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## **APPENDIX A: LABORATORY TESTING METHODS**

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

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

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

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

• <u>*Field-collected*</u> sample is a general label that includes *Storage* and *Pavement* collected samples from the TRANSCEND facility, Lewistown, Montana. All *field-collected* samples are handled similarly throughout the entirety of this project.

This document consists of ten test methods aimed to characterize the pH, chloride concentration, inhibitor concentration, instantaneous corrosivity, 72-hour average corrosivity, thermal properties of the deicer solution, conductivity, total phosphorus, inhibitor degradation by ultraviolet radiation, and inductively coupled plasma mass spectrometry. The details of each test method are provided. **A1. Test Method for Determining pH of an Undiluted Deicer Solution** 

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

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

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

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

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

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

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

#### Mohr's method to determine chloride ion concentration by titration:

This method determines the chloride ion concentration	Equipment Needed
of a solution by titration with silver nitrate. As the silver	burette and stand
chloride forms.	10 and 20 mL pipettes
$\Delta \sigma^+ + C \downarrow^- \longrightarrow \Delta \sigma C \downarrow$	100 mL volumetric flask
The end point of the titration ensure when all the	250 mL conical flasks
The end point of the titration occurs when all the	10 mL and 100 mL measuring cylinders

chloride ions are precipitated	1. Then additional chloride	
Scan Definition	Ell Definition	
Waveform:       I1         0	Comment Applies a constant current, while measuring the resulting potential. Instrument Instrument Set: Model 263A at address 15 • PowerBooster Working Electrode Type: [unspecified] • Area: 2.75 cm <sup>2</sup> Density: 0.000 g/ml Equivalent Weight: 0.000 g	<b>ded</b> ion:(0.1 mol L <sup>-1</sup> ) If possible, dry 5 g of at 100°C and allow to cool. Accurately of solid AgNO <sub>2</sub> and dissolve it in 250 er in a conical flask. Store the solution <b>te indicator solution:</b> (approximately e 1 g of K <sub>2</sub> CrO <sub>4</sub> dissolved in 20 mL
<ul> <li><u>Back</u></li> <li><u>N</u>ext &gt;</li> <li>Finish</li> <li>Cancel</li> <li>Help</li> </ul>	Reference Electrode Type: Ag, AgCl / KCl (sal'd) Offset Potential vs Normal Hydrogen Electrode: 0.197 Volts	LT was titrated with 0.01 M as FreezGard CI Plus and CCB $n 0.1 \text{ M AgNO}_3$ .

#### Titration

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

#### Results Calculations

- 1. Determine the average volume of silver nitrate used from the concordant titres.
- 2. Calculate the moles of silver nitrate reacting.
- 3. Determine the moles of chloride ions reacting.
- 4. Calculate the concentration of chloride ions in the diluted deicer solution and then the original identify the first appearance of red-brown colouration. Figure 2 Color change observed during titration. storage-collected deicer solution.

gives the clear solution a lemon-yellow colour.



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

#### Additional Notes

- 1. Silver nitrate solution will stain clothes and skin. Any spills should be rinsed with water immediately.
- 2. Residues containing silver ions are usually saved for later recovery of silver metal. Check this with laboratory manager.
- 3. The Mohr titration should be carried out under conditions of pH 6.5 - 9. At higher pH silver ions may be removed by precipitation with hydroxide ions, and at low pH chromate ions may be removed by acid-base reaction to form hydrogen chromate ions or dichromate ions affecting the

accuracy of the end point.

4. It is a good idea to first carry out a "rough" titration in order to become familiar with the color change at the end point.

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

#### Method

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

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

#### Step 1- Fabrication of the Chloride Sensor

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

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

For diameter, d = 2.03 mm & length, l = 35mm:  

$$SA = \pi \times d \times l$$
  
 $SA = 3.142 \cdot 2.03 \text{mm} \cdot 35 \text{mm} = 223.2391 \text{ mm}^2$   
 $223.2391 \text{ mm}^2 \cdot \left(\frac{1 \text{ cm}^2}{100 \text{ mm}^2}\right) = 2.2324 \text{ cm}^2$ 

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

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

- Instrument
  - Instrument Set: Original Model 263A at address xx
- Working Electrode
  - *Type:* (unspecified)
  - Area: Input the surface area calculated previously, SA, in units of cm<sup>2</sup>
  - Density: 0.000 g/ml
  - Equivalent Weight: 0.000 g
- Reference Electrode
  - Type: Ag AgCl/KCl (saturated)

*Type: 115, 11501 (Saturated)* 

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

For Run 1

•

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

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

#### Step 2- Standard Curves and Sensor Calibration

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

For each type of chloride-based deicer (MgCl<sub>2</sub>, CaCl<sub>2</sub> and NaCl), the research team will prepare standard solutions with known chloride concentration (using water as the solvent) and subject them to an Ag/AgCl electrode. The presence of the chloride will give a reading (*E*) proportional to the concentration. As such, a standard calibration curve can be established for each chloride. For any field samples with unknown chloride concentration, the electrode's response to the sample can be compared against the calibration curve to derive the chloride concentration. For example, Figure 5 shows a calibration curve for a chloride sensor prepared by the WTI CSIL researchers. This data provides the chloride sensor calibration curve established using the NaCl+GLT deicer, which shows a strong linear correlation between the natural logarithm of the chloride concentration in the deicer and the electrochemical potential reading of the chloride sensor placed in the deicer (in mV). The same correlation also held well for standard solutions made from reagent-grade NaCl (as indicated by the empty dots in the graph).



Figure 5 Calibration curve for chloride sensor in NaCl solutions.

Due to the logarithmic relationship between the Galvanostatic Coated Silver-wire and the SCE Reference Electrode, a new standard curve was required for each deicer on the day of testing. The

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

#### Step 3- Sample Preparation and Analysis

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

#### Data Analysis

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

#### Molarity Method

The molarity method will be demonstrated using FreezGard CI Plus and MgCl<sub>2</sub> information and formulae.

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

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

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

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

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

#### **Dilution Rate Method**

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

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

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

For 
$$D = 86.7\%$$
  
M = 0.867 · 6.305 = 5.466

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

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

Deicing Product	Experimental Malarity	Molecular Weight of the Salt
	Moranty	(g/mor)
NaCl+GLT	4.81	58.443
ССВ	3.92	110.984
FreezGard	6.305	95.211
IceSlicer Elite	N/A	58.443

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

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

The ultraviolet-visible spectroscopy or spectrophotometry (UV-Vis) method has been routinely used in the quantitative determination of solutions of transition metal ions and highly conjugated

organic compounds. Organic compounds, especially those with a high degree of conjugation, also absorb light in the UV or visible regions of the <u>electromagnetic spectrum</u>. The research team will identify the *characteristic* UV-absorption peak for each of the selected corrosion inhibitors possibly without knowing their exact chemical composition. The inhibited NaCl liquid deicer (with Shield GLT<sup>TM</sup>), the inhibited CaCl<sub>2</sub> liquid deicer (CCB<sup>TM</sup>) and the inhibited MgCl<sub>2</sub> liquid deicer (FreezGard CI Plus<sup>TM</sup>) each showed a characteristic UV-absorption peak near 275 nm, 264 nm and 260 nm respectively.

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

#### Method

The UV-VIS instrumentation is Spectromax 384 Plus form Molecular Devices. Data acquisition and transfer are performed via SoftMax Pro 4.3.1 software on Mac OS 9.2. Final analysis is computed using Microsoft Excel<sup>®</sup>. The spectrophotometer is set to collect the full spectrum 190 to 750 t Figure 3 Silver sire electrode plating set-up screen. nple. Each ucreer is ran at the enupoint (peak wavelengur) determined from the method development. A DI water sample is run as a reference sample for each UV-Vis analysis. Each deicer-inhibitor solution has a specific set of standard dilutions and sample dilutions as well as a specific peak adsorption wavelength. A standard curve, a correlation between the inhibitor concentration and the UV signal intensity, is generated with the endpoint data from the series of standard dilutions. For any field samples with unknown inhibitor concentration, the measured UV-Vis absorbance of the sample is compared against the calibration curve to derive the inhibitor concentration. On each testing day, an inhibitor concentration standard curve is established for each deicer type, using at least five standard solutions with known inhibitor concentration. These procedures are detailed below for each deicer/inhibitor used in this research project.

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

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





Figure 7 UV-Vis spectra of FreezGard CI Plus deicer solutions diluted to various degrees.

Please note the following definitions:

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

#### FreezGard CI Plus

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

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

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

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

Pavement-collected samples were tested without further dilution. The pavement samples are stored in seven dram snap-cap sample vials and labeled with collection date plot number and deicer type.

Prior to test the pavement samples are inverted once to ensure analysis of a homogenous sample.

#### Calcium Chloride with Boost

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

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

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

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

#### NaCl+GLT

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

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

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

#### $y = -37.53 \ln(x) - 20.895$

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

 IceSlicer Elite
 Figure 6 An example of a standard curve correlating salt molarity with

 We experimented wi
 sensor potential.
 ared

 into 23 wt% solution
 y be
 y be

liquid solution, and the poor solubility of its inhibitor. As such, the inhibitor concentration in IceSlicer Elite solutions was determined by measuring the total phosphorus concentration instead (as detailed in Appendix A9).

#### Data Analysis

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



(a)



(b)



(c)

Figure 8 UV-Vis standard curves correlating the characteristic absorption strength as a function of inhibitor concentration: a) FreezGard CI Plus corrosion inhibitor, b) CCB corrosion inhibitor, and

#### c) GLI corrosion initionor.

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

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



Figure 9 Potentiodynamic polarization curves of a steel sample in a simulated deicer solution, as a function of inhibitor presence.

#### Method

Please note the following definitions:

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



Figure 10 Counter electrode.



Figure 11 Reference electrode.

#### Preparation of the working electrode

A sheet of mild steel (ASTM A36) is laser cut into 1 cm square coupons. To make the working

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

#### Test Procedure

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

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

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

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

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

As such, the Potentiostat software is used to fit the measured weak polarization curve and obtain the four key parameters,  $E_{corr}$ ,  $i_{corr}$ ,  $b_a$  and  $b_k$ . For any known metal, the corrosion rate can be easily

converted from current density (mA/cm<sup>2</sup>) to weight loss (MPY or milli-inches per year).

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

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

#### General Method:

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

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

#### Method

#### Step 1- Preparation of the Coupons

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

- 1. Wipe the coupon with a suitable solvent to remove grease and oil.
- 2. Examine each coupon closely and reject those that are subject to flaws or metallurgical abnormalities.
- 3. All coupons are tested by the vendor prior to shipment for Rockwell Hardness of C 38-45; coupons having hardness values outside of this range are rejected.
- 4. Coupons deemed acceptable for testing are stamped for identification.
- 5. Coupons are then acid-etched (cleaned) with 1+1 hydrochloric acid (HCl) for approximately 2-3 minutes.
- 6. The coupons are then quickly rinsed with tap water, DI water, wiped dry and placed in chloroform.
- 7. When removed from the chloroform, the coupons are placed on a tray lined with paper towels and are not touching each other. The coupons are air dried in a ventilated hood for a minimum of 15 minutes.
- 8. Coupons are measured as specified in Step 2. (Note: gloves must be worn during cleaning and measuring to prevent the transfer of oil or other residues onto the coupons. If the coupons are handled with ungloved hands, the coupons should be re-cleaned using the method above prior to weighing.)
- 9. Each coupon will be weighed to a constant weight. The constant weight shall be two consecutive weights of each coupon within a minimum of 0.5 milligrams of each other.

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

#### Step 2-Measuring of the Coupons

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

A = (3.1416/2)'(D2 - d2) + 3.1416t' D + 3.1416t' d

# t = average thickness

Example:

 $A = 1.5708 \quad (1.9044-0.3136) + 0.4768949 + 0.1935226$   $A = 1.5708 \quad 1.5908 + 0.4768949 + 0.1935226$  A = 2.4988286 + 0.4768949 + 0.1935226 A = 3.1692461 square inches (Total surface area of the coupon.)A = 3.17 square inches

#### Step 3—Preparation of the Solutions

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

#### Step 4—The Corrosion Test

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

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

#### Step 5—Cleaning of the Coupons after Corrosion Test

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

#### Siep 0 - Evaluation of Corrosion

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

MPY = (weight loss (milligrams)) (534) / ((area) (time) (metal density))

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

#### Step 6-Additional Information

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

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

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

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

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

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

#### Step 8–Negative Numbers

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

#### Data Analysis

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

Example:

Magic Melter II has a corrected value of 10.15 Salt has a corrected value of 45.00 Therefore: (10.15 / 45.00) ´ 100 = 22.6% Pass Acme Melter has a corrected value of 19.99 Therefore: (19.99 / 45.00) ´ 100 = 44.4% Fail

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

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

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

Method:

#### Step 1- Deicer Preparation

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

#### Step 2- Sample Preparation

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

#### Step 3- DSC Test Parameter

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

#### Step 4- Replication

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

#### Step 5- Integration

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

#### Step 6- Calculations

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

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

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

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

Where

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

T<sub>i</sub> is peak temperature (°F) for test i

n is number of replicate tests

#### Step 7- Analysis

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

#### Interpretation:

#### Step 1- Characteristic Temperature

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

#### Step 2- Predicted Ice Melting Performance:

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

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

Where:

IMC = Ice Melting Capacity (expected volume of brine that will be collected in Modified SHRP Ice Melting Test after 60 minutes (mL))  $\Delta H$  = 334 J/g minus average heat flow (H<sub>avg</sub> in J/g) T = average peak temperature (T<sub>avg</sub> in °F)

#### A8. Test Method for Determining Conductivity of a Deicing Solution

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

#### Method:

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

#### Step 1- Instrument Calibration

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

#### Step 2- Sample Measurement

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

key.

#### Analysis:

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

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

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

#### Method- For Collecting Total Phosphorus Data:

Due to the phosphate characteristic of the IceSlicer Elite inhibitor and the difficulty of putting the corrosion-inhibitor into solution, two Total Phosphorous testing methods were used to determine the inhibitor concentration of each sample. The first method described below determined the total phosphate concentration following Method 10127 from the Hach® Colorimeter Testing Handbook. Essentially, a test represents one blank standard of de-ionized water and three repetitions of one sample. Prior to adding to the "Test 'N Tube<sup>TM</sup>" vials, the samples are diluted to an appropriate level to ensure that their measurements fall within 10.0-100.0 mg/L PO<sub>4</sub><sup>3-</sup>. The dilution rates were typically around 3% to achieve an acceptable reading. The vials are filled with sample, a Potassium Persulfate Pillow for Phosphonate, and run through a hydrolysis process where the vials are subjected to 150°C for 30 minutes in the DRB200 reactor unit. Once the hydrolysis process is complete and the vials are allowed to cool to room temperature, a ratio of sodium hydroxide and Molybdovanadate Reagent is added to each vial. Within 7-9 minutes the measurement must be taken and is done with the Hach® DR/890 Colorimeter.

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

#### Step 1- Sample Preparation

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

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

#### Step 2-Processing the Samples

Following the cooling process of the vials, add 2 mL of sodium hydroxide to each vial including the standard using a TenSette<sup>®</sup> Pipette. Add 0.5 mL of Molybdovanadate to each vial including the standard using a Bulb Pipette. Replace each vials cap and invert to mix. Then allow the mixed vials to rest for seven to nine minutes before taking a measurement. Remove the cover from the colorimeter to insert the vial labeled "blank". Replace colorimeter cover securely and press "Zero"

to calibrate the measurements. Repeat this process with the remaining sample vials pressing "Read" instead of "Zero.

#### Step 3-Standardization and Measurement

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

#### Method- For Differentiating Orthophosphate and Pyrophosphates:

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

#### Step 1-Sample Preparation

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

#### Analysis:

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

$$\left(70\frac{mg}{L}PO_4^{3-}\right)*\left(\frac{100\%}{3\%}\right)=2333.\overline{333}\frac{mg}{L}PO_4^{3-}$$

#### A10. Test Method for Determining Inhibitor Degradation by Ultraviolet Radiation

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

#### Method:

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

exposure. The second shelf is for samples that are exposed both UV-a + UV-b wavelengths. The third and fourth shelves are the UV-a and UV-b exposures, respectively.

#### Step 1- Sample Preparation

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

#### Step 2- Sample Testing

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

#### Analysis:

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

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

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

#### **B1. Liquid Deicer Mixing and Sampling Methods**

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

#### Tank Mixing

The three "mixed" tanks will be mixed once a week for one hour for the first month of testing and twice monthly for one hour thereafter. Equipment needed for the mixing includes; a flat-head screw driver, robber boots, 220-volt extension cord, chemical resistant gloves, cordless power drill with Torv25 drill bit and paper towals

TOTX25 drift bit, and paper towers.

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

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

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

#### Tank Sampling

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

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

#### **B2.** Solid Deicer Sampling Methods

The sampling method for the solid NaCl deicer (IceSlicer Elite) includes collecting samples from both the storage enclosure and the pile left outside following the ASTM D 632 method, which requires at least three sub-samples to be selected at random from the top, middle and bottom profiles of each storage pile. This is to ensure a representative cross-section of the material being collected. A sub-sample will be obtained from a randomly chosen area within the top third, at the midpoint, and at the bottom third of the total volume of material. Following the specifications provided by the Washington State DOT, we will use a sampling tube for sub-sample collection to ensure a cross sectional representation of the materials. The sample tube will be constructed of thick-walled PVC pipe 1  $\frac{1}{2}$ " 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 will be collected by scraping aside the top layer of material to a depth of at least one inch then driving the sampling tube into the material to a depth of no less than six inches to collect a total target sample of at least five pounds. The collected sub-samples of the solid deicer will be thoroughly mixed in the 5-gallon bucket to make up one composite sample representative of the storage pile.

#### APPENDIX C. STORM EVENTS AND FIELD SAMPLING METHODS

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

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

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

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



Figure 12 Clearing and washing test sections on the driving surface area using a plow truck and high pressure hose.

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

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

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



Figure 13 Raised tank filled with warm well water connected to the trailer to flush the system (a) and replacing clean nozzles for final flush with the next anti-icer (b).

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



Figure 14 Diagram of test lanes and sample plot layout





Figure 15 Example of sample boxes (32"x32") laid out on the asphalt surface using silicone sealant in test sections.

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

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

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



Figure 16 Sample test boxes shown after addition of 1 L of DI water (a) and sample test box agitation technique (b).





Figure 17 Sample collection using a vacuum with squeegee attachment.

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

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

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

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

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

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

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

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

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

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



Figure 18 Diagram of test lanes and sample plot layout.

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





Figure 19 Example of a sample box (18 by 18 inches) laid out on the asphalt surface within a test lane using silicone sealant.

Each sample plot represents one of seven timed sample events. Immediately following the snowmaking activities each sample plot will be leveled off to a known depth of ½ inches using a metal frame with dimensions 18 ¼ by 18 ¼ by ½ inches. The frame will be placed on the sample plot cutting through the manmade snow. A flat metal bar 20 by ½ by 1/8 inches will be used to uniformly skim the excess snow off the top to attain a uniform snow depth for each sample plot of ½ inches. All sample boxes will be leveled off immediately following snow making activities. For the manmade storm event the first sample will be collected immediately following leveling of the "Sample dep 1" events dep 1" events and extended off the sample dep 1" events and

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

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

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

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

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

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

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

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

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

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

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

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

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





Figure 20 Diagram of test lanes and sample plot layout.

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

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

The sample collection process will begin by first collecting and melting the snow remaining in the sample plot. Based on typical snow water equivalent values, natural spring snow typically has a snow water density between 20 and 40%. With sample plot dimensions of 18 by 18 by  $\frac{1}{2}$  inches the volume of water from the snow melt will range between 550 mL and 1061 mL of water. The melted snow will be measured in a graduated cylinder and then placed in a labeled 1 L plastic bottle. The volume of water collected in the form of snow melt on sample day one will replace the addition of DI water to the sample plot unless the snow melt is less than 1 L at which point the difference will be added as DI water. Dilution rates for the remaining six day sample period will be based on the addition of 1 L of DI water. Depending on the weather following "day one" sampling, if the measured amount of snow melt does not equal 1 L it will be subtracted from 1 L of DI water, and this amount of DI water will be added to the sample plot and vacuum collected (see Figure 16a).

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

two personnel will carry out sample collection procedures throughout the seven day period.

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

#### APPENDIX D. FIELD OPERATION TEST REPORTS

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

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

#### Test Section Preparation

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



Figure 21 Condition of pavement after washing (a) and test lane layout using safety cones (b)

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



Figure 22 Silicone sample plot construction (a) and test section layout with sample plot completion (b)

#### Anti-Icer Application

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

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

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





Figure 23 Petri-dish set placement near sample plot prior to application of the anti-icer NaCl+GLT (a) and drill mark patterns of the anti-icer FreezGard obvious in the sunlight (b).

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

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

FreezGard Calcs (Set 1)	Results	Units	FreezGard Calcs (Set 2)	Results	Units	FreezGard Calcs (Set 3)	Results	Units
Deicer weight in 5 dishes	0.92	grams	Deicer weight in 5 dishes	1.69	grams	Deicer weight in 5 dishes	1.79	grams
Deicer density	10.79	lb/gallon	Deicer density	10.79	lb/gallon	Deicer density	10.79	lb/gallon
Deicer specific gravity	1.30		Deicer specific gravity	1.30		Deicer specific gravity	1.30	
Desired applied rate	30	gplm	Desired applied rate	30	gplm	Desired applied rate	30	gplm
Actual applied rate	17.82	gplm	Actual applied rate	32.74	gplm	Actual applied rate	34.68	gplm
Actual applied rate/box	7.57	mL	Actual applied rate/box	13.91	mL	Actual applied rate/box	14.73	mL
Dilution rate	0.75	%	Dilution rate	1.37	%	Dilution rate	1.45	%
CCB Calcs (Set 1)	Results	Units	CCB Calcs (Set 2)	Results	Units	CCB Calcs (Set 3)	Results	Units
Deicer weight in 5 dishes	1.60	grams	Deicer weight in 5 dishes	1.69	grams	Deicer weight in 5 dishes	1.70	grams
Deicer density	11.12	lb/gallon	Deicer density	11.12	lb/gallon	Deicer density	11.12	lb/gallon
Deicer specific gravity	1.34		Deicer specific gravity	1.34		Deicer specific gravity	1.34	
Desired applied rate	30	gplm	Desired applied rate	30	gplm	Desired applied rate	30	gplm
Actual applied rate	30.06	gplm	Actual applied rate	31.75	gplm	Actual applied rate	31.94	gplm
Actual applied rate/box	12.77	mL	Actual applied rate/box	13.49	mL	Actual applied rate/box	13.57	mL
Dilution rate	1.26	%	Dilution rate	1.33	%	Dilution rate	1.34	%

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

GLT Calcs (Set 1)	Results	Units	GLT Calcs (Set 2)	Results	Units	GLT Calcs (Set 3)	Results	Units
Deicer weight in 5 dishes	1.70	grams	Deicer weight in 5 dishes	1.81	grams	Deicer weight in 5 dishes	1.69	grams
Deicer density	9.86	lb/gallon	Deicer density	9.86	lb/gallon	Deicer density	9.86	lb/gallor
Deicer specific gravity	1.19		Deicer specific gravity	1.19		Deicer specific gravity	1.19	
Desired applied rate	30	gplm	Desired applied rate	30	gplm	Desired applied rate	30	gplm
Actual applied rate	36.02	gplm	Actual applied rate	38.35	gplm	Actual applied rate	35.80	gplm
Actual applied rate/box	15.30	mL	Actual applied rate/box	16.29	mL	Actual applied rate/box	15.21	mL
Dilution rate	1.51	%	Dilution rate	1.60	%	Dilution rate	1.50	%

#### Field Sampling

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

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



Figure 24 The anti-icer NaCl+GLT after application obvious in plots and test lanes (a) No anti-icer FreezGard CI Plus is visible after collection of "Sample day 1", plot #1 (b).







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

"Sample day 3," February 12, 2010, test section conditions upon arrival were dry and clear with an ambient air temperature of  $42^{\circ}$ F. Applied liquid deicer remained visibly present in all test lanes. Wind speeds were 10 mph from the w(**(a)**) rement conditions were clear and dry, th **(b)** s no evidence of blowing snow, no precipitation was recorded in the plots or gauges, and croud cover was 100%. Sampling began at 11:20 a.m. and was completed at 12:33 p.m.





Figure 26 Test section conditions upon arrival with free water in the sample plots (a) collection of free water prior to addition of DI water (b) and measuring volume of free water for DI water addition (c).

"Sample day 4," February 13, 2010, test sections upon arrival were wet with obvious precipitation

accumulation in the sample plots (Figure 26a). The test lanes were visibly wet and with no indication of applied liquid deicer. Close observation of the test plots indicated deicer suspended in the free standing water within the CCB test plot (Figure 26b). Wind speeds were 7 mph from the north northwest, pavement conditions were wet with light snow falling. There was no evidence of blowing snow, approximately <sup>1</sup>/<sub>4</sub>" of precipitation in the form of snow was recorded in the precipitation collection pans from the overnight and early morning precipitation event, and cloud cover was 100%. Sampling began at 11:00 a.m. with the removal of free water from the test plot prior to the addition of DI water (Figure 26b). Collected free water was poured into a graduated cylinder to get a total volume of free water already present in the plot (Figure 26c). The collected free water was then poured into a 1 L labeled plastic bottle. To reach a total sample volume of 1000 mL, the volume of free water collected was subtracted from a total target sample volume of 1000 mL. The remainder of sample volume needed to obtain a total of 1000 mL was measured out as DI water then poured onto the sample plot to proceed with the two minute agitation process. The DI sample was vacuum collected and added to the one liter plastic bottle containing the previously collected free water.



Figure 27 Sample day 5 (a) snow accumulation, (b) clearing of snow from sample boxes, (c) a cleared sample box, (d) a cleared sample box with melted ice on pavement surface.

"Sample day 5" February 14, 2010, test sections were covered with  $\frac{1}{2}$ " of snow upon arrival. The ambient air temperature was 16°F with 62% relative humidity. Wind speeds were approximately 3 mph from the south, pavement was 100% covered with new snow, there was no evidence of blowing snow,  $\frac{1}{2}$ " of precipitation was recorded in the plots and collection pans, and cloud cover was 5% (Figure 27a). Sampling began at 11:40 a.m. and was completed at 1:30 p.m. Beneath the layer of fresh snow was a thin layer of ice. Because of the layer of ice beneath the new snow each test plot was cleared of the new snow prior to sampling by gently brushing with a clean 4" paint brush limiting the removal of any anti-icer from box (Figure 27(b and c)). The ice melted in each sample plot prior to the addition of DI water but no free liquid was present in the plots after ice melt (Figure 27d). DI water was added and agitated as usual.

"Sample day 6" February 15, 2010, test sections were damp with free water visible in sample plots

upon arrival. The ambient air temperature was 28°F and 63% relative humidity. Winds were calm, pavement was damp, there was no evidence of blowing snow, there was no evidence of 24 hr precipitation, and cloud cover was 60%. No liquid deicers were visibly present in the test lanes. Sampling began at 11:55 a.m. and was completed at 12:45 p.m.

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

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

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

#### Test Section Preparation

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



Figure 28 Condition of pavement after washing (a) and test lane layout using safety cones (b).

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

#### Anti-Icer Application

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

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



Figure 29 Raised tank filled with warm well water connected to the trailer to flush the system (a) and final flush with the next anti-icer (b).

Actual application rates were based on weight measurements and the specific gravity of each anti-

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

FreezGard Calcs (Set 1)	Results	Unit	FreezGard Calcs (Set 2)	<i>Results</i>	Unit	FreezGard Calcs (Set 3)	Results	Unit	FreezGard Calcs (Set 4)	Results	Unit
Deicer weight in 5 dishes Deicer	2.88	gram	Deicer weight in 5 dishes Deicer	2.87	grams	Deicer weight in 5 dishes Deicer	2.93	grams	Deicer weight in 5 dishes Deicer	2.95	grams
density Deicer specific gravity	10.79	lb/gallon	density Deicer specific gravity	10.79	lb/gallon	 density Deicer specific gravity	10.79	lb/gallon	 density Deicer specific gravity	10.79	lb/gallon
Desired applied rate	60	gplm	Desired applied rate	60	gplm	Desired applied rate	60	gplm	Desired applied rate	60	gplm
Actual applied rate Actual	56	gplm	Actual applied rate	56	gplm	Actual applied rate	57	gplm	Actual applied rate	57	gplm
applied rate/box	7.50	mL	Actual applied rate	7.47	mL	Actual applied rate	7.63	mL	Actual applied rate	7.68	mL
Dilution rate	0.74	%	Dilution rate	0.74	%	 Dilution rate	0.76	%	Dilution rate	0.76	%
CCB Calcs (Set 1)	Results	Units	CCB Calcs (Set 2)	Results	Units	CCB Calcs (Set 3)	Results	Units	CCB Calcs (Set 4)	Results	Units
Deicer weight in 5 dishes	2.45	grams	Deicer weight in 5 dishes	2.63	grams	Deicer weight in 5 dishes	2.66	grams	Deicer weight in 5 dishes	2.46	grams
Deicer density Deicer	11.12	lb/gallon	Deicer density Deicer	11.12	lb/gallon	Deicer density Deicer	11.12	lb/gallon	Deicer density Deicer	11.12	lb/gallon
specific gravity	1.34		specific gravity	1.34		specific gravity	1.34		specific gravity	1.34	
Desired applied rate Actual applied rate	60 46	gplm gplm	Desired applied rate Actual applied rate	60 49	gplm gplm	 Desired applied rate Actual applied rate	60 50	gplm gplm	 Desired applied rate Actual applied rate	60 46	gplm gplm
Actual applied rate/box	6.19	mL	Actual applied rate/box	6.64	mL	Actual applied rate/box	6.72	mL	Actual applied rate/box	6.21	mL
Dilution rate	0.62	%	Dilution rate	0.66	%	Dilution rate	0.67	%	 Dilution rate	0.62	%
GLT Calcs (Set 1)	Results	Units	GLT Calcs (Set 2)	Results	Units	GLT Calcs (Set 3)	Results	Units	GLT Calcs (Set 4)	Results	Units
Deicer weight in 5 dishes	2.54	grams	Deicer weight in 5 dishes	2.61	grams	Deicer weight in 5 dishes	2.58	grams	Deicer weight in 5 dishes	2.46	grams
Deicer density	9.86	lb/gallon	Deicer density	9.86	lb/gallon	Deicer density	9.86	lb/gallon	Deicer density	9.86	lb/gallon
specific gravity	1.19		specific gravity	1.19		specific gravity	1.19		specific gravity	1.19	
Desired applied rate	60	gplm	Desired applied rate	60	gplm	Desired applied rate	60	gplm	Desired applied rate	60	gplm
Actual applied rate	54	gplm	Actual applied rate	55	gplm	Actual applied rate	55	gplm	Actual applied rate	52	gplm
applied rate/box	7.23	mL	applied rate/box	7.43	mL	applied rate/box	7.35	mL	applied rate/box	7.01	mL
Dilution note	0.72	07	Dilution note	0.74	07	Dilution and	0.72	07	Dilution and	0.70	07

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

#### Snow Making

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



Figure 30 Snow guns making snow over test sections.

#### Field Sampling

Leveling of the sample plots following snowmaking activities began at 1:30 a.m. on March 19, 2010. Each sample plot was leveled off to a known depth of  $\frac{1}{2}$  inches using a metal frame with dimensions 18  $\frac{1}{4}$  by 18  $\frac{1}{4}$  by  $\frac{1}{2}$  inches. The frame was placed on the sample plot cutting through the man-made snow along the outer dimensions of the silicone test box. A flat metal bar 20 by  $\frac{1}{2}$  by 1/8 inches was used to uniformly skim the excess snow off the top to attain a uniform snow depth for each sample plot of  $\frac{1}{2}$  inches (Figure 31(a)). The artificial snow broke away from the pavement easily and in larger "sheets" (see Figure 31(a)) while removing it from around the sample plots suggesting successful elimination of the snow to pavement bond. Leveling of all sample boxes was completed at 2:45 a.m.



Figure 31 Example of sample box with snow leveled off to ½ inches (a) example of snow sheets around the sample box and visible coloring from the deicer on the upturned snow column (b).

Collection of the first set of samples, "Sample-day 1", began at 7:53 a.m. on March 20, 2010 approximately 14 hours after anti-icer application. The sample collection process began by first collecting and melting the  $\frac{1}{2}$  inches of snow remaining in the sample plots. Snow in the sample plots was visually clean on the top of the snow column; however, when the snow was collected the bottom of the snow column demonstrated coloring by the deicer suggesting slight upward migration of the deicer into the snow column (Figure 31(b)). The melted snow, collected from the test plot, was measured in a graduated cylinder. The volume of water from snow melt equaled 1420

mL, 1050 mL, 1325 mL, and 1325 mL in the FreezGard, NaCl+GLT, CCB, and Control test plots respectively. After the snow was melted and a volume recorded, it was replaced back into the appropriate test plot for agitation and vacuum recovery processes (Figure 32(a)). Total sample volumes following vacuum recovery were 935 mL, 950 mL, 1010 mL, and 940 mL of FreezGard, CCB, NaCl+GLT, and Control samples respectively. Samples were collected in a labeled 1 L plastic bottle. Sample collection was completed from all four test lanes at 10:30 a.m. Each sample was labeled "Sample-day 1" with plot number, date, time, collector's initials, anti-icer type, and volume recovery. Sample collection equipment was thoroughly washed and rinsed with DI water prior to use with the next sample plot. DI water for sampling activities was provided daily by the Corrosion and Sustainable Infrastructure Laboratory in Bozeman, MT. Ambient air temperature on "Sample day 1" was 28-35° F. Wind speeds were negligible; pavement conditions were snow covered early in the morning and clear and dry by late morning, there was no evidence of blowing snow, and cloud cover was approximately 20%.

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



Figure 32 Sample test box shown after melting snow accumulation, replacement, agitation, and vacuum sample collection (a) and a test section with no snow and deicer visible in the un-sampled test plot (b).

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

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

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

containing the collected free water. Day 4 sampling was completed at 12:30 p.m.



Figure 33 Sample test box containing free standing water in the day 4 FreezGard test lane.

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



Figure 34 Evidence of the applied liquid deicer NaCl+GLT remains in the test box

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

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

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

The following field report has been prepared by the Corrosion and Sustainable Infrastructure Laboratory (CSIL) at the Western Transportation Institute, Montana State University (WTI/MSU) and is based on the application and sampling of deicers or anti-icers in a field situation using deicers investigated in the Pooled Fund Study led by the Pacific Northwest Snowfighters (PNS)

Standard Operating Procedure (SOP) developed through pilot field and laboratory efforts within this project's scope. Samples collected from this field test will be analyzed according to the SOPs detailed in the Laboratory Standard Operating Procedures.

#### Test Section Preparation

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



Figure 35 Clearing and washing chosen test section within the driving surface area using a plow truck and high pressure hose.

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

#### Anti-Icer Application

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

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



Figure 36 Garden hose with spray nozzle used for rinsing (a) and final flush with the next anti-icer (b).

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

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

FreezGard Calcs (Set											
1)	Results	Unit	2)	Results	Unit	3)	Results	Unit	4)	Results	Unit
Deicer weight in 5 dishes	2.84	grams	Deicer weight in 5 dishes	3.05	grams	Deicer weight in 5 dishes	3.21	grams	Deicer weight in 5 dishes	2.9	grams
Deicer density	10.79	lb/gallon									
Deicer specific gravity	1.30		Deicer specific gravity	1.30		Deicer specific gravity	1.30		Deicer specific gravity	1.30	
Desired applied rate	60	gplm									
Actual applied rate	55	gplm	Actual applied rate	59	gplm	Actual applied rate	62	gplm	Actual applied rate	56	gplm
Actual applied rate/box	7.40	mL	Actual applied rate	7.94	mL	Actual applied rate	8.36	mL	Actual applied rate	7.55	mL
Dillution rate	0.73	%	Dillution rate	0.79	%	Dillution rate	0.83	%	Dillution rate	0.75	%
CCB Calcs (Set 1)	Results	Units	CCB Calcs (Set 2)	Results	Units	CCB Calcs (Set 3)	Results	Units	CCB Calcs (Set 4)	Results	Units

Deicer weight in 5	2.62	~~~~	Deicer weight in 5	2.19	~~~~~		Deicer weight in 5	1 02	~	Deicer weight in 5	2.60	~~~~
Daiaar	2.03	granis	Dejeer	2.10	grams		Dajaar	2.63	grams	Daiaar	2.09	grams
density	11.12	lb/gallon	density	11.12	lb/gallon		density	11.12	lb/gallon	density	11.12	lb/gallon
Deicer		8	Deicer				Deicer		8	Deicer		8
specific			specific				specific			specific		
gravity	1.34		gravity	1.34			gravity	1.34		gravity	1.34	
Desired			Desired				Desired			Desired		
applied rate	60	gplm	applied rate	60	gplm		applied rate	60	gplm	applied rate	60	gplm
Actual			Actual				Actual			Actual		
applied rate	49	gplm	applied rate	41	gplm		applied rate	53	gplm	applied rate	51	gplm
Actual			Actual				Actual			Actual		
applied		_	applied		_		applied		_	applied		_
rate/box	6.64	mL	rate/box	5.51	mL		rate/box	7.15	mL	rate/box	6.79	mL
Dillution rate	0.66	%	Dillution rate	0.55	%		Dillution rate	0.71	%	Dillution rate	0.67	%
OT TO A			CLT Calas				GLT Cales			CI T Cales		
GLT Cales			GLI Calcs				OLI Cales			ULI Cales		
GLT Calcs (Set 1)	Results	Units	(Set 2)	Results	Unite	L	(Set 3)	Results	Units	(Set 4)	ts	Units
(Set 1) Deicer	Results	Units	(Set 2) Deicer	Results	$\frac{U^{aite}}{(a)}$	ŀ	(Set 3) Deicer	Results	Units	 (Set 4) Deicer (b	) ts	Units
(Set 1) Deicer weight in 5	Results	Units	(Set 2) Deicer weight in 5	<i>Results</i>	Unite (a)		(Set 3) Deicer weight in 5	Results	Units	(Set 4) Deicer weight in 5	) ts	Units
GLT Calcs (Set 1) Deicer weight in 5 dishes	Results	<i>Units</i> grams	(Set 2) Deicer weight in 5 dishes	Results	(a)		(Set 3) Deicer weight in 5 dishes	<i>Results</i> 2.86	<i>Units</i> grams	(Set 4) Deicer weight in 3 dishes	2.88	<i>Units</i> grams
GLT Calcs (Set 1) Deicer weight in 5 dishes Deicer	Results	Units grams	(Set 2) Deicer weight in 5 dishes Deicer	Results	(a)		(Set 3) Deicer weight in 5 dishes Deicer	Results	<i>Units</i> grams	(Set 4) Deicer weight in 3 dishes Deicer	)	<i>Units</i> grams
GLT Calcs (Set 1) Deicer weight in 5 dishes Deicer density	<i>Results</i> 2.56 9.86	Units grams lb/gallon	(Set 2) Deicer weight in 5 dishes Deicer density	<i>Results</i> 2.76 9.86	grams		(Set 3) Deicer weight in 5 dishes Deicer density	<i>Results</i> 2.86 9.86	Units grams lb/gallon	(Set 4) Deicer weight in 3 dishes Deicer density	2.88 9.86	Units grams lb/gallon
GLT Calcs (Set 1) Deicer weight in 5 dishes Deicer density Deicer	<i>Results</i> 2.56 9.86	Units grams lb/gallon	(Set 2) Deicer weight in 5 dishes Deicer density Deicer	<i>Results</i> 2.76 9.86	(a) grams lb/gallon		(Set 3) Deicer weight in 5 dishes Deicer density Deicer	<i>Results</i> 2.86 9.86	Units grams lb/gallon	(Set 4) Deicer weight in 3 dishes Deicer density Deicer	) <u>2.88</u> 9.86	Units grams lb/gallon
GLT Calcs (Set 1) Deicer weight in 5 dishes Deicer density Deicer specific	<i>Results</i> 2.56 9.86	Units grams lb/gallon	(Set 2) Deicer weight in 5 dishes Deicer density Deicer specific	<i>Results</i> 2.76 9.86	(a) grams lb/gallon		(Set 3) Deicer weight in 5 dishes Deicer density Deicer specific	<i>Results</i> 2.86 9.86	Units grams lb/gallon	(Set 4) Deicer weight in 3 dishes Deicer density Deicer specific	)	Units grams lb/gallon
GLT Calcs (Set 1) Deicer weight in 5 dishes Deicer density Deicer specific gravity	<i>Results</i> 2.56 9.86 1.19	Units grams lb/gallon	(Set 2) Deicer weight in 5 dishes Deicer density Deicer specific gravity	<i>Results</i> 2.76 9.86 1.19	(a) grams lb/gallon		(Set 3) Deicer weight in 5 dishes Deicer density Deicer specific gravity	Results           2.86           9.86           1.19	Units grams lb/gallon	(Set 4) Deicer weight in 5 Deicer density Deicer specific gravity	)	Units grams lb/gallon
GLT Calcs (Set 1) Deicer weight in 5 dishes Deicer density Deicer specific gravity Desired	Results           2.56           9.86           1.19	Units grams lb/gallon	(Set 2) Deicer weight in 5 dishes Deicer density Deicer specific gravity Desired	Results           2.76           9.86           1.19	(a) grams lb/gallon		(Set 3) Deicer weight in 5 dishes Deicer density Deicer specific gravity Desired	<i>Results</i> 2.86 9.86 1.19	Units grams lb/gallon	(Set 4) Deicer weight in 5 Deicer density Deicer specific gravity Desired	) <u>1.19</u>	Units grams lb/gallon
GLT Calcs (Set 1) Deicer weight in 5 dishes Deicer density Deicer specific gravity Desired applied rate	Results           2.56           9.86           1.19           60	Units grams lb/gallon gplm	GLT Cates (Set 2) Deicer weight in 5 dishes Deicer density Deicer specific gravity Desired applied rate	Results           2.76           9.86           1.19           60	(a) grams lb/gallon gplm		(Set 3) Deicer weight in 5 dishes Deicer density Deicer specific gravity Desired applied rate	Results           2.86           9.86           1.19           60	Units grams lb/gallon gplm	(Set 4) Deicer weight in 9 Deicer density Deicer specific gravity Desired applied rate	2.88 9.86 1.19 60	Units grams lb/gallon gplm
GLT Calcs (Set 1) Deicer weight in 5 dishes Deicer density Deicer specific gravity Desired applied rate Actual	Results           2.56           9.86           1.19           60	Units grams lb/gallon gplm	GLT Cates (Set 2) Deicer weight in 5 dishes Deicer density Deicer specific gravity Desired applied rate Actual	Results           2.76           9.86           1.19           60	(a) grams lb/gallon gplm		(Set 3) Deicer weight in 5 dishes Deicer density Deicer specific gravity Desired applied rate Actual	<i>Results</i> 2.86 9.86 1.19 60	Units grams lb/gallon gplm	(Set 4) Deicer weight in 9 Deicer density Deicer specific gravity Desired applied rate Actual	2.88 9.86 1.19 60	Units grams lb/gallon gplm
GLT Calcs (Set 1) Deicer weight in 5 dishes Deicer density Deicer specific gravity Desired applied rate	Results           2.56           9.86           1.19           60           54	Units grams lb/gallon gplm gplm	GLT Cates (Set 2) Deicer weight in 5 dishes Deicer density Deicer specific gravity Desired applied rate Actual applied rate	Results           2.76           9.86           1.19           60           58	(a) grams lb/gallon gplm gplm		(Set 3) Deicer weight in 5 dishes Deicer density Deicer specific gravity Desired applied rate Actual applied rate	Results           2.86           9.86           1.19           60           61	Units grams lb/gallon gplm gplm	(Set 4) Deicer weight in 9 Deicer density Deicer specific gravity Desired applied rate Actual applied rate	)(s 2.88 9.86 1.19 60 61	Units grams lb/gallon gplm gplm
GLT Cales (Set 1) Deicer weight in 5 dishes Deicer density Deicer specific gravity Desired applied rate Actual applied rate	Results           2.56           9.86           1.19           60           54	Units grams lb/gallon gplm gplm	GLT Catcs (Set 2) Deicer weight in 5 dishes Deicer density Deicer specific gravity Desired applied rate Actual applied rate	Results           2.76           9.86           1.19           60           58	(a) grams lb/gallon gplm gplm		(Set 3) Deicer weight in 5 dishes Deicer density Deicer specific gravity Desired applied rate Actual Actual	Results           2.86           9.86           1.19           60           61	Units grams lb/gallon gplm gplm	(Set 4) Deicer weight in 9 Deicer density Deicer specific gravity Desired applied rate Actual applied rate	2.88 9.86 1.19 60 61	Units grams lb/gallon gplm gplm
GLT Calcs (Set 1) Deicer weight in 5 dishes Deicer density Deicer specific gravity Desired applied rate Actual applied rate	Results           2.56           9.86           1.19           60           54	Units grams lb/gallon gplm gplm	GLT Cates (Set 2) Deicer weight in 5 dishes Deicer density Deicer specific gravity Desired applied rate Actual applied	Results           2.76           9.86           1.19           60           58	(a) grams lb/gallon gplm gplm		(Set 3) Deicer weight in 5 dishes Deicer density Deicer specific gravity Desired applied rate Actual applied	Results           2.86           9.86           1.19           60           61	Units grams lb/gallon gplm gplm	(Set 4) Deicer weight in 9 Deicer density Deicer specific gravity Desired applied rate Actual applied	)(s 2.88 9.86 1.19 60 61	Units grams lb/gallon gplm gplm
GLT Calcs (Set 1) Deicer weight in 5 dishes Deicer density Deicer specific gravity Desired applied rate Actual applied rate Actual applied rate/box	Results           2.56           9.86           1.19           60           54           7.29	Units grams lb/gallon gplm gplm mL	GLT Catcs (Set 2) Deicer weight in 5 dishes Deicer density Deicer specific gravity Desired applied rate Actual applied rate Actual applied rate/box	Results           2.76           9.86           1.19           60           58           7.86	(a) grams lb/gallon gplm gplm mL		(Set 3) Deicer weight in 5 dishes Deicer density Deicer specific gravity Desired applied rate Actual applied rate Actual applied rate/box	Results           2.86           9.86           1.19           60           61           8.15	Units grams lb/gallon gplm gplm mL	(Set 4) Deicer weight in 9 dishes Deicer density Deicer specific gravity Desired applied rate Actual applied rate Actual applied rate/box	) [15] 2.88 9.86 1.19 60 61 8.20	Units grams lb/gallon gplm gplm mL

#### The Natural Storm Event

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



Figure 37 Snow falling outside of the shop area (a) snow depth measurement from the test area (b).

#### Field Sampling

Leveling of the sample plots following the natural storm event began at 10:30 a.m. on April 13, 2010. Each sample plot was leveled off to a known depth of  $\frac{1}{2}$  inches using a metal frame with dimensions 18  $\frac{1}{4}$  by 18  $\frac{1}{4}$  by  $\frac{1}{2}$  inches. The research team had to locate each sample test plot within each test section prior to applying the metal frame used in the leveling process (Figure 38(a)). Once all the test plots had been located the frame was placed on the sample plot cutting through the heavy wet snow along the outer dimensions of the silicone test box. A flat metal bar 20 by  $\frac{1}{2}$  by 1/8 inches was used skim the excess snow off the top to attain a uniform snow depth for

very difficult. Snow leveling of all sample boxes was completed at 12:45 p.m.

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



Figure 38 Removing snow surround sample test plots (a), example of test plot after leveling (note how wet the snow appears) (b), height of visible deicer in snow column denoted by gray line (c), detail of deicer discovered in snow column (d).

Collection of the first set of samples, "Sample-day 1", began at 12:45 a.m. on April 13, 2010 approximately 19.5 hours after anti-icer application. The  $\frac{1}{2}$  inches of snow remaining in the sample plots after leveling existed as a snow/slush mixture. The mixture maintained enough free water for agitation without removal or the addition of DI water (Figure 39(a)). Each sample plot was immediately agitated for two minutes then vacuum collected (Figure 39(b)). The mixture was allowed to melt before recovery volumes were measured and recorded. Total sample volumes following vacuum recovery were 5730 mL, 1970 mL, 2680 mL, and 3540 mL of FreezGard, CCB, NaCl+GLT, and Control samples requestively. The discrepancy in sample volumes collection  $\frac{1}{(b)}$ d be from the varying amount  $a^{(a)}$ w/slush mixture within each sample plot from the d associated with uniform leveling of heavy wet snow. Samples were collected and labeled in new 2.5-gallon plastic buckets with lids. Sample collection was completed from all four test lanes at 2:00 p.m. Each sample was labeled "Sample-day 1" with plot number, date, time, collector's initials, anti-icer type, and volume recovery. Sample collection equipment was thoroughly washed and rinsed with DI water prior to use with the next sample plot. DI water for sampling activities was provided daily by the Corrosion and Sustainable Infrastructure Laboratory in Bozeman, MT.





Figure 39 Sample plot after agitation (a) collection of snow/slush mixture (b).

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

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



Figure 40 Test area  $\frac{1}{(a)}$  ew windblown snow accumulation.

(b)

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

"Sample day 3," April 15, 2010, test section conditions upon arrival were damp and patches of snow remained from the wind storm event the previous day. Free water was noted in the test plots. Sampling began at 10:55 a.m. with the removal of free water from the test plot prior to the addition of DI water. Collected free water was poured into a graduated cylinder to get a total volume of free water already present in the plot. Subsequently, 0 to 1000 mL of de-ionized water was added to the 18x18 inch sampling box depending on the amount of precipitation in the sampling box. In all cases, each sampling day would yield typically 1000 mL of liquids collected from the pavement, providing adequate volumes for laboratory testing. The DI sample was agitated, vacuum collected, and added to the one liter plastic bottle containing the collected from in gauges or collection pans. The ambient air temperature was 52° F. Wind speeds were 10 mph from the north, and cloud cover was 0%.

"Sample day 4," April 16, 2010, test sections upon arrival were dry and clear with an ambient air temperature of 45° F. Observation of the test area revealed little visible evidence of applied deices remaining within the test sections (Figure 41). No precipitation was recorded. Calm winds were

p.m.



Figure 41 Sample test lane with little visible deicer remaining.

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

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

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

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#### **APPENDIX E. DEICER PERFORMANCE – FOT PHOTOS**





FreezGard Day 3: Conditions for sample collection





FreezGard Day 4: Before sample collection 2010:02:13 10:43:45



FreezGard Day 6: Before sample collection





Deicer Application showing Petri dish location



CCB Day 2: Before sample collection







FreezGard Day 7: Before sample collection



CCB Day 1: After sample collection 2010:02:10 11:50:34



CCB Day 3: Conditions for sample collection







CCB Day 5: Before sample collection





CCB Day 6: Before sample collection





CCB Day 7: After sample collection



E3. Black Ice Event Photo Sheet – NaCl+GLT Deicer Application showing Petri dish location Deicer Application showing Petri dish location



GLT Day 2: Before sample collection



GLT Day 4: Before sample collection



GLT Day 6: Before sample collection

(a)



GLT Day 3: After sample collection



GLT Day 5: After sample collection



GLT Day 7: Before sample collection







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



FreezGard Day 2: Before sample collection



FreezGard Day 4: Before sample collection



FreezGard Day 6: Before sample collection



FreezGard Day 1: Before sample collection





FreezGard Day 3: Before sample collection





FreezGard Day 7: Before sample collection



E5. Man Made Snow Event Photo Sheet – Calcium Chloride with Boost Snow making over test section CCB Day 1: After sample collection





CCB Day 2: Conditions before sample collection CCB Day 3: Before sample collection





CCB Day 4: Before sample collection



CCB Day 6: Before sample collection



CCB Day 5: Before sample collection







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

Snow making over test sections



(a)





GLT Day 2: Before sample collection

GLT Day 3: Before sample collection



GLT Day 4: Before sample collection



GLT Day 6: Before sample collection





GLT Day 5: Before sample collection



GLT Day 7: Before sample collection



#### E7. Natural Storm Event Photo Sheet – FreezGard CI Plus

Deicer Application



FreezGard Day 2: Before sample collection



FreezGard Day 4: Conditions for sample





FreezGard Day 3: Before sample collection



FreezGard Day 5: After sample collection

#### collection



FreezGard Day 6: Before sample collection



FreezGard Day 7: Before sample collection



E8. Natural Snow Event Photo Sheet - Calcium Chloride with Boost Deicer Application showing Petri dish location



CCB Day 2: During sample collection



CCB Day 4: Before sample collection



CCB Day 1: During sample collection



CCB Day 3: Before sample collection



**(a)** 

CCB Day 5: Before sample collection



**(b)** 

CCB Day 6: After sample collection



CCB Day 7: After sample collection



### E9. Natural Snow Event Photo Sheet – NaCl+GLT

Deicer Application showing Petri dish location



GLT Day 2: During sample collection



(a)

GLT Day 1: Before sample collection







GLT Day 4: Before sample collection



GLT Day 6: Before sample collection



GLT Day 5: Before sample collection



GLT Day 7: Before sample collection



#### **APPENDIX F. ETHANOL FOR SAMPLE RECOVERY**

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

#### Ethanol Recovery of Anti-Icer Application in Laboratory Testing

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

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

#### Ethanol Recovery of Anti-Icer Application in Field Testing

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

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

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





Figure 42 Sample test box shown after addition of 250 mL of ethanol.

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



Figure 43 Effect of dilution on the pH reading of deicer samples, showing generally higher pH reading of FreezGard and CCB after dilution and lower pH reading of NaCl+GLT after dilution.



(a)





(b)

Figure 44 Effect of salt concentration on the pH reading of the aqueous solution containing 12% and 2% inhibitor for: (a) CCB, and (b) FreezGard respectively, showing generally lower pH reading at higher salt concentrations.









Chemical absorbed to the bottom layer of snow



Sunrise after the all-night snow event



Collect the samples from the collection squares





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



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

![](_page_63_Picture_3.jpeg)

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

![](_page_63_Picture_5.jpeg)

![](_page_64_Picture_0.jpeg)