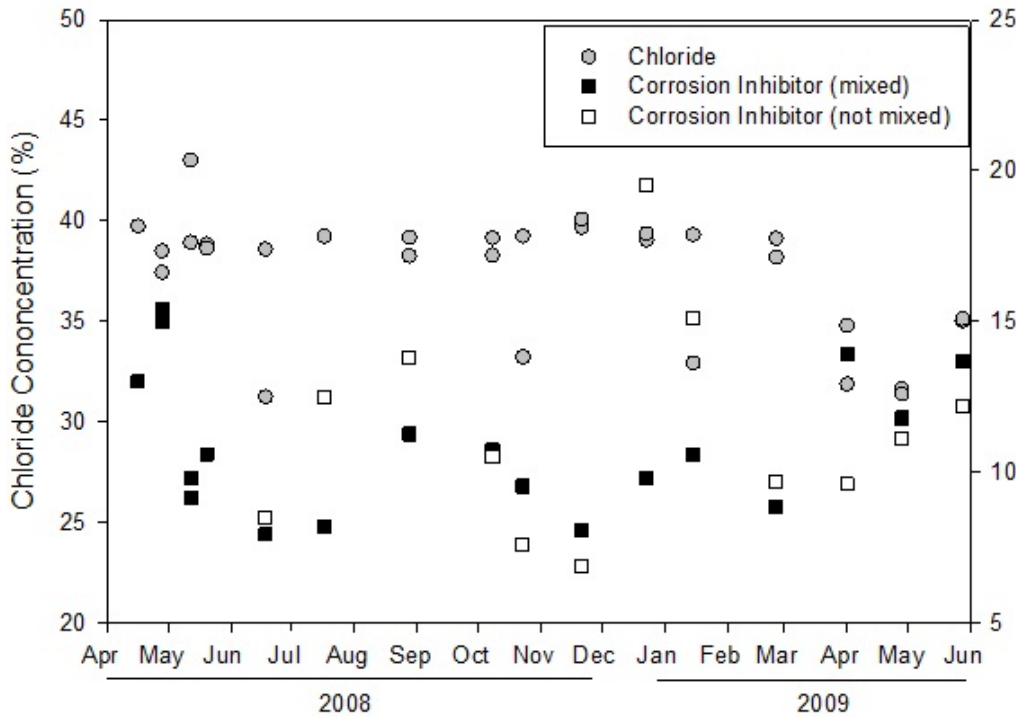


FIGURE 9 Temporal evolution of chloride and inhibitor concentrations in the CCB deicer tanks.

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 $9.3 \pm 1.7\%$ and $11.2 \pm 3.3\%$ respectively, with the mixed tanks showing lower readings 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.

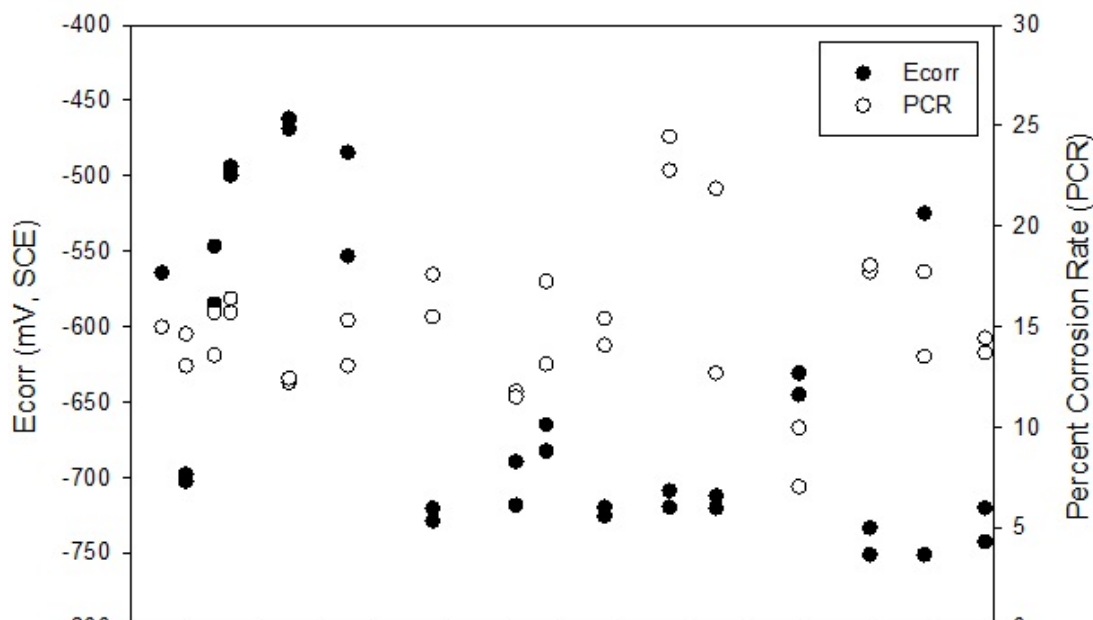


FIGURE 10 Temporal evolution of deicer corrosivity to steel (indicated by E_{corr} and PCR) in the CCB deicer tanks.

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 $15.0 \pm 3.3\%$. 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.

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 ± 4.2 mS/cm respectively. The DSC-derived characteristic temperature (T_c) and ice melting capacity ($IMC_{30^\circ F, 60min}$) of the CCB deicer samples remained very consistent within 11.2 ± 1.2 °F and 3.8 ± 0.1 mL/mL (snowmelt/deicer) respectively, 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 $IMC_{30^\circ F}$). 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 $14.8 \pm 5.0\%$. 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, which helps to explain why the measured chloride concentrations were lower than the target concentration (20% by weight).

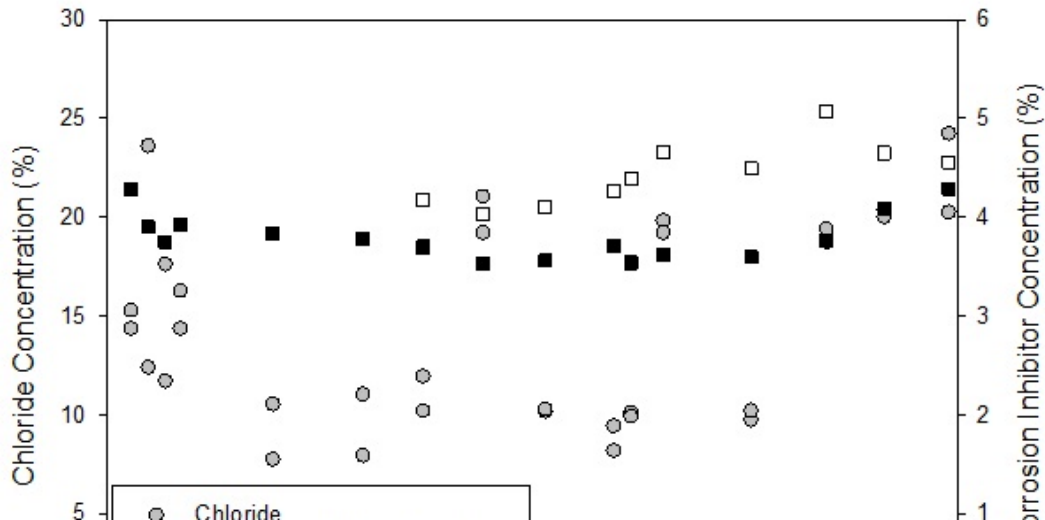
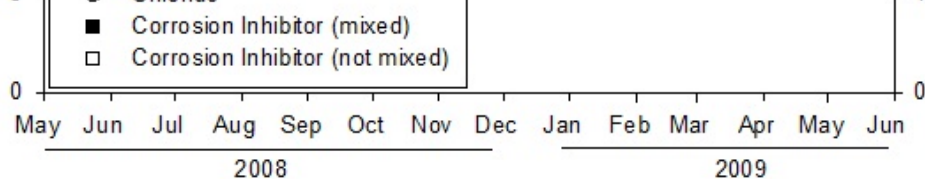


FIGURE 11 Temporal evolution of chloride and inhibitor concentrations in the NaCl+GLT deicer tanks.

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 $3.8 \pm 0.2\%$ and $4.3 \pm 0.4\%$ respectively, again with the mixed tank showing lower readings 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.

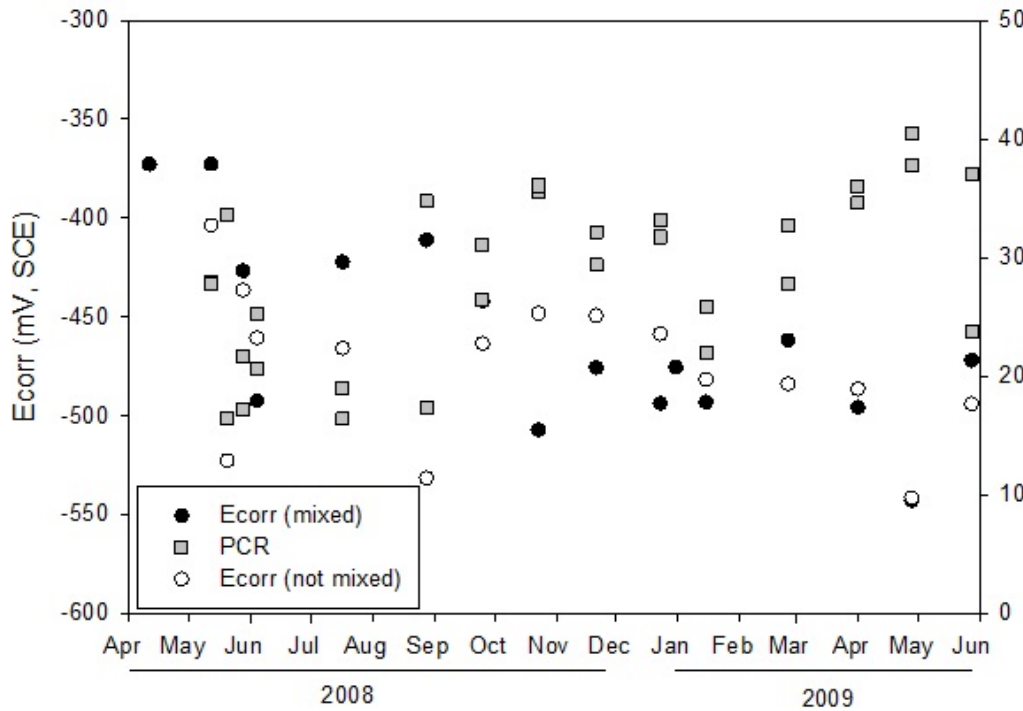


FIGURE 12 Temporal evolution of deicer corrosivity to steel (indicated by E_{corr} and PCR) in the NaCl+GLT deicer tanks.

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.

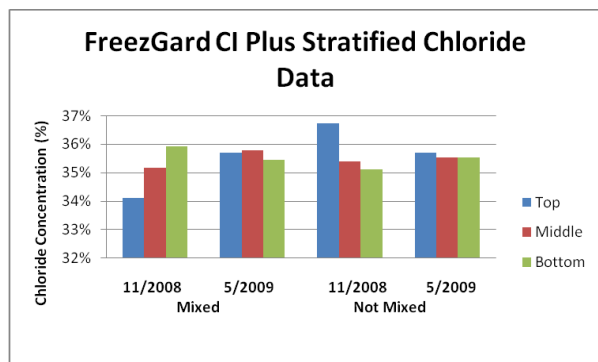
Finally, during the field storage months the pH and electrical conductivity of the NaCl+GLT deicer samples remained within 7.6 ± 0.6 and 189.5 ± 19.9 mS/cm respectively. The DSC-derived characteristic temperature (T_c) and ice melting capacity ($IMC_{30^\circ F, 60min}$) of the NaCl+GLT deicer samples remained very consistent within 23.5 ± 1.9 °E and 3.8 ± 0.2 mL/ml (snowmelt/deicer)

samples remained very consistent within 25.5 ± 1.9 F and 5.8 ± 0.2 mL/mL (shown in deicer) respectively, suggesting higher T_c and similar $IMC_{30^\circ F}$ 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.

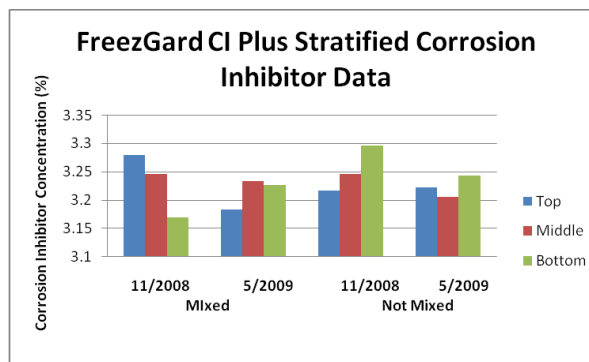
2.2.5. Stratified Sampling of Liquid Deicer Tanks

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.

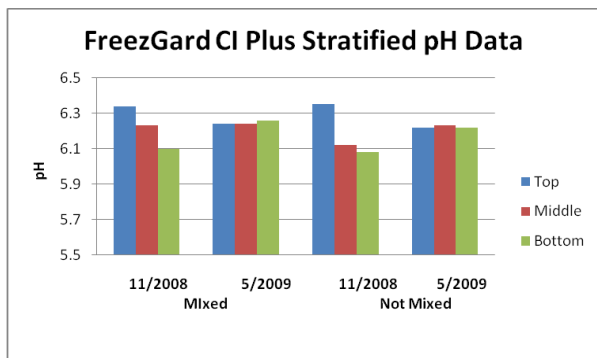
Figures 13(a) and 13(b) show that after the first seven months of storage the non-mixed FreezGard deicer tank featured the lowest chloride concentration and the highest inhibitor concentration at the bottom of the tank, whereas the mixed FreezGard deicer tank featured the opposite tendency for unknown 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.



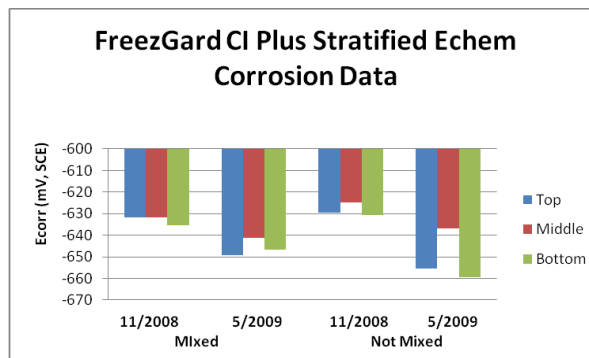
(a)



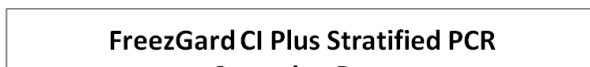
(b)

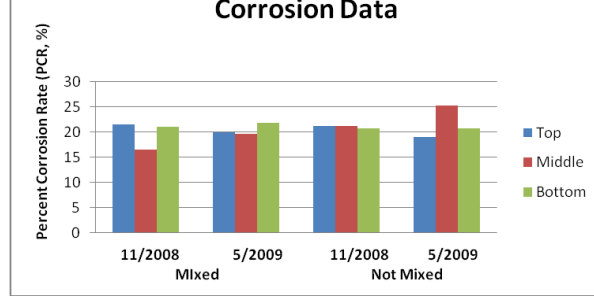


(c)



(d)

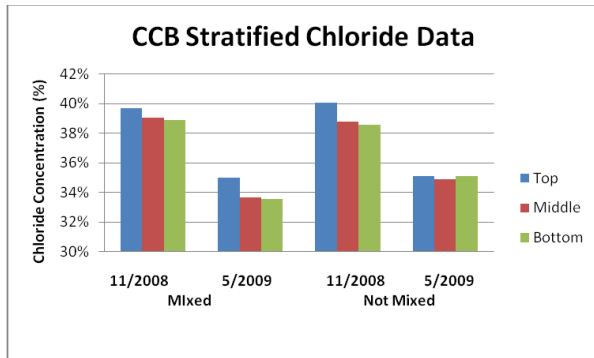




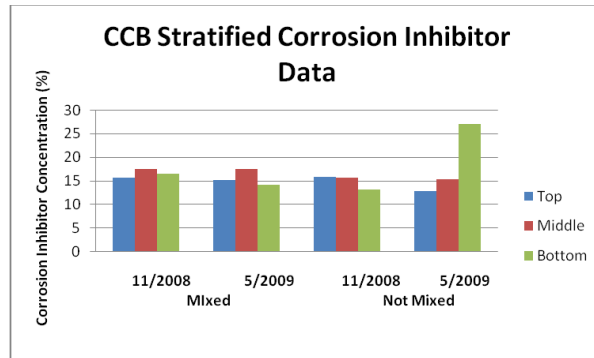
(e)

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.

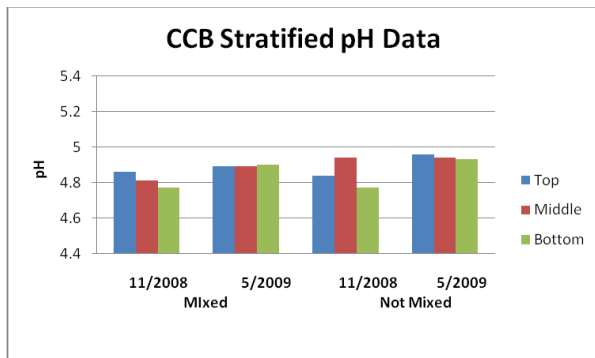
Figures 14(a) and 14(b) show that after the first seven months of storage both the mixed and non-mixed CCB deicer tanks featured the lowest chloride concentration at the bottom of the tank, whereas the inhibitor concentration along the tank depth showed little trend. The 13-months-old deicer samples 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.



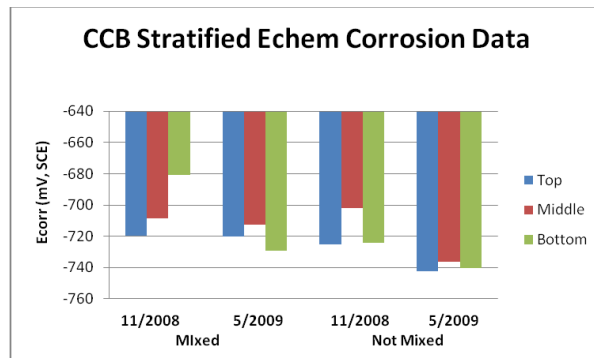
(a)



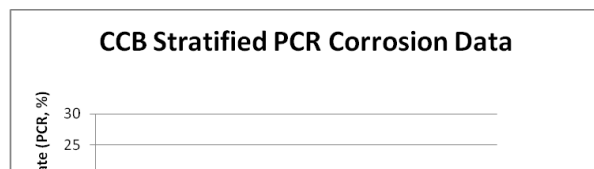
(b)



(c)



(d)



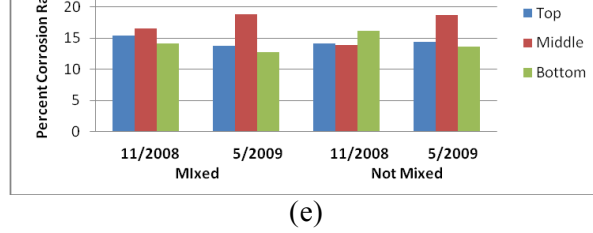


FIGURE 14 Properties of stratified samples obtained from the top, middle and bottom of the CCB deicer tanks: (a) chloride concentration; (b) inhibitor concentration; (c) pH; (d) E_{corr} of mild steel; and (e) PCR.

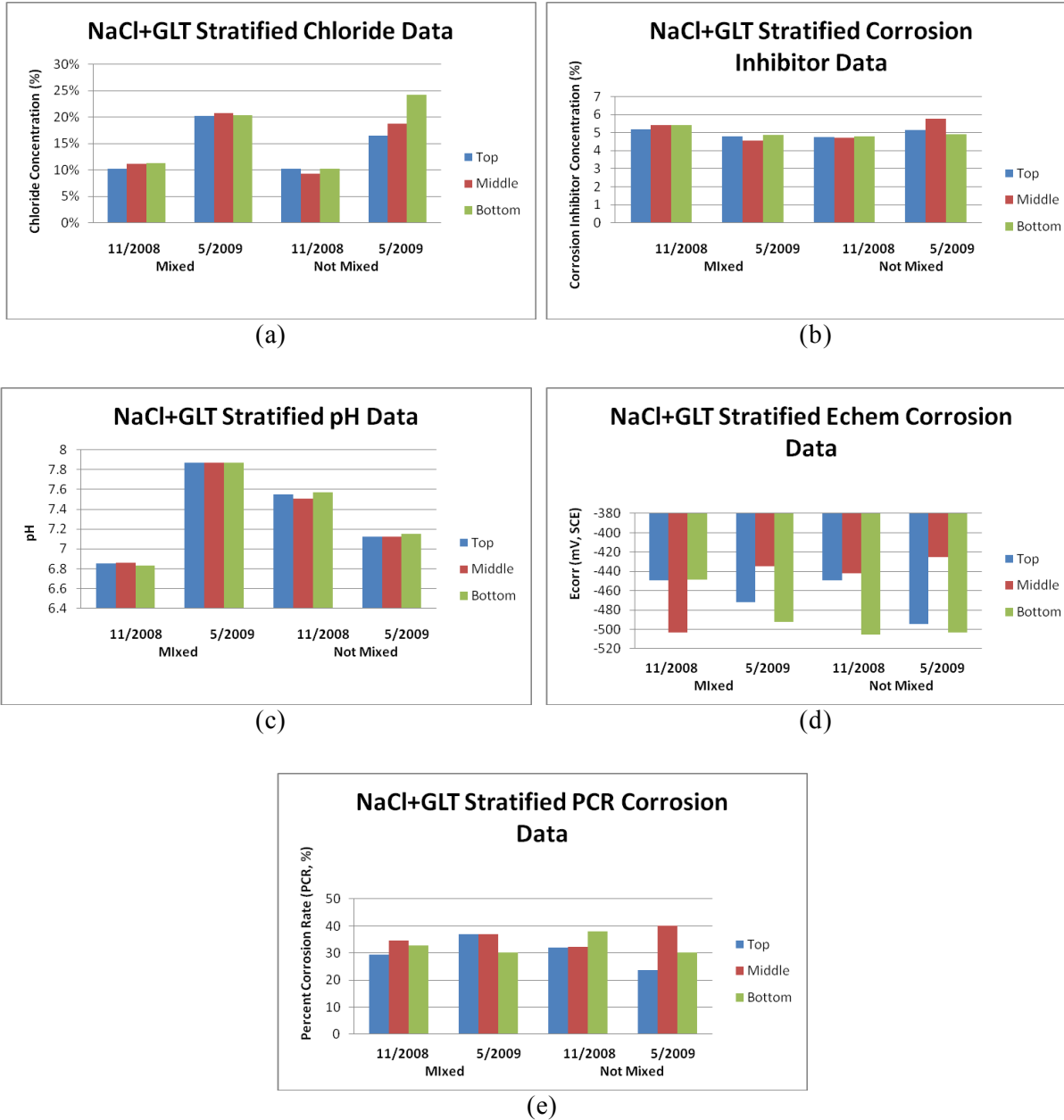


FIGURE 15 Properties of stratified samples obtained from the top, middle and bottom of the NaCl+GLT deicer tanks: (a) chloride concentration; (b) inhibitor concentration; (c) pH; (d) E_{corr} of mild steel; and (e) PCR.

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 at the bottom and middle of the tank, respectively. Figure 15(c) shows that for

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 $IMC_{30°F}$). 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.

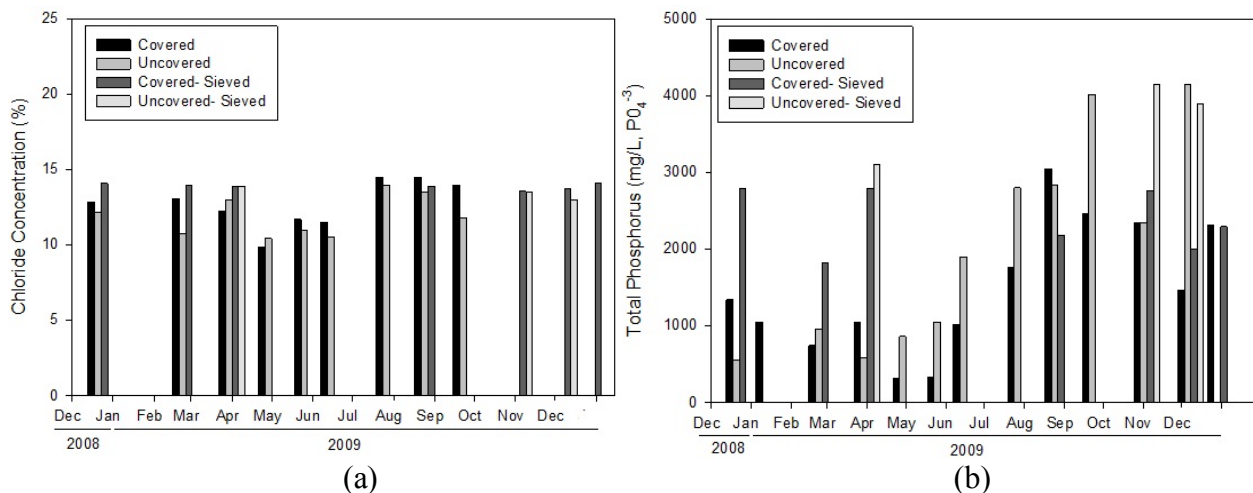


FIGURE 16 Temporal evolution of (a) chloride and (b) inhibitor concentrations in the IceSlicer piles. Note that the concentrations were based on the 23% IceSlicer solution, instead of its solid form.

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.

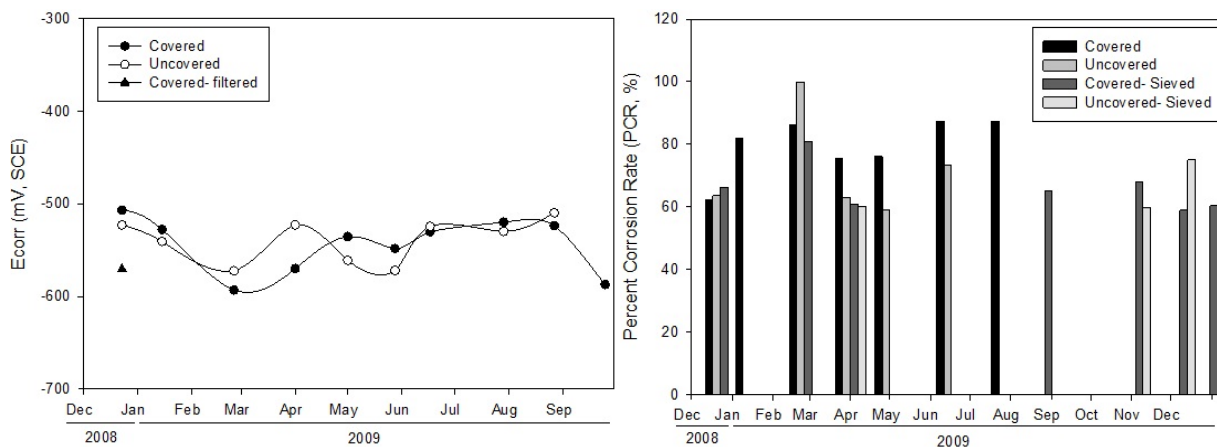


FIGURE 17 Temporal evolution of deicer corrosivity to steel (indicated by E_{corr} and PCR) in the NaCl+GLT deicer tanks.

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 . 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 ($IMC_{30^\circ F, 60min}$) of the IceSlicer deicer samples remained very consistent over the duration of sampling, within 27.6 ± 4.2 °F and 3.6 ± 0.7 mL/mL for the covered samples and 26.1 ± 2.3 °F 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 $IMC_{30^\circ F, 60min}$ (by SHRP Ice Melting Test) was 21.8 ± 0.1 °F 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 30°F, relative to the NaCl+GLT liquid deicer and the 23% NaCl solution. 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 the leaching rate of chloride from the uncovered pile exceeded that of the corrosion inhibitor.

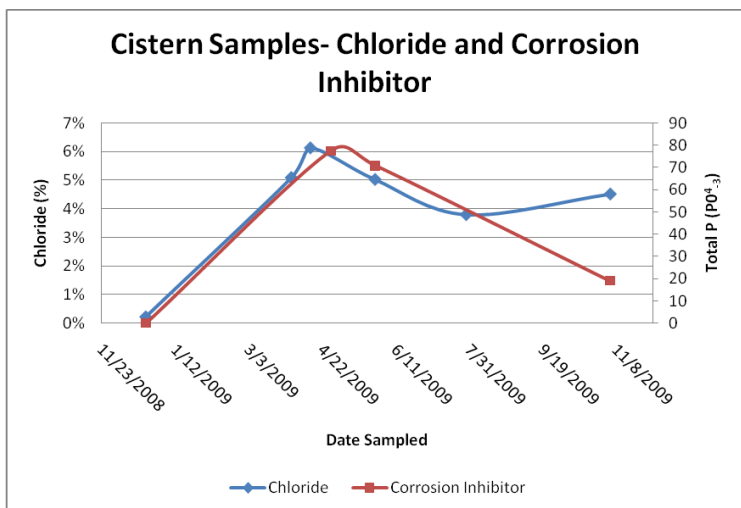


FIGURE 18 Temporal evolution of chloride and inhibitor concentrations in the IceSlicer cistern.

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.

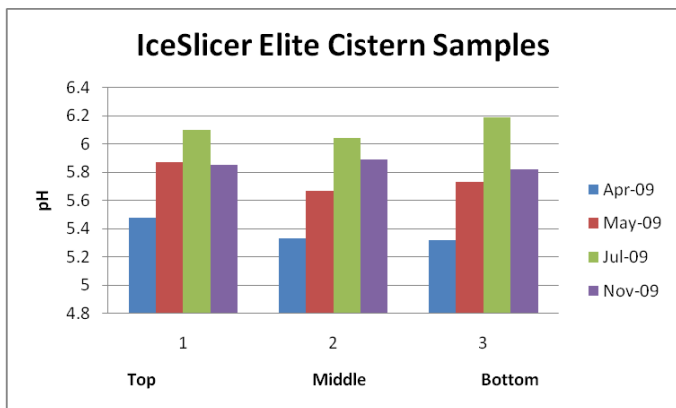
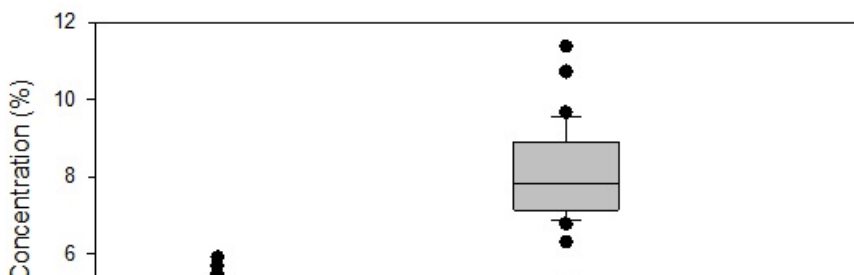


FIGURE 19 Temporal evolution of pH in the IceSlicer cistern.

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).



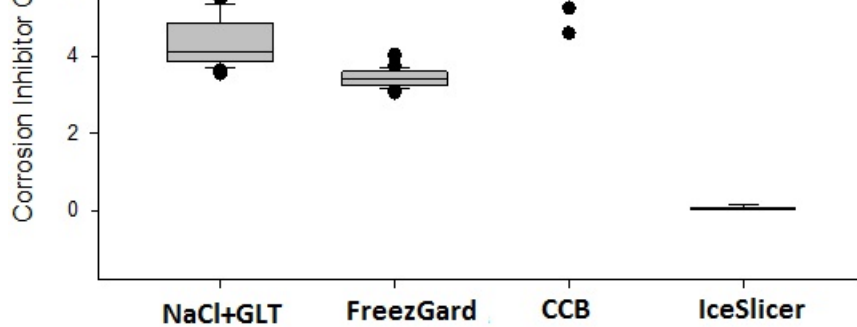


FIGURE 20 Box plot showing the corrosion inhibitor concentration following various exposure experiments as detailed in Table 3.

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.

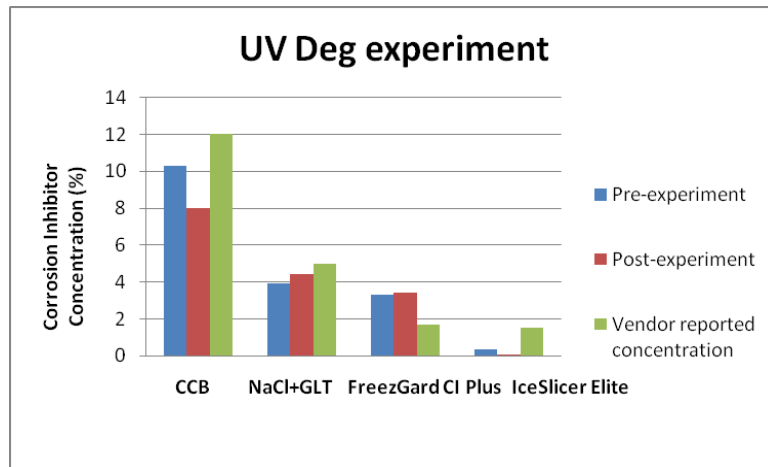


FIGURE 21 Inhibitor concentration in deicers before and after the laboratory degradation experiments.

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

Note that the most severe exposure conditions during the laboratory degradation experiments entailed the air temperature of 40°C (104°F) 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/m². 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 70°F (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/m² (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 overfitting 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].

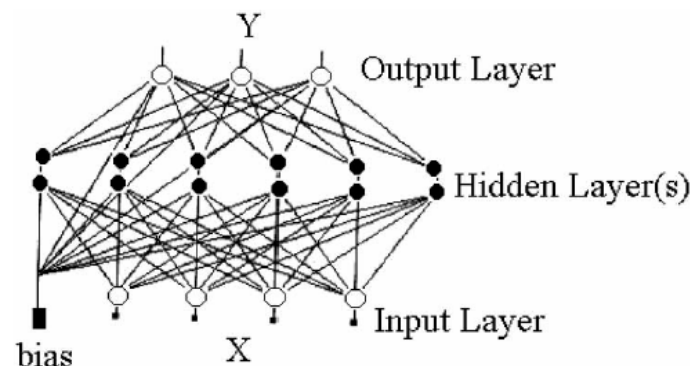


FIGURE 22 A typical multi-layer feed-forward ANN architecture.

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	Deicer Type	Relative i_{corr}	Relative E_{corr} (mV)	Solution Conductivity (mS)	PCR
1	0.63	16.8	5.1	21.3	3	1.69	107.8	99.7	23.5
1	0.70	40.1	9.8	28.1	3	2.88	73.3	100.6	27.2
1	0.68	28.2	14.4	25.5	3	3.00	65.4	99.4	17.1
1	0.84	81.4	18.7	24.3	3	1.73	85.3	98.8	26.8
1	1.25	60.8	24.1	28.0	3	1.88	65.1	99.6	17.5
1	1.00	0.0	14.7	93.3	3	3.32	70.3	100.2	20.0
3	0.76	40.9	7.5	41.7	3	2.30	78.3	99.8	19.7
3	1.00	144.6	14.9	28.2	3	2.16	72.7	99.5	21.9
3	1.05	39.8	22.6	15.7	3	2.04	96.2	98.9	21.2
3	0.81	55.5	28.2	14.5	3	1.84	67.8	104.0	23.0
3	0.98	133.6	34.6	10.0	3	2.61	139.7	98.0	16.9
3	0.83	33.2	22.8	45.9	3	1.55	81.8	97.2	15.5
2	0.48	230.0	7.9	34.5	3	1.09	97.7	99.6	16.5
2	0.45	329.9	15.7	21.0	3	3.43	135.9	98.9	15.5
2	0.53	225.8	23.7	15.9	3	3.51	131.0	98.0	17.6
2	0.85	287.6	30.4	10.6	3	2.81	52.9	98.5	17.2
2	1.39	187.4	36.9	13.5	3	3.03	74.3	100.3	22.5
2	1.03	7.0	25.0	87.1	3	1.39	89.9	100.0	21.3
2	0.65	155.3	131.1	15.0	3	1.48	94.8	100.6	21.2
2	0.83	16.9	130.8	13.1	3	1.22	88.9	100.0	20.8
2	1.08	134.7	131.2	13.6	3	0.99	78.4	99.7	16.6
2	1.06	220.0	130.6	16.4	3	0.93	86.1	97.8	28.0
2	0.85	257.6	131.5	12.2	3	2.71	85.7	98.9	26.2
2	1.12	166.3	131.5	13.1	3	2.25	71.4	100.6	14.3
2	0.23	-9.2	131.6	15.5	3	3.18	69.6	99.6	27.8
2	0.51	1.1	131.7	11.8	3	1.65	69.5	98.2	15.1
2	1.89	54.5	132.4	17.3	3	3.03	63.8	99.6	19.1
2	0.47	0.0	133.4	15.4	3	2.70	82.6	100.3	25.3
2	1.00	10.7	132.5	16.5	3	3.30	59.9	99.6	20.8
2	0.97	38.7	132.5	14.1	3	2.85	99.4	99.9	17.2
2	0.18	5.1	132.6	14.5	1	0.11	346.7	145.0	1.6
2	0.99	10.7	133.9	22.8	1	1.18	-94.7	131.7	28.0
2	0.19	7.2	132.1	21.9	1	0.52	292.6	157.5	16.5
2	1.34	88.7	133.5	7.1	1	0.88	226.9	167.6	21.7
2	0.22	-13.9	132.8	17.7	1	0.64	297.1	173.2	25.3
2	0.89	194.7	132.6	17.7	1	0.43	308.3	189.6	16.4
2	0.46	-0.6	133.4	13.7	1	0.60	277.3	196.7	17.4
2	0.41	7.0	132.4	18.8	1	0.41	212.1	199.9	31.1
2	0.41	-9.8	132.1	12.7	1	0.55	243.7	200.0	35.5
2	0.22	4.2	132.1	13.1	1	0.62	270.0	191.5	29.4
2	1.05	213.5	132.4	11.0	1	0.54	216.1	193.3	34.6
2	1.11	21.8	131.0	14.6	1	0.59	270.7	192.2	32.7
2	1.37	172.7	132.2	15.7	1	0.57	225.7	200.0	35.6
2	0.98	225.7	132.8	15.7	1	0.94	243.9	200.0	31.7
2	0.85	250.6	132.1	12.4	1	0.83	226.2	200.0	25.8
2	0.74	234.9	129.2	15.3	1	0.24	257.6	200.0	27.8
2	0.27	-0.8	123.9	17.6	1	0.69	223.6	200.0	36.0
2	1.17	30.1	133.0	11.5	1	0.83	176.6	200.0	40.5
2	1.34	37.0	133.4	13.2	1	0.53	247.5	200.0	37.0

2	0.29	-5.9	134.0	14.1	1	0.66	284.7	200.0	37.0
2	0.86	17.3	134.6	13.9	1	0.62	226.9	200.0	30.3
2	0.63	-5.0	134.1	16.1	1	0.33	217.2	200.0	30.7
2	0.32	-8.6	133.9	16.6	1	0.58	267.9	200.0	33.5
2	0.15	-0.2	121.5	24.5	1	0.41	315.7	146.8	27.8
2	0.20	-0.8	122.2	12.7	1	0.99	196.7	200.0	33.6
2	1.71	74.5	128.7	10.0	1	0.46	283.0	136.6	17.1
2	0.35	-31.6	132.0	18.1	1	0.30	258.9	143.9	20.7
2	0.36	-31.6	130.8	13.5	1	0.62	253.6	200.0	19.0
2	0.37	-23.0	135.1	14.4	1	1.00	187.8	200.0	34.7
2	0.55	-17.0	134.1	18.7	1	0.36	255.8	189.0	26.4
2	0.46	-20.7	123.7	13.6	1	0.65	271.1	200.0	36.1
2	1.01	4.9	130.7	11.4	1	0.61	270.0	200.0	32.2
3	1.74	97.0	99.0	18.4	1	0.40	277.5	200.0	32.4
3	2.28	176.4	98.4	14.2	1	0.52	213.7	200.0	38.0
3	1.62	82.2	98.8	13.9	1	0.53	259.4	200.0	35.9
3	1.44	94.6	99.0	16.2	1	0.78	260.8	200.0	33.2
3	1.50	89.5	98.2	15.9	1	0.82	237.8	200.0	22.0
3	3.16	169.2	98.8	17.4	1	0.25	235.5	200.0	32.7
3	2.85	57.9	98.8	18.4	1	0.72	232.9	200.0	34.6
3	1.14	71.0	99.2	19.0	1	0.75	177.8	200.0	37.8
3	1.46	87.8	99.8	21.6	1	0.49	225.3	187.5	23.8
3	1.68	87.8	99.3	16.6	1	0.59	294.1	197.3	40.2
3	1.19	84.1	99.5	21.2	1	0.69	216.1	200.0	30.3
3	2.23	105.0	99.2	19.4	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+GLTTM, 2 for CCBTM, and 3 for FreezgardTM 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.

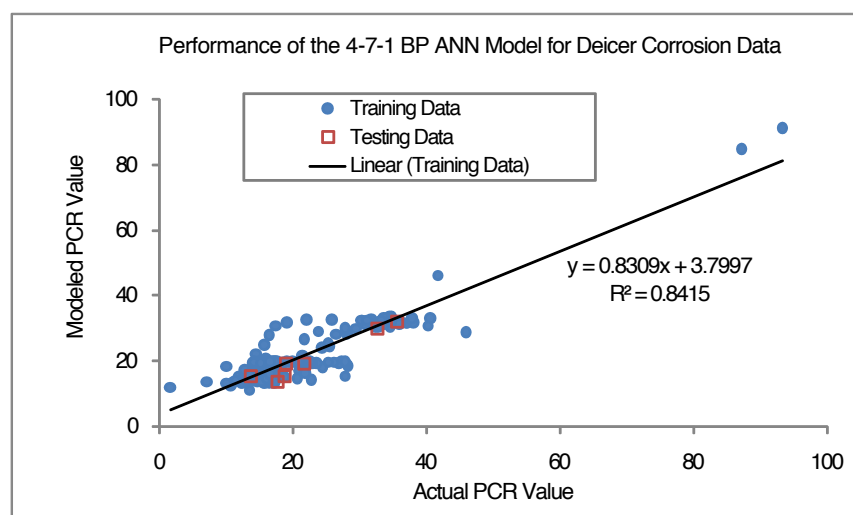
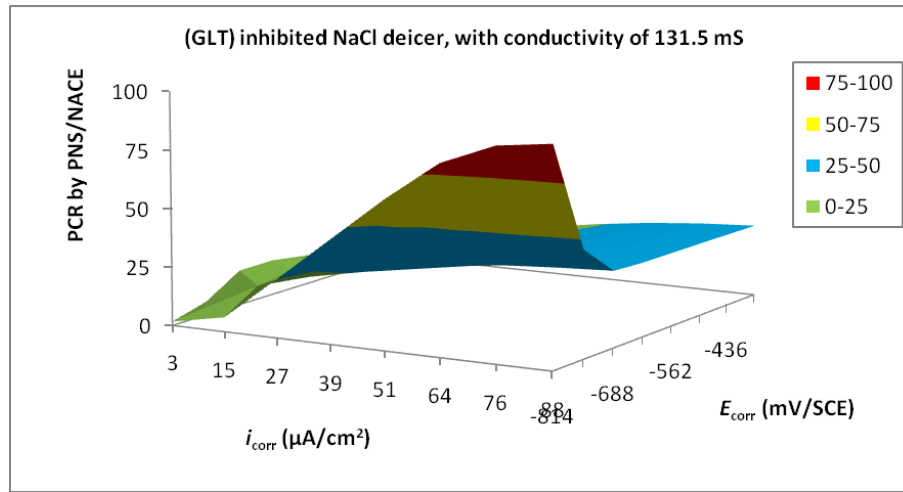


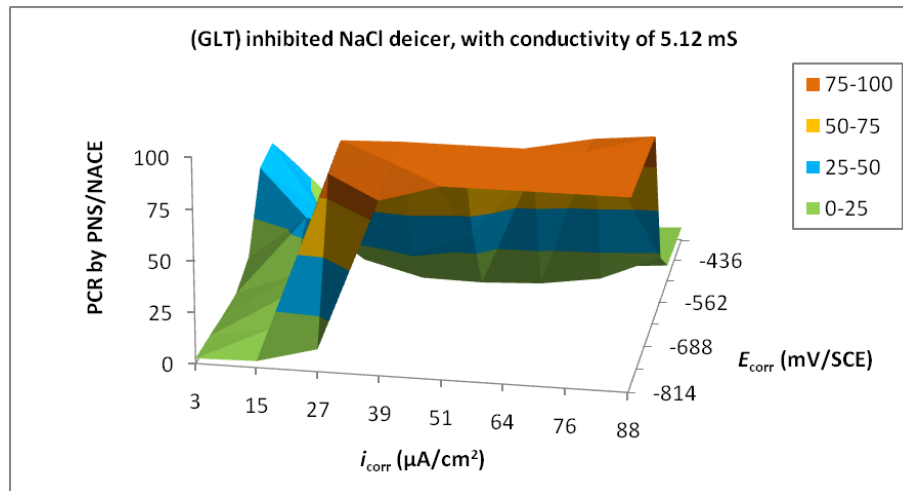
FIGURE 23 Relationship between the measured *PCR* of steel in deicer samples and the *PCR* modeled by the corrosion ANN model.

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.



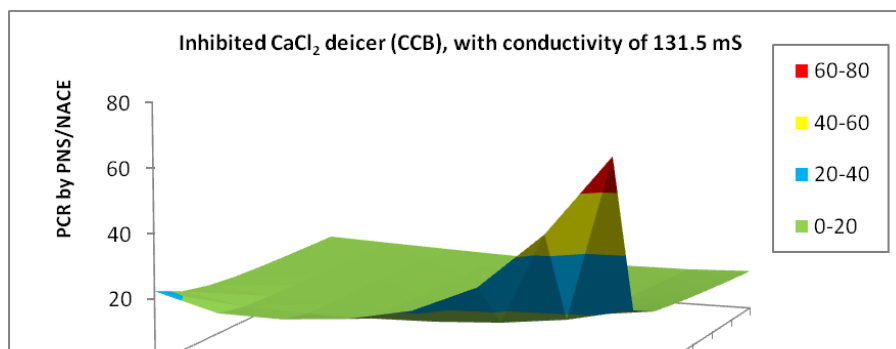
(a)

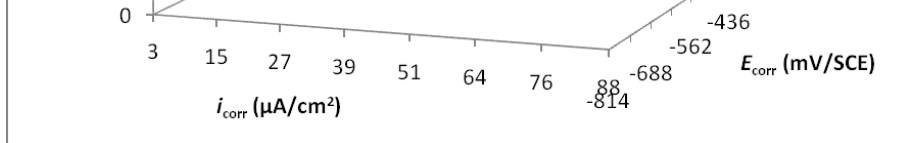


(b)

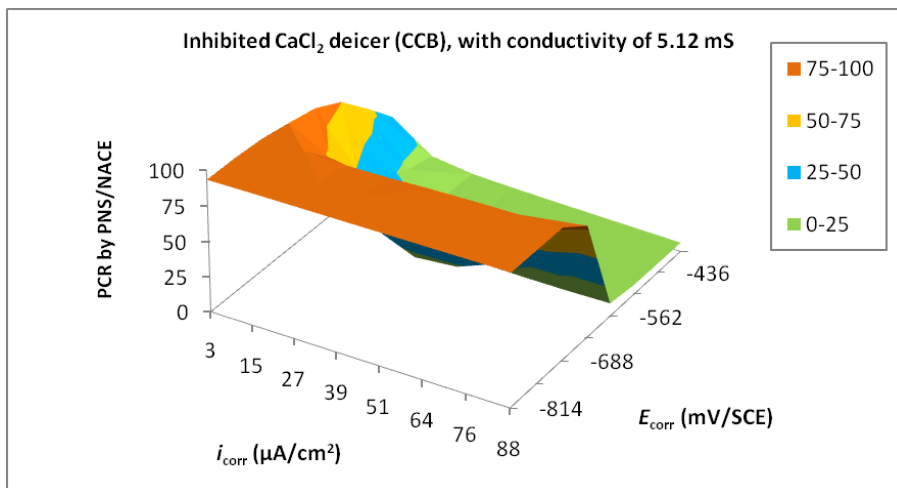
FIGURE 24 Predicted PCR as a function of i_{corr} and E_{corr} for GLT-inhibited NaCl deicer, with conductivity of (a) 131.5 mS/cm, or (b) 5.12 mS/cm.

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.





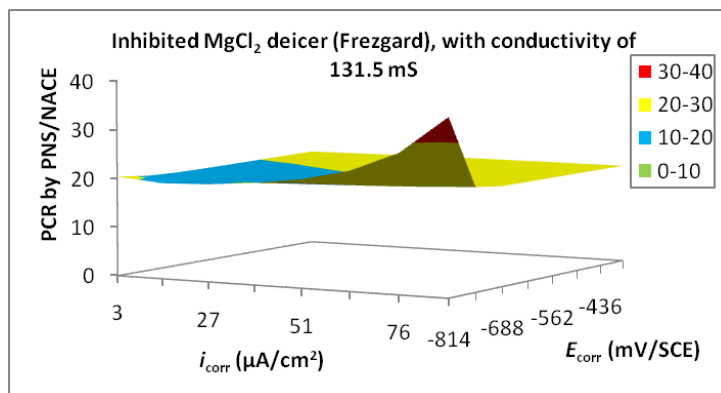
(a)



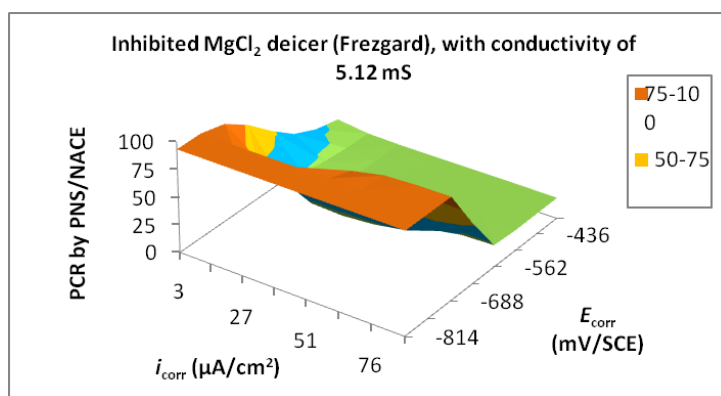
(b)

FIGURE 25 Predicted PCR as a function of i_{corr} and E_{corr} for inhibited $CaCl_2$ deicer (CCBTM), 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 relatively 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™), 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.

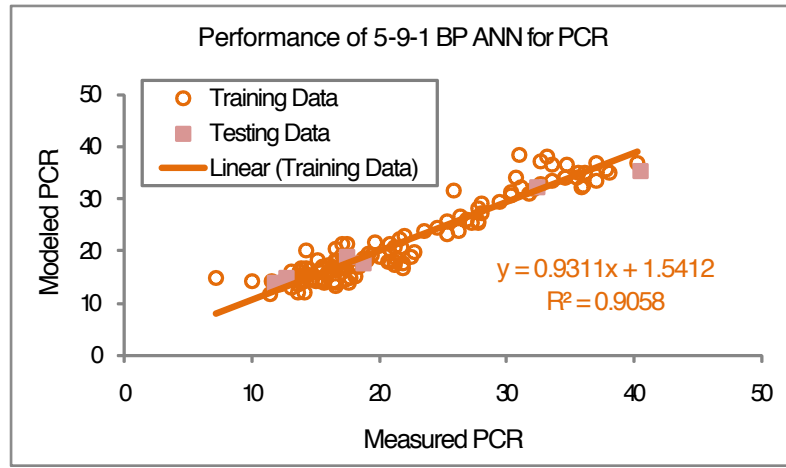
2.2.9. Correlating the Composition with the Corrosivity and Performance of Liquid Deicers

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 30°F regardless of deicer composition. All the DSC-derived $IMC_{30}^{\circ F}$ values remained within 3.79 ± 0.14 mL/mL; and this lack of diversity disqualified $IMC_{30}^{\circ F}$ as an output factor for ANN modeling.

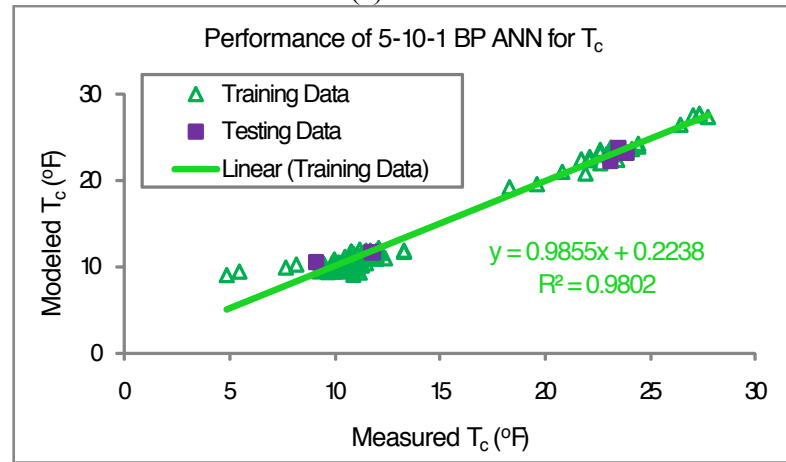
The data set used for the training and testing of the two ANN models include 120 and 6 records respectively. Through trial and error, a 5-9-1 model and a 5-10-1 model were used to capture the relationship between the deicer composition and the PCR and the T_c respectively. The training and testing SMSE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



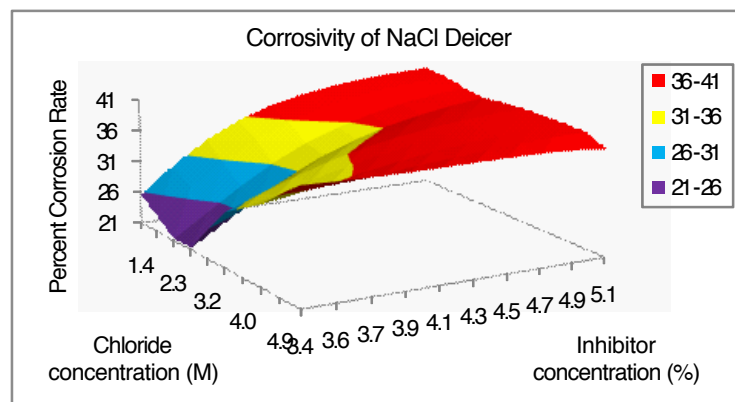
(a)



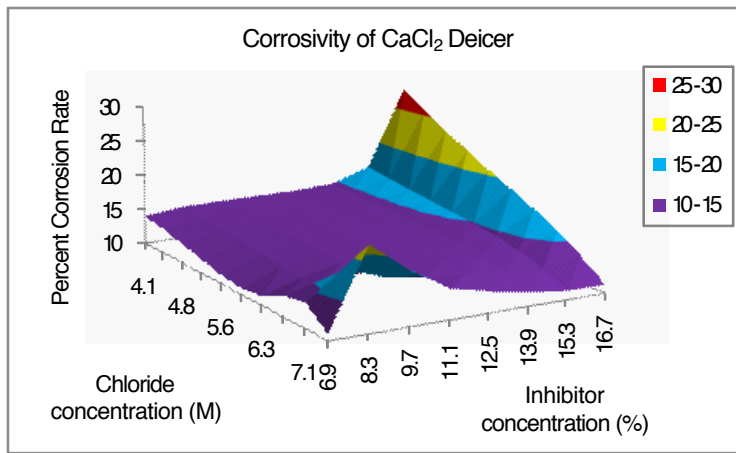
(b)

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

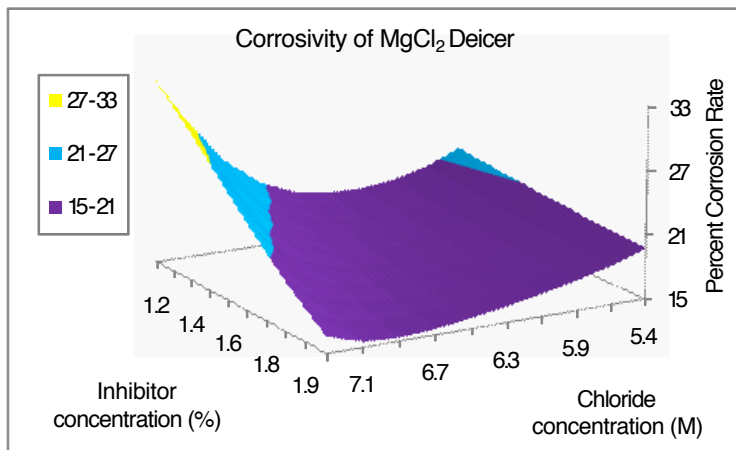
Figure 28 presents the predicted PCR value a function of chloride and inhibitor concentrations for the three liquid deicers, with pH and conductivity fixed at the median levels for each deicer, which were 7.56 and 200.0 mS respectively for NaCl+GLT, 4.92 and 132.1 mS/cm respectively for CCB, and 6.24 and 99.4 mS/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)

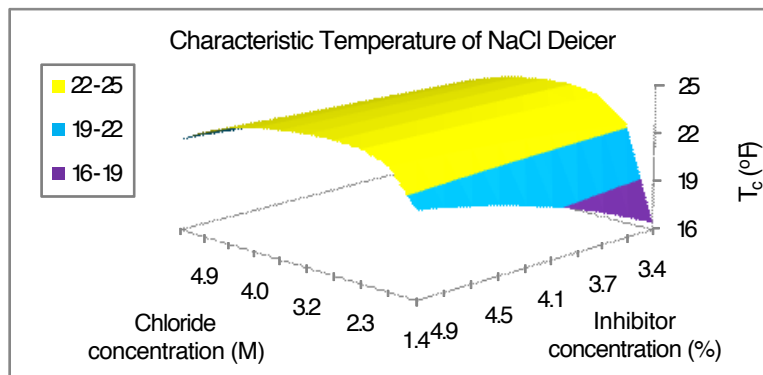


(b)

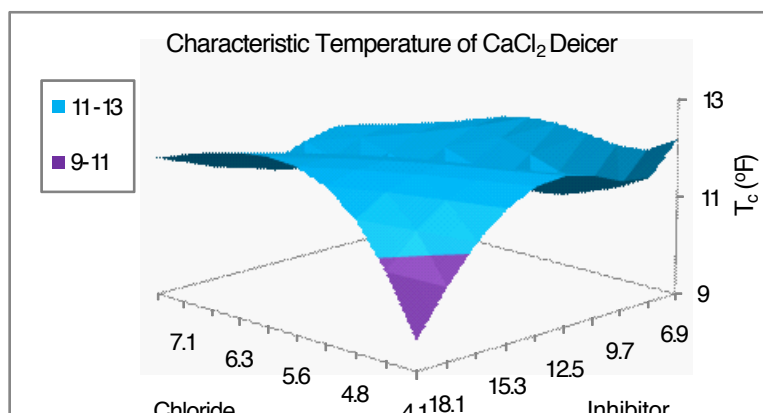


(c)

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)



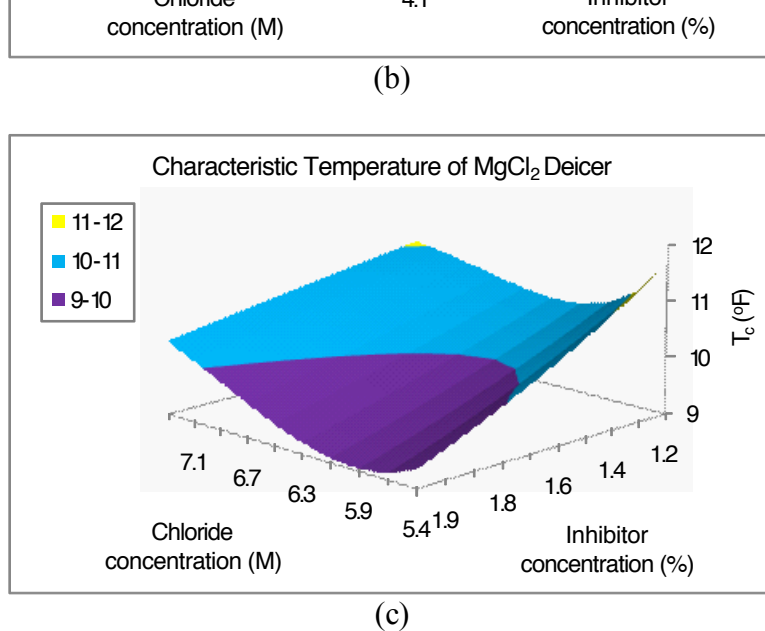


FIGURE 29 Predicted T_c as a function of chloride and inhibitor concentrations for (a) NaCl+GLT, (b) CCB, and (c) FreezGard, with pH and conductivity fixed at the median levels for each deicer.

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) 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)
<i>NaCl+GLT (with 4.3% inhibitor)</i>	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
<i>CCB (CaCl₂-based, with 11.1% inhibitor)</i>	154.3±1.6	13.7	191
Non-inhibited CCB brine	142.8±2.6	11.5	202

Non-inhibited CCB Brine (provided by the vendor)	142.6±2.9	11.9	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 FreezGard Brine (provided by the vendor)	130.4±5.1	10.3	215
Corrosion inhibitor only	165±38.3	32.6	169

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 (MgCl₂-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_{cor} and PCR), pH, electrical conductivity, and performance parameters (T_c and $IMC_{30^\circ\text{F}}$). 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 $IMC_{30^\circ\text{F}, 60\text{min}}$ of the FreezGard deicer samples remained very consistent within 10.2±1.2 °F and 3.7±1.1 mL/mL (snowmelt/deicer) respectively.
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 $9.3\pm 1.7\%$ and $11.2\pm 3.3\%$ 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 $IMC_{30^\circ\text{F}, 60\text{min}}$ of the CCB deicer samples remained very consistent within 11.2 ± 1.2 °F 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 $3.8\pm 0.2\%$ and $4.3\pm 0.4\%$ 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 $IMC_{30^\circ\text{F}, 60\text{min}}$ of the NaCl+GLT deicer samples remained very consistent within 23.5 ± 1.9 °F and 3.8 ± 0.2 mL/mL (snowmelt/deicer) respectively, suggesting higher T_c and similar $IMC_{30^\circ\text{F}}$ 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.

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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 man-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 CaCl₂ liquid deicer (Calcium Chloride with Boost, or CCBTM), and the inhibited MgCl₂ liquid deicer (FreezGard CI PlusTM). 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.

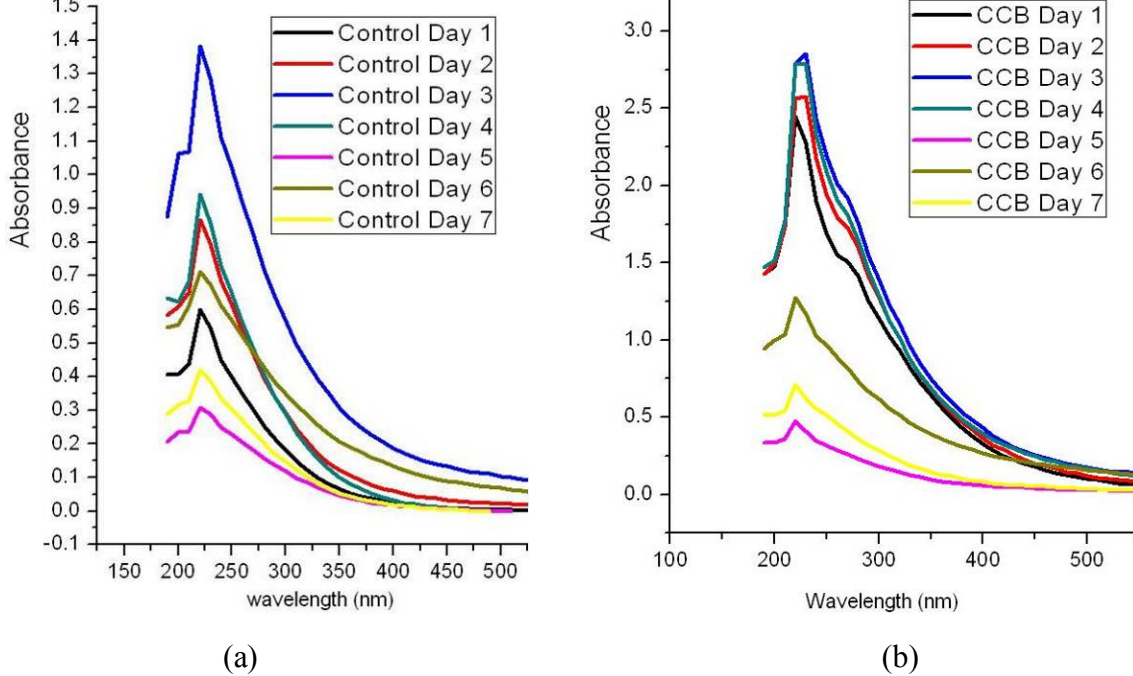


FIGURE 30 Measured UV-vis spectra of samples collected over the 7 days after deicer application for the black ice event: (a) from the control lane (with no deicer applied); (b) from the CCB lane.

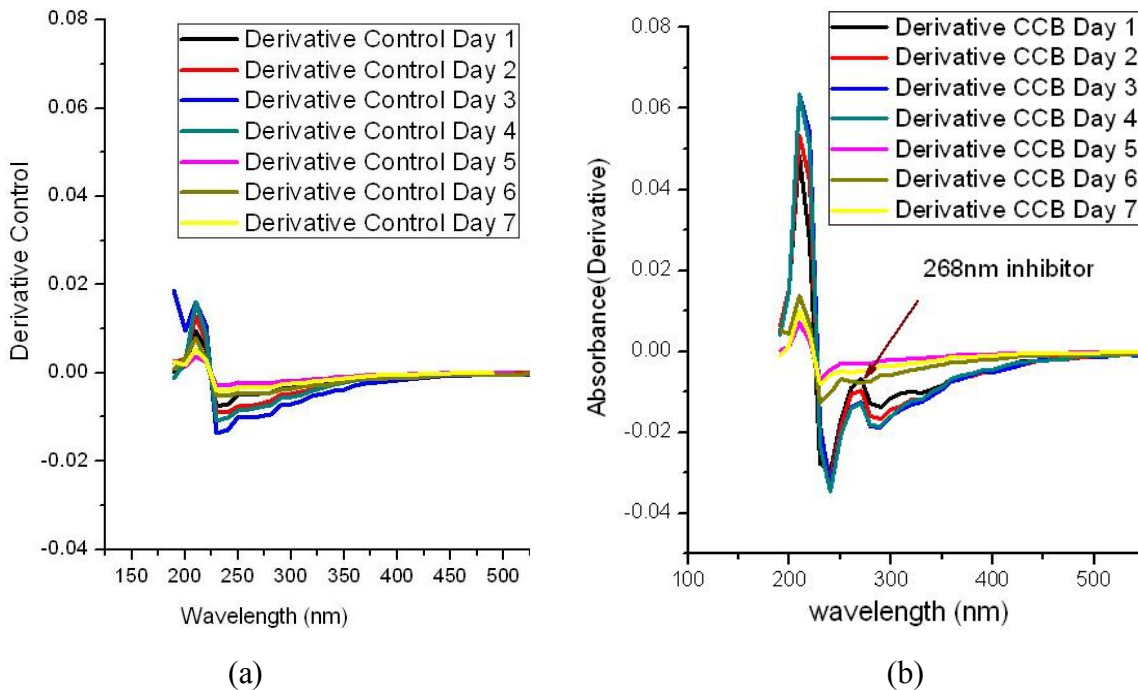


FIGURE 31 First-order derivative UV-vis spectra of samples collected over the 7 days after deicer application for the black ice event: (a) from the control lane (with no deicer applied); (b) from the CCB lane.

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 (see Figure 22), which features a climate chamber and a weathering facility that

(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.

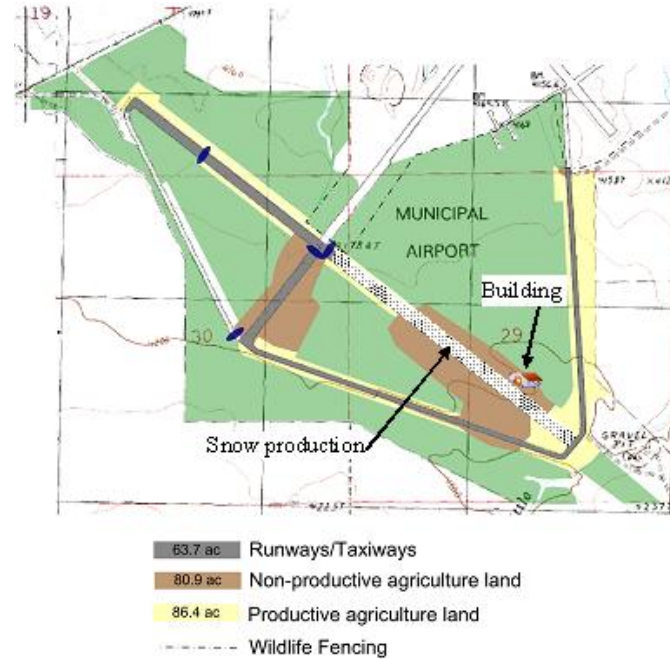


FIGURE 32 Marked aerial photo of the TRANSEND controlled field test-bed.

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.

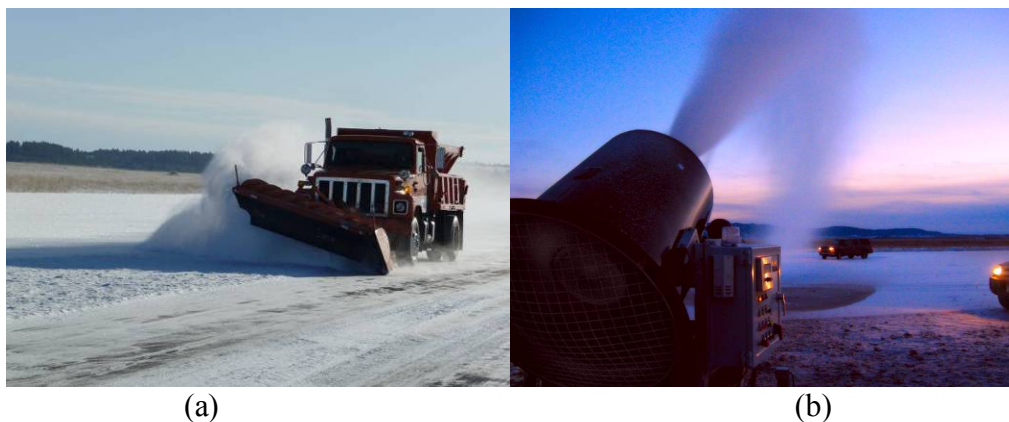


FIGURE 33 (a) Snowplowing and (b) practice of snowmaking at the TRANSEND facility during the 2009-2010 winter season.

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

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

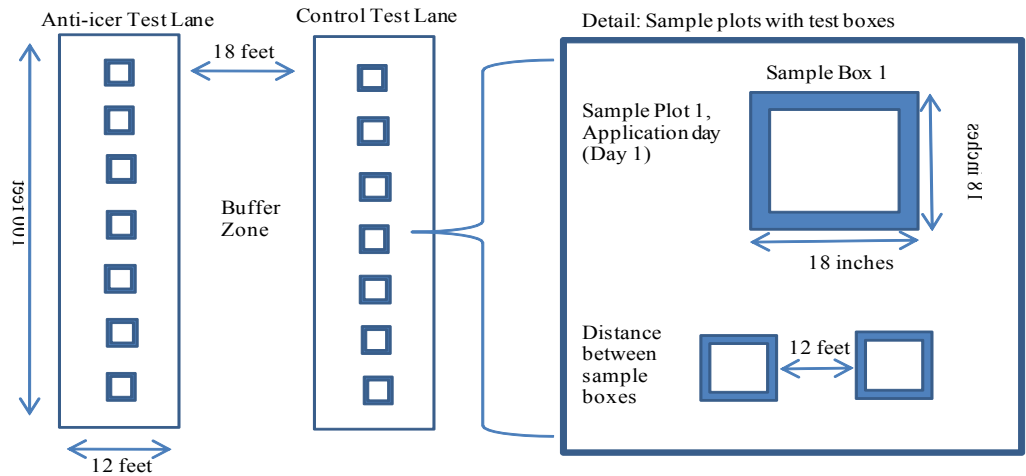


FIGURE 34 Diagram of test lanes and sampling plot layout. For the black ice event however, the boxes were of 32 by 32 inches.



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	AccmIn.
Black Ice Event 10-Feb-10 30 g/lb-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/lb-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	-	-	-	-
Natural Snow Event 12-Apr-10 20 g/lb-m 20-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	-	-	-	-

60 g/in-m	5	17-Apr-10	6:50 AM	110.3	-	-	-	-
45-min	6	18-Apr-10	12:30 PM	140.0	-	-	-	-
	7	19-Apr-10	10:45 AM	162.2	-	-	-	-

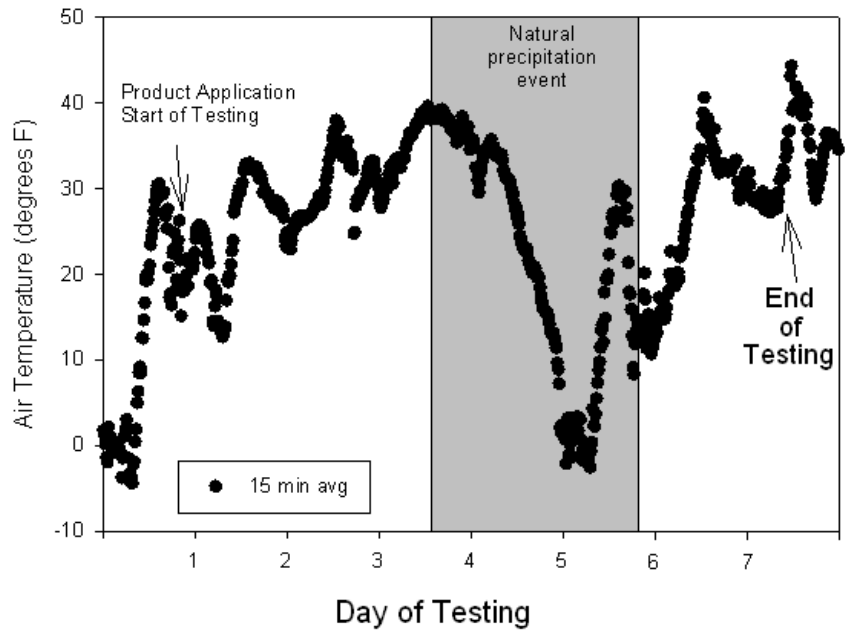


FIGURE 37 Temporal evolution of average air temperature during the black ice event.
BLACK ICE EVENT

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 0°F and 40°F). The air temperature on day 3 ranged between 28°F and 38°F, during which some rain precipitation occurred. On day 4 and day 5, the air temperature dropped to as low as -4 °F, 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 25°F and 50°F and gradually decreased over the first six days of the black ice event. There were many hours during which the pavement temperature dropped below 32°F, 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/m². 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/m², 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 20°F and 60°F). Immediately after the natural snow precipitation on day 3 and day 4, the air temperature dropped to the range of 34°F and 46°F.

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 25°F and 80°F 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 32°F, 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/m². 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 30°F and 46°F); thereafter, it showed a clear trend of daily fluctuations mostly between 30°F and 65°F. 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.

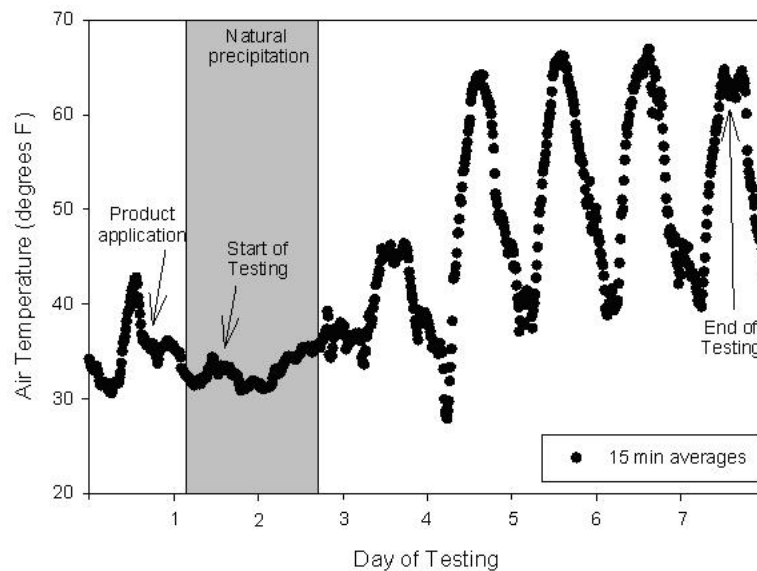


FIGURE 45 Temporal evolution of average pavement temperature during the natural snow event.

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 38°F and 48°F in the first 3.5 days and then increased in the range of 38°F and 56°F in daily cycles, suggesting that the ground was not frozen. The pavement surface temperature showed a trend of daily fluctuations mostly between 35°F and 95°F, except for the days of natural snow precipitation during which the pavement temperature remained mostly near 36°F, 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/m². 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.

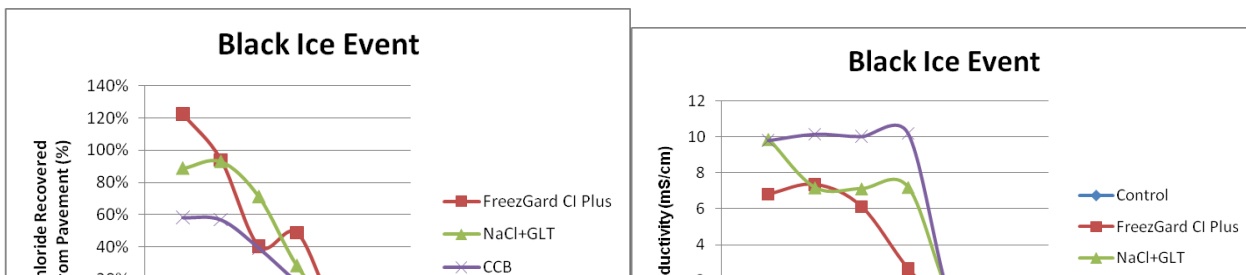
3.2.2. Longevity of Chlorides on the Pavement and Temporal Evolution of Solution Conductivity

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).



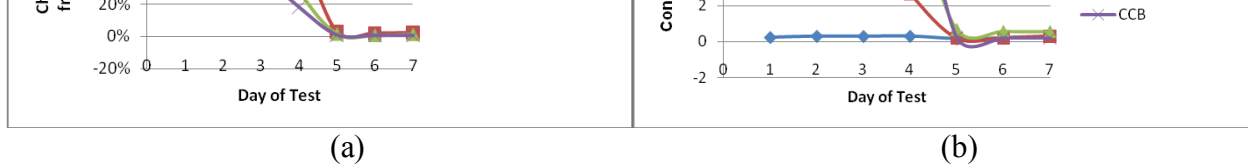


FIGURE 49 Temporal evolution of (a) chloride recovery efficiency and (b) electrical conductivity of samples collected from the asphalt pavement during the black ice event.

For the man-made snow event, the target deicer application rate was 60 gallons/lane-mile, 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.

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 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.

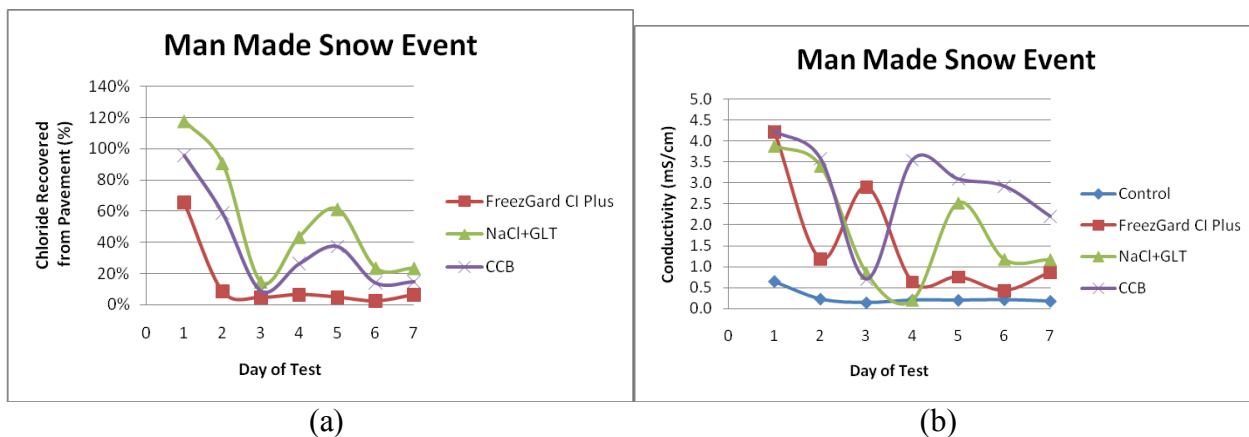


FIGURE 50 Temporal evolution of (a) chloride recovery efficiency chloride concentration and (b) electrical conductivity of samples collected from the asphalt pavement during the man-made snow event.

For the natural snow event, the target deicer application rate was 60 gallons/lane-mile, 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 residuals consistently showed 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.

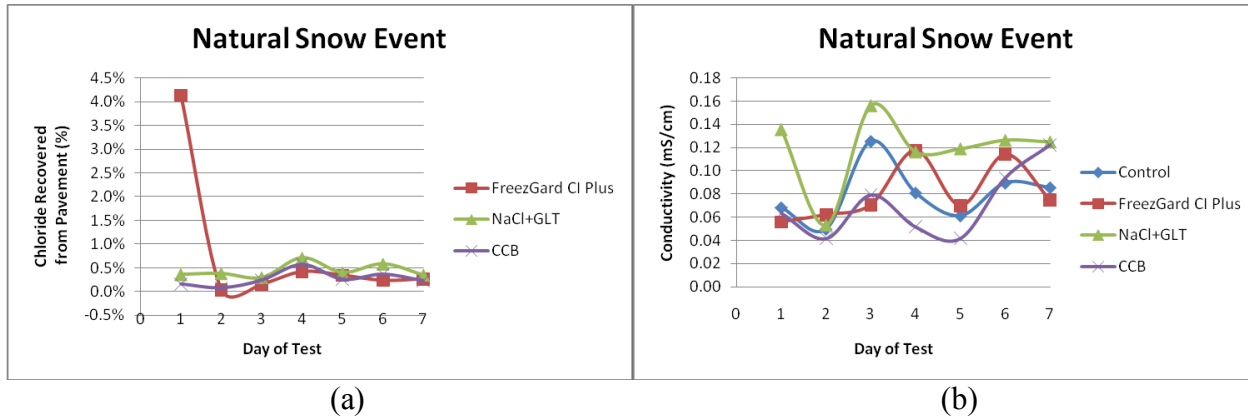


FIGURE 51 Temporal evolution of (a) chloride recovery efficiency chloride concentration and (b) electrical conductivity of samples collected from the asphalt pavement during the natural snow event.

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 3.5-4² of natural snow in the first 24 hours and about 0.75² of blowing snow on day 2. For the man-made snow event, however, the sampling boxes only received 1² of artificial snow and a total of 0.26² 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.

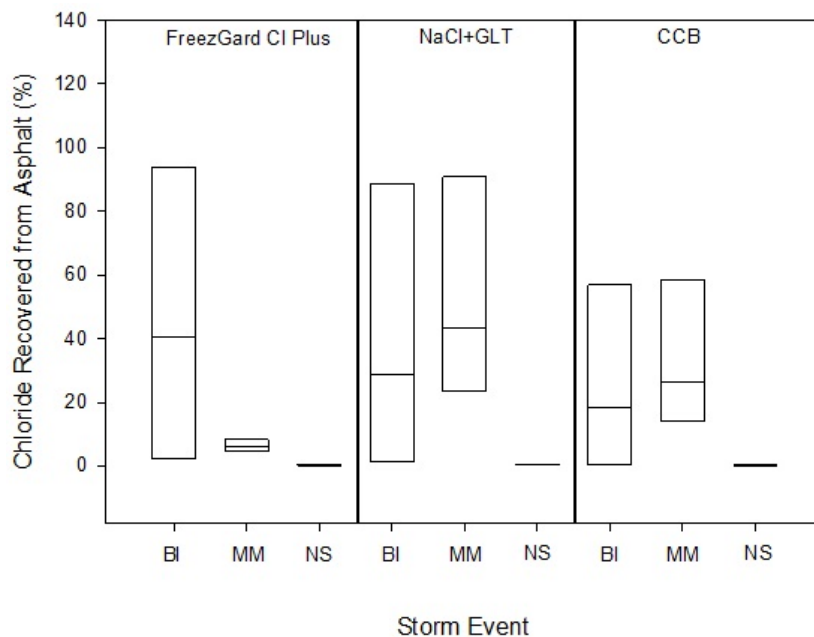
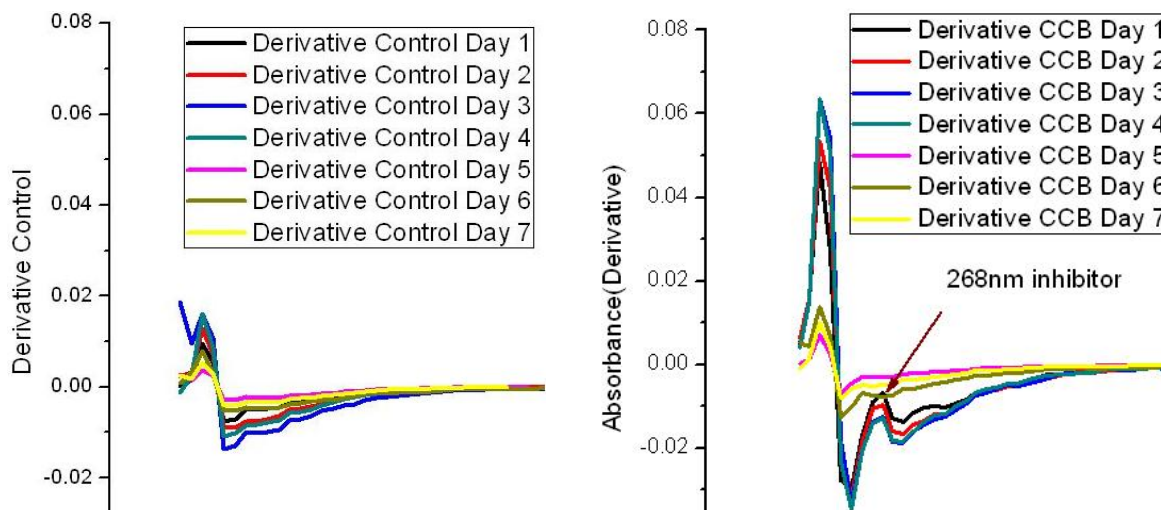


FIGURE 53 Box plot of chloride recovery efficiency on the asphalt pavement over the 7 days of sampling for each storm event.

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).



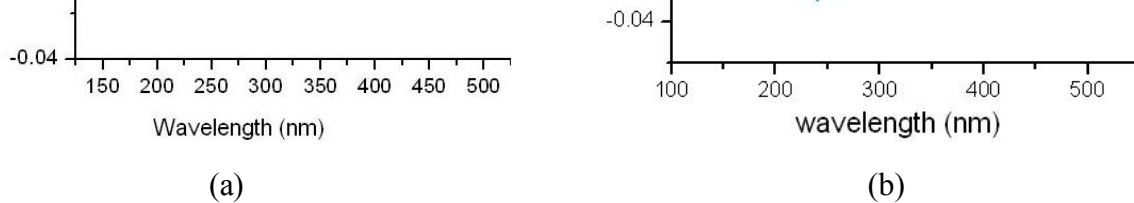


FIGURE 54 First-order derivative UV-vis spectra of samples collected over the 7 days after deicer application for the black ice event: (a) from the control lane (with no deicer applied); (b) from the CCB lane.

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).

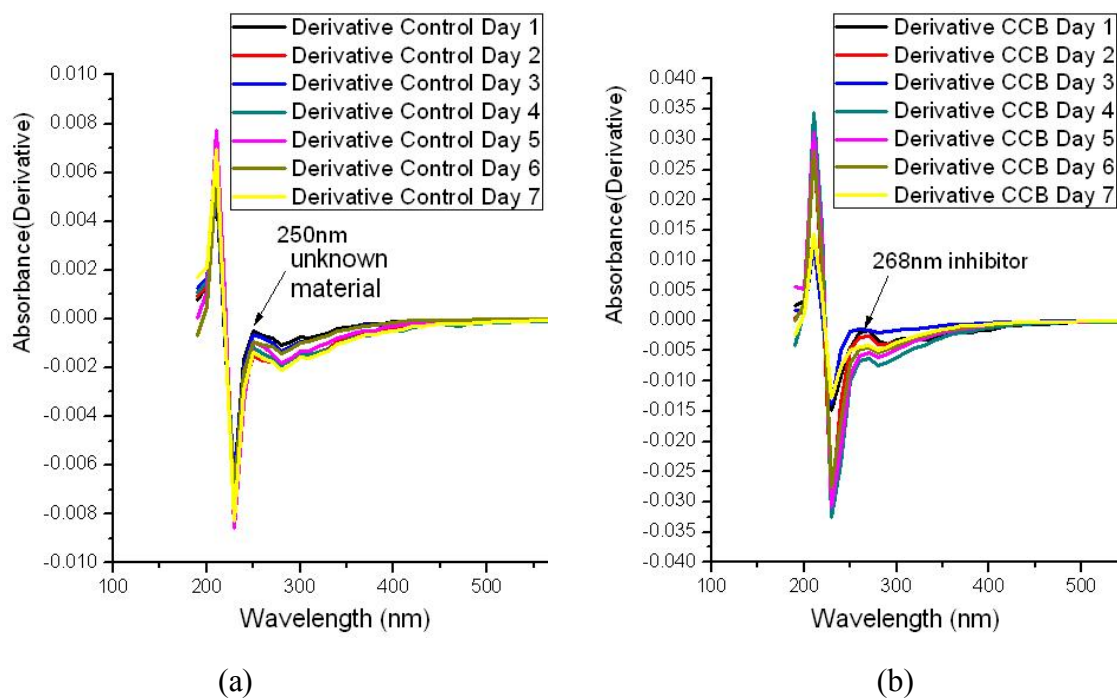
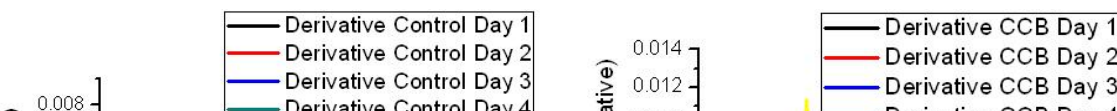


FIGURE 55 First-order derivative UV-vis spectra of samples collected over the 7 days after deicer application for the man-made snow event: (a) from the control lane (with no deicer applied); (b) from the CCB lane.



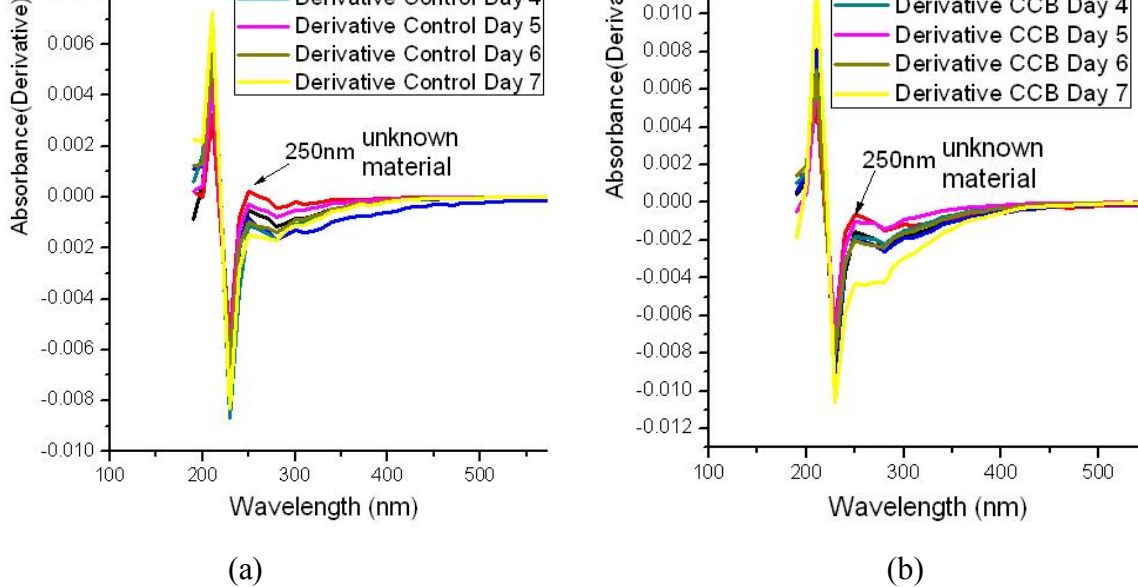


FIGURE 56 First-order derivative UV-vis spectra of samples collected over the 7 days after deicer application for the natural snow event: (a) from the control lane (with no deicer applied); (b) from the CCB lane.

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.

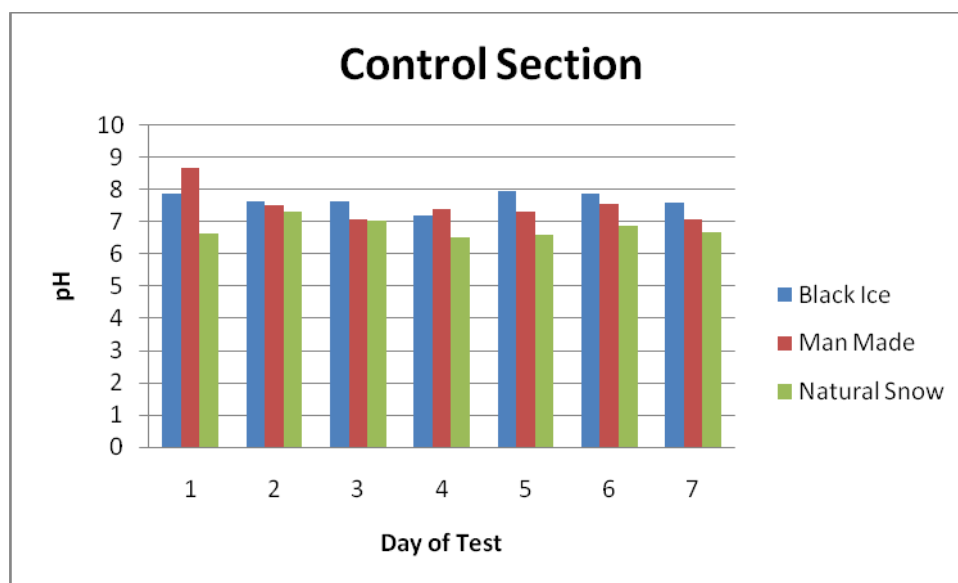


FIGURE 57 pH of samples from the control test lane for each storm

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). 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 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.

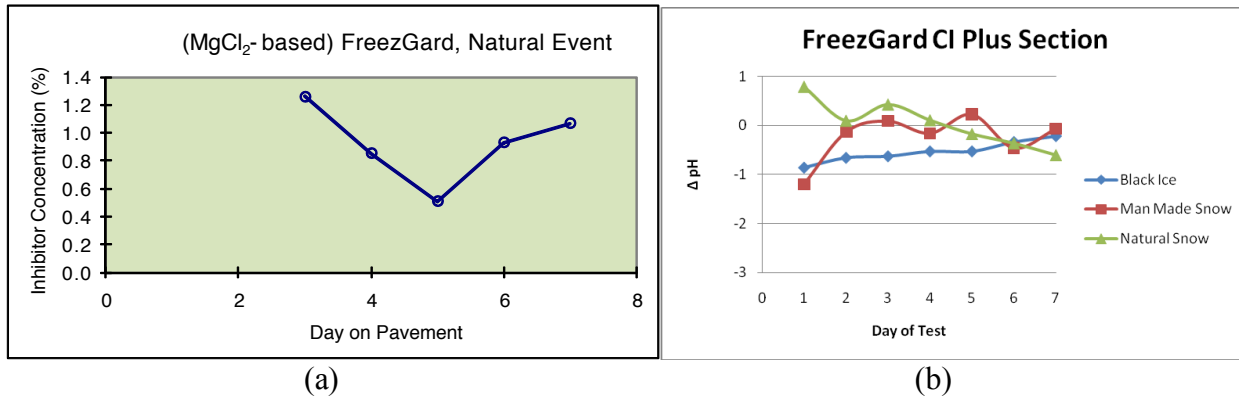


FIGURE 58 Temporal evolution of (a) inhibitor concentration and (b) relative pH of samples collected from the FreezGard deicer test lanes. Note that the FreezGard inhibitor signals for the black ice event and man-made event were not detectable for unknown reasons.

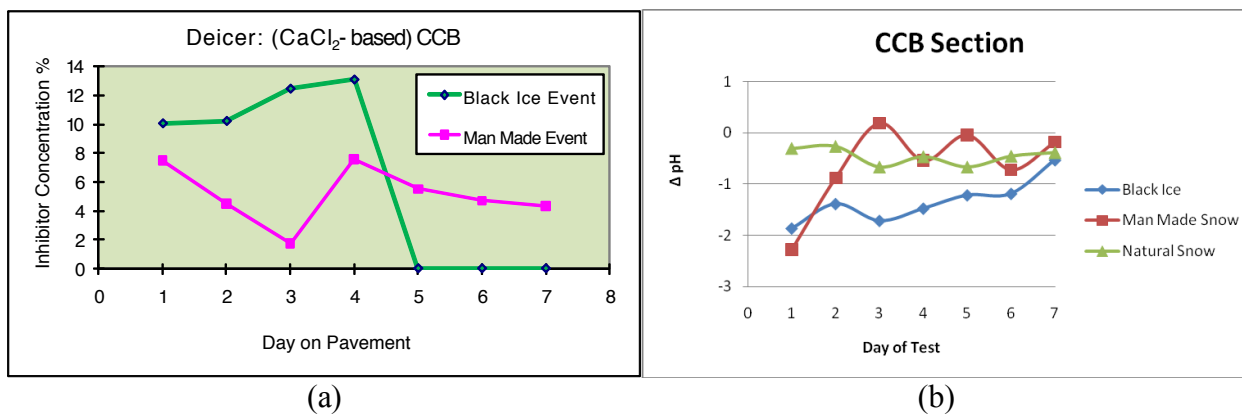


FIGURE 59 Temporal evolution of (a) inhibitor concentration and (b) pH of samples collected from the CCB deicer test lanes. Note that the CCB inhibitor signals for the natural snow event were not detectable for unknown reasons.

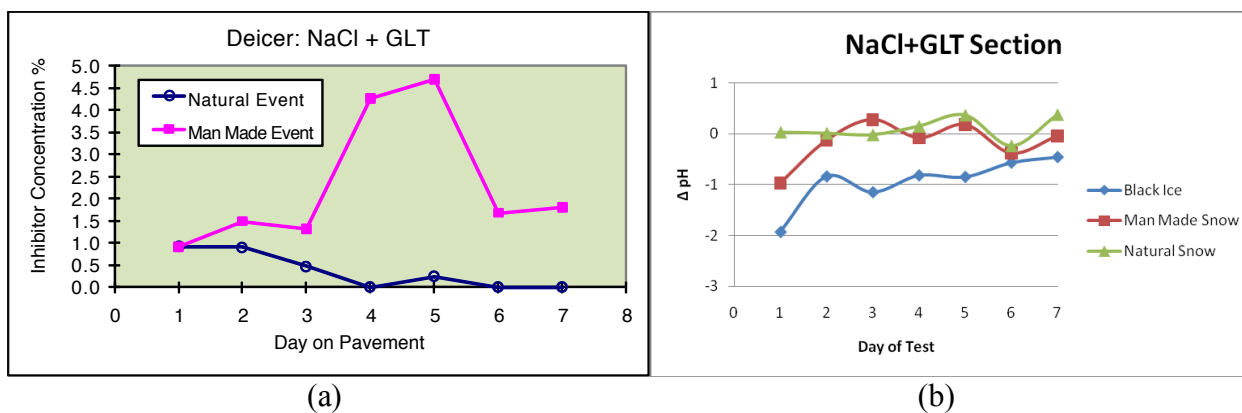


FIGURE 60 Temporal evolution of (a) inhibitor concentration and (b) pH of samples collected from the NaCl+GLT deicer test lanes. Note that the GLT inhibitor signals for the black ice event were not detectable for unknown reasons.

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

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 pavement test lanes over the sampling period. Note that unlike the field data

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)

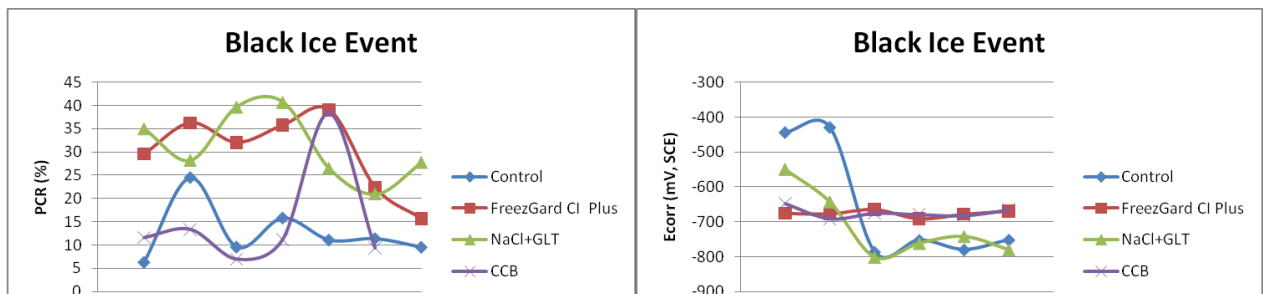




FIGURE 61 Temporal evolution of (a) PCR and (b) E_{corr} of samples collected from the asphalt pavement during the black ice event.

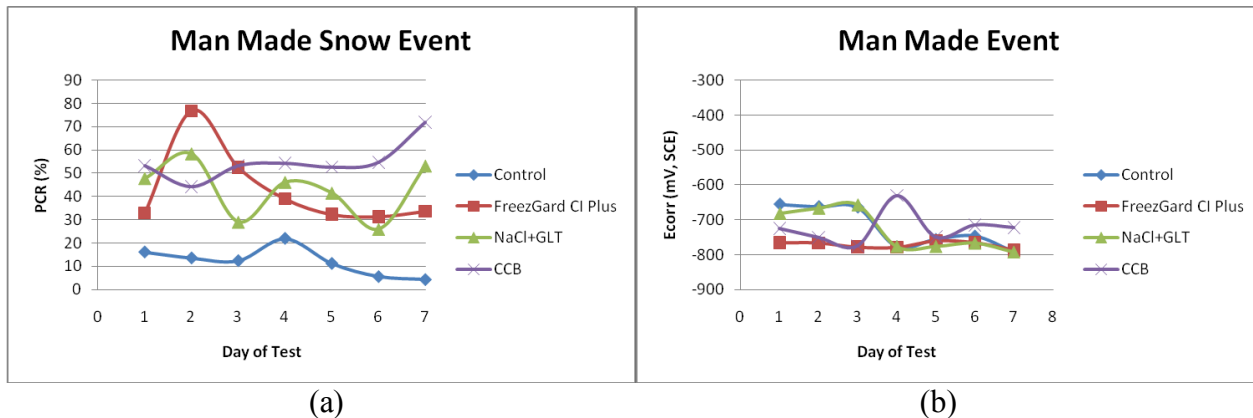


FIGURE 62 Temporal evolution of (a) PCR and (b) E_{corr} of samples collected from the asphalt pavement during the man-made snow event.

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.

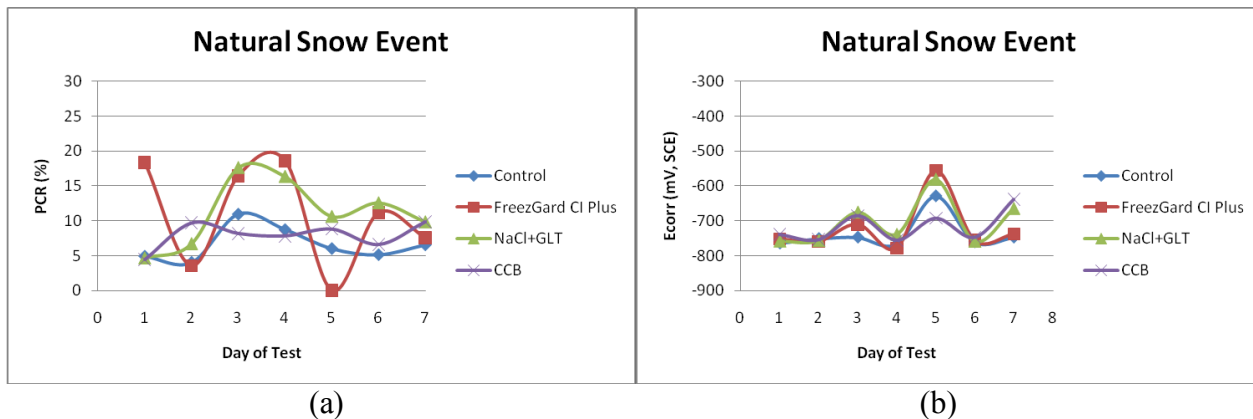


FIGURE 63 Temporal evolution of (a) PCR and (b) E_{corr} of samples collected from the asphalt pavement during the natural snow event.

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 $-562 \text{ mV}_{\text{SCE}}$ generally corresponded to PCR values lower than 30. It should be noted, however, that an E_{corr} value lower than $-562 \text{ mV}_{\text{SCE}}$ 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.

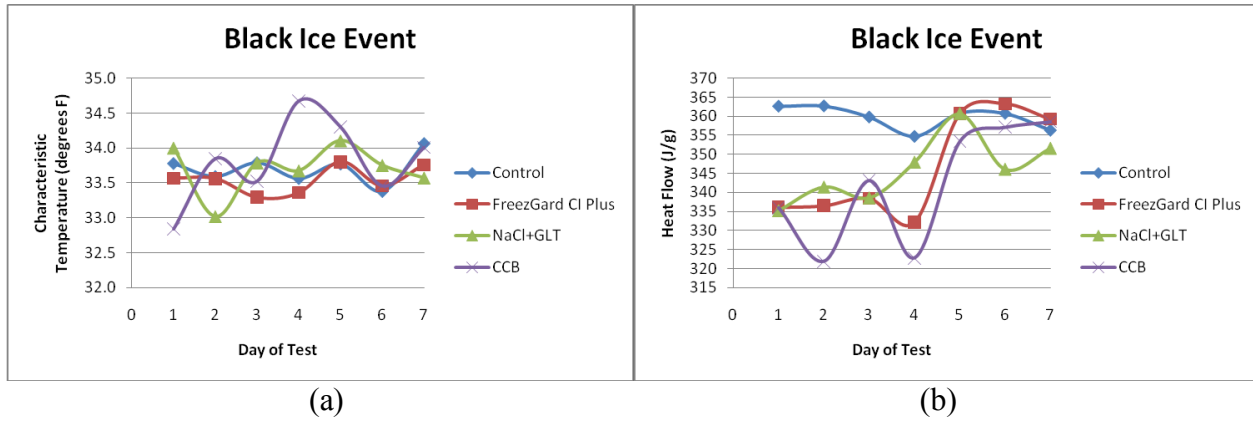


FIGURE 65 Temporal evolution of (a) T_c and (b) H of samples collected from the asphalt pavement during the black ice event.

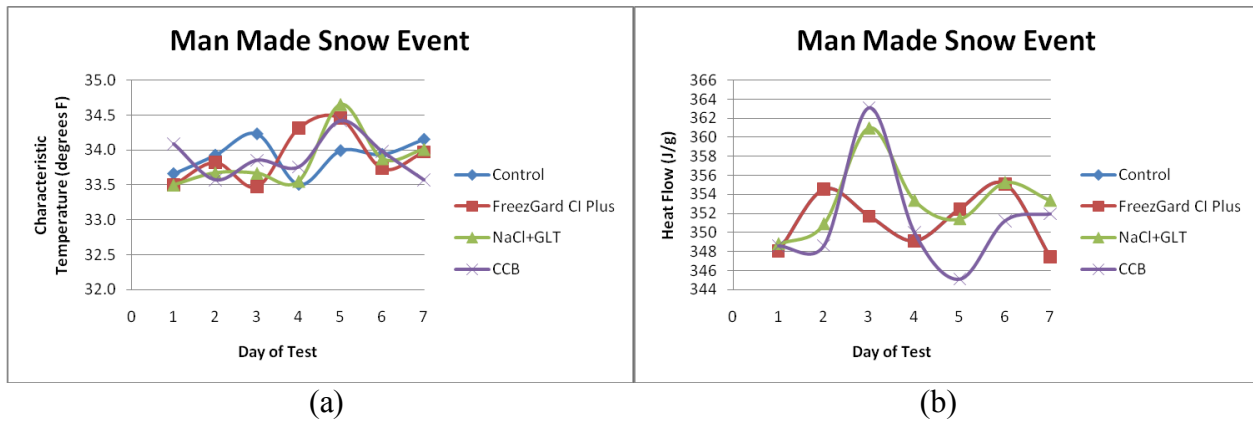


FIGURE 66 Temporal evolution of (a) T_c and (b) H of samples collected from the asphalt pavement during the man-made snow event.

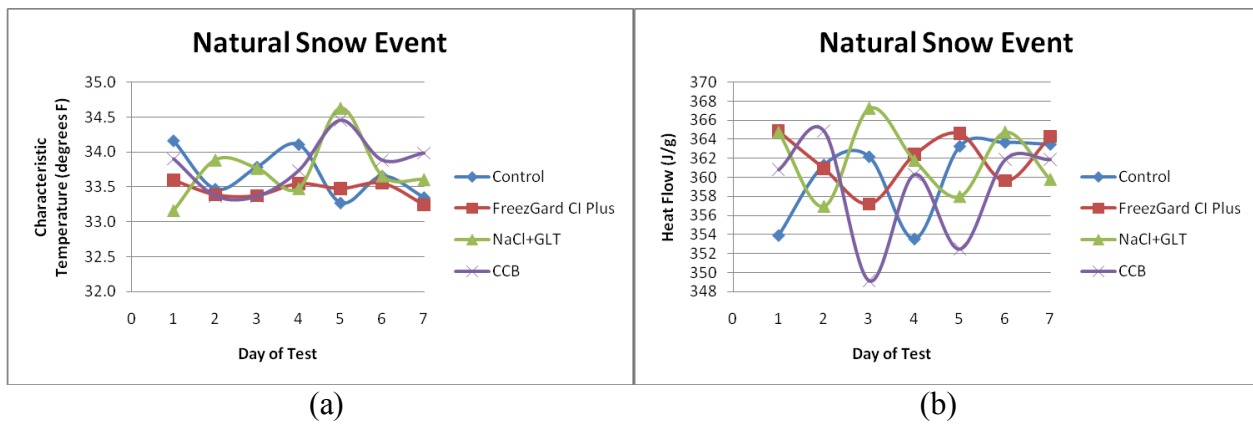


FIGURE 67 Temporal evolution of (a) T_c and (b) H of samples collected from the asphalt pavement during the natural snow event.

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 $IMC_{30^{\circ}\text{F}, 60\text{min}}$ of 21.7°F, 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 °F and ΔH values between -1 and -22 J/g, which were unable to be used to predict meaningful $IMC_{30^{\circ}\text{F}, 60\text{min}}$ 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 °F respectively) and positive ΔH values (10.3, 3.6, and 6.4 J/g respectively), corresponding to predicted $IMC_{30^{\circ}\text{F}, 60\text{min}}$ 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 $IMC_{30^{\circ}\text{F}, 60\text{min}}$ of 13.7°F, 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 °F and ΔH values between -4 and -20 J/g, which were unable to be used to predict meaningful $IMC_{30^{\circ}\text{F}, 60\text{min}}$ 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 °F respectively) and positive ΔH values (7.8, 23.2, 1.9, and 22.3 J/g respectively), corresponding to predicted $IMC_{30^{\circ}\text{F}, 60\text{min}}$ 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 $IMC_{30^{\circ}\text{F}, 60\text{min}}$ of 11.2°F, 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 °F and ΔH values between -3 and -20 J/g, which were unable to be used to predict meaningful $IMC_{30^{\circ}\text{F}, 60\text{min}}$ 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 °F respectively) and positive ΔH values (18.6, 8.5, 6.6, and 12.8 J/g respectively), corresponding to predicted $IMC_{30^{\circ}\text{F}, 60\text{min}}$ 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 $IMC_{30^{\circ}\text{F}, 60\text{min}}$ 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 0.75^2 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 1^2 of artificial snow and a total of 0.26^2 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 $3.5-4^2$ of natural snow in the first 24 hours and about 0.75^2 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.

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 (MgCl₂-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 $IMC_{30^\circ\text{F}}$). 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 $35.6\pm 0.8\%$ and $1.7\pm 0.3\%$ 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 $IMC_{30^\circ\text{F}, 60\text{min}}$ of the FreezGard deicer samples remained very consistent within 10.2 ± 1.2 °F and 3.7 ± 1.1 mL/mL (snowmelt/deicer) respectively.
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 $9.3\pm 1.7\%$ and $11.2\pm 3.3\%$ 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 $IMC_{30^\circ\text{F}, 60\text{min}}$ of the CCB deicer samples remained very consistent within 11.2 ± 1.2 °F 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 $3.8 \pm 0.2\%$ and $4.3 \pm 0.4\%$ 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 $IMC_{30^\circ\text{F}, 60\text{min}}$ of the NaCl+GLT deicer samples remained very consistent within 23.5 ± 1.9 °F and 3.8 ± 0.2 mL/mL (snowmelt/deicer) respectively, suggesting higher T_c and similar $IMC_{30^\circ\text{F}}$ relative to the MgCl₂- or CaCl₂-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

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 0.75^2 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 1^2 of artificial snow and a total of 0.26^2 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 $3.5\text{-}4^2$ of natural snow in the first 24 hours and about 0.75^2 of blowing snow on day 2. The percent of chloride recovered from the pavement was less

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.

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 (MgCl₂-based FreezGard, CaCl₂-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.

