Development of Standardized Test Procedures for Evaluating Deicing Chemicals

Western Transportation Institute, Montana State University

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16. Abstract

This project aims to develop and/or identify a series of standard laboratory testing procedures and ranges that can be used to evaluate the performance of deicing chemicals, additives and mixtures used on roadways and other transportation facilities. A literature review and survey were conducted to provide the scope and direction for laboratory tests. The results of the survey indicate relatively modest implementation of the deicer performance tests developed under the Strategic Highway Research Program (SHRP) and ASTM freezing point test. As such, several test methods were experimented for the purpose of refining or developing a promising test protocol, including: Differential Scanning Calorimetry (DSC) thermogram test for liquid deicers, Modified SHRP Ice Melting Test for solid and liquid deicers, Modified SHRP Ice Penetration Test for solid and liquid deicers, and a modified ice undercutting test developed by Minnesota DOT for solid and liquid deicers. These tests shed light on the complexity and challenges in evaluating various deicers, especially the poor reliability inherent in conventional test methods.

The DSC-based method was demonstrated to be very reproducible for each deicer at a given dilution rate and heating rate, and thus may serve as a "fingerprint" tool for quality assurance of deicers. The DSC data also showed strong correlation with the Modified SHRP Ice Melting Test data, which hold the promise of establishing the DSC-based method for evaluating the performance of liquid deicers (both in terms of characteristic temperature and ice melting capacity). The Modified SHRP Ice Melting Test incorporates a control substance and some checks to determine acceptability of the data. While not essential, a round robin test involving multiple laboratories is recommended to assess the between-laboratory variability of these improved or newly developed tests for deicing chemicals.

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EXECUTIVE SUMMARY

This project aims to develop and/or identify a series of standard laboratory testing procedures and ranges that can be used to evaluate the performance of deicing chemicals, additives and mixtures used on roadways and other transportation facilities. A literature review and survey were conducted to provide the scope and direction for laboratory tests. Test methods for the effects of deicers on infrastructure and the environment were considered secondary to deicer performance. The literature review identified many possible test methods for deicer performance and impacts that could be used to screen potential deicer products and blends. Some of the test methods seem to be more widely used, while others have inherent limitations. The relationship between laboratory tests that measure deicer performance to potential field performance was notably absent from the literature. Furthermore, most of the laboratory test methods neglected several parameters that likely play a role in the field performance of deicers, including: traffic, humidity, wind, active precipitation, and often pavement. However, the focus of this project was to develop relatively simple and straightforward laboratory test methods that could be used to screen potential deicing products and blends prior to more elaborate and expensive field tests.

The survey results indicate modest implementation of the deicer performance tests developed under the Strategic Highway Research Program (SHRP) and the ASTM (American Society for Testing and Materials) freezing point test. While five separate state DOTs have tried the most popular SHRP Ice Melting Test, only two indicate they currently use the test. State DOTs rated the SHRP Ice Melting Test between somewhat useful and very useful, while five manufacturers rated the test between not useful and very useful. The reliability of the test method often rated lower than the usefulness of the test. As such, for this project several test methods were experimented for the purpose of refining or developing a promising test protocol, including: Differential Scanning Calorimetry (DSC) thermogram test for liquid deicers, modified SHRP Ice Melting Test for solid and liquid deicers, modified SHRP Ice Penetration Test for solid and liquid deicers, and modified ice undercutting test for solid and liquid deicers. These tests shed light on the complexity and challenges in evaluating various deicers, especially the poor reliability inherent in conventional test methods.

The DSC-based method was demonstrated to be very reproducible for each deicer at a given dilution rate and heating rate, and thus may serve as a “fingerprint” tool for quality assurance of deicers. The DSC data also showed strong correlation with the modified SHRP Ice Melting Test data, which hold the promise of establishing the DSC-based method for evaluating the performance of liquid deicers (both in terms of characteristic temperature and ice melting capacity). The ice undercutting test and the SHRP ice penetration test were found to be not reliable and thus are not recommended in the suite of test methods. While not essential, a round robin test involving multiple laboratories is recommended before full implementation of the test protocols in order to assess the between-laboratory variability of the improved or newly developed tests for deicing chemicals.

1. INTRODUCTION

Laboratory testing can provide valuable information for evaluating the performance and effects of deicing chemicals, additives and mixtures, although it is difficult to relate laboratory performance to actual field performance. In many cases, field testing is costly and non-reproducible in light of uncontrollable and non-uniform weather and traffic conditions; and experiments need to be carefully designed to allow direct comparisons between various chemicals. In contrast, the uniform and well-controlled conditions in a laboratory setting can facilitate direct comparison of deicing products and allow for quality control. In controlled laboratory tests, variations in pavement type, temperature, wind, dynamic traffic, and many other variables are held constant or ignored altogether. This facilitates comparison of deicing and anti-icing chemicals (hereinafter referred to as deicers) when tested in different labs at different times.

The objective of this project was to develop and/or identify a suite of standard laboratory testing procedures and ranges that can be used to evaluate the performance of deicing chemicals, additives, and mixtures used on roadways and other transportation facilities. The project was initiated because departments of transportation (DOTs) are frequently approached by manufacturers and suppliers with unsubstantiated claims about their products. Users do not currently have a comprehensive methodology for evaluating the performance of new products prior to purchasing. A standard set of performance tests that can be conducted by independent or DOT laboratories will help agencies anticipate how products may work in their specific environment.

A literature review and survey were conducted to provide the scope and direction for laboratory tests. The objective of the literature review was to identify existing laboratory test methods for evaluating deicers. Chapter 2 provides a literature review of test methods for deicer performance, impacts to materials found on roads, and environmental impacts. The test methods are described individually, noting the testing conditions, use of controls, and notable advantages and disadvantages. The tests and quantifiable deicer characteristics identified from the literature review served as the basis for the design of a survey, which was developed and distributed to winter maintenance practitioners in Clear Roads member states and other stakeholder groups. The blank survey form is reproduced in Appendix A and an analysis of the survey responses is in Chapter 3. The testing methodologies for the laboratory investigation are described in Chapter 4. While the tests were primarily developed and refined using the three primary chloride-based deicers on the market—sodium chloride (NaCl), calcium chloride ($CaCl_2$) and magnesium chloride ($MgCl_2$)—baseline testing was performed on a variety of deicer blends.

2. LITERATURE REVIEW

A comprehensive literature search was carried out to identify all existing methods used to evaluate deicers. Several test methods are standardized by various consortiums, such as ASTM International, American Association of State and Highway Transportation Officials (AASHTO), Strategic Highway Research Program (SHRP), among others. The literature search was performed using a variety of tools, including *TRIS Online*, *E-Science Server*, *TRB Annual Meeting CD-ROMs*, *Google Scholar*, *Google Patents*, *Google*, *Montana State University Library*, and *Local Technical Assistance Program library*. Standardized test methods were identified as well as laboratory methods developed for individual research projects. Determination of deicer performance was designated the main priority by the project Technical Advisory Subcommittee (TAS). Test methods for the effects of deicers on infrastructure and the environment were considered secondary to deicer performance and are provided in Appendix A of this report.

There have been several test methods developed to measure the performance of a deicing chemical. In 1992 the Strategic Highway Research Program (SHRP) sponsored the development of the *Handbook of Test Methods for Evaluating Chemical Deicers* (referred to as SHRP *Handbook* from this point forward) that provided test methods for eight principal features of deicers, including deicing performance. Three types of test methods for deicing performance were created: Ice Melting Test for solid and liquid deicers (SHRP H-205.1 and H-205.2, respectively), Ice Penetration Test for solid and liquid deicers (SHRP H-205.3 and H-205.4, respectively), and Ice Undercutting Test for solid and liquid deicers (SHRP H-205.5 and H-205.6, respectively) (Chappelow et al., 1992). However, the scientific literature provides many other tests that have been developed for specific research projects, some of which resemble the standardized SHRP tests while others are more unique.

2.1. Ice Melting Tests

The SHRP Ice Melting Test (H-205.1 and H-205.2) measures the amount of ice melted by deicers at 10, 20, 30, 45, and 60 minutes after application. The test should be conducted three times for each deicer at each temperature of interest. It is performed in a dry cold box equipped with hand ports in a cold room or upright freezer. A flat 9-in. diameter and ¾-in. thick Plexiglas® dish is constructed and filled with 130 mL of water to create ⅛-in. thick ice. The surface is melted with a piece of aluminum and the dish swirled and tilted to redistribute the water. Refreezing the sample will then produce a more uniform ice sample. The deicer is then applied by uniformly spreading 4.170 g of solid deicer or 3.8 mL of liquid deicer with a syringe. At the required times, the liquid is removed with a syringe for volume measurements. The process of removing and replacing the liquid should be completed in less than 2.5 minutes.

Additional details for this test, including preparation of the liquid deicers and data analysis, are available in the *Handbook* (Chappelow et al., 1992).

The SHRP Ice Melting Test was modeled after tests conducted by McElroy et al. (1988a, b, c) because a review of several other possible tests indicated limitations or lack of documentation to reproduce the tests. However, there are inherent difficulties presented by any ice melting test, such as the inability to separate the entire melted portion from the remaining ice due to entrapment within ice cavities and absorption of brine on the ice surface and undissolved deicer particles. Other factors affecting reproducibility include the dependence on the rate of dissolution of solid deicers (which also depends on the particle size) and the amount of brine needed for reasonably accurate measurements. Reducing the surface area of the ice can limit the errors resulting from absorption but also the amount of brine generated. Thus, ice melting tests try to strike a balance of generating enough brine for accurate measurements, but avoiding too much deicer which may not represent a realistic application rate for highway operations (Chappelow et al., 1993). Chappelow et al. (1992) decided that the testing of solid deicers with rates about three times higher than highway deicing are the most appropriate. Thus, the standard test incorporates the equivalent of 1,320 lb/lane-mile for solid deicers. For liquid deicers, the application of 3.8 mL of deicer is equivalent to approximately 144 gallons per lane-mile. Finally, although the test method used by McElroy et al. (1988a, b, c) was only performed on solid deicers, Chappelow et al. (1992) found the test to be suitable for liquid deicers. In this case, the data analysis required different computations, but the standard errors were less (Chappelow et al., 1993).

Nixon et al. (2005) performed the SHRP Ice Melting Test with a few deviations on seven liquid deicers and found the test to be sufficient for product comparison and for product selection based on desired performance criteria. The deviations were: 80 mL of water to form ice (instead of 130 mL), 5 mL of liquid deicer applied (instead of 3.8 mL), and a funnel and graduated cylinder were used to decant the melted portion (instead of a syringe). No deviation from the standard 9-in. diameter dish was noted. According to Nixon et al. (2005), because the test is performed at four different temperatures, the best product can be selected for the expected temperatures. Furthermore, the volume of melted ice can be compared against the cost of the deicer such that the most cost-effective deicer can be identified.

Goyal et al. (1989) developed an ice melting test before the standardized test procedures were published in the SHRP *Handbook*. After initial attempts to decant the melted portion, the researchers decided to use blotter paper to absorb and weigh the melted portion. Two methods of blotting the melted portion were tested: Blotter-S and Blotter-Z. In the Blotter-S method, weighed blotter paper was placed on the surface of the ice sample at the desired time (at 4, 8, 15, or 30 minutes) for about 10 seconds, and then placed in a plastic bag until just before it was weighed again. Any visible solid unmelted deicers picked up by the blotter paper were brushed off before weighing. The researchers noted that sometimes two or three pieces of blotter paper were needed. In the Blotter-Z method the system was inverted and shaken upside down for 5–10 seconds after the blotter paper was placed on the surface. This was done in order to collect the water trapped in pores, and was found necessary for solid deicers, whereas the Blotter-S method was adequate for liquid deicers (Goyal et al., 1989). More specimen samples were needed with this method because the melted portion was not returned to the samples for continued testing. Perhaps the increased collectability of the melted portion is negated by the need to use different ice specimens for the different collection times.

Variations in results were explained by Goyal et al. (1989) as: 1) variations in experimental temperatures up to ±3.6°F, and 2) variations in ice characteristics. In the SHRP *Handbook*, the former is addressed by restricting temperature variation in dry box enclosures to within ±0.5°F. The latter is addressed by melting the surface of the ice and refreezing the specimen.

Ganjyal et al. (2007) used a digital camera to test the effectiveness of alternative deicers to melt snow and ice outdoors. Aluminum pans topped with 5 cm of a snow–ice mixture compacted to approximately 0.75 g/cm^3 were placed outside with an average temperature of 27°F. Dry powders of sodium levulinate, calcium levulinate, and magnesium levulinate in amounts ranging from 2 to 5 percent of the weight of the snow–ice mixture were applied. Digital photos taken every five minutes provided the only indication of melting.

2.2. Ice Penetration Tests

The SHRP Ice Penetration Tests (H-205.3 and H-205.4), presented in the SHRP *Handbook*, were developed by Chappelow et al. (1992) to test the ability of deicers to penetrate “ice layers likely to be encountered in highway deicing” (p.139). A literature review by Chappelow et al. (1993) revealed a few tests, some using a sheet of ice and others in which ice was confined in small cavities that could force the deicer particles to melt vertically. In other cases, penetration data was reported but the methodology was not. Because various deicers exhibit dissimilar penetration patterns (size, shape, and degree of horizontal penetration), a penetration test is particularly difficult to define. Two studies by McElroy et al. (1988b and 1990) conducted in Plexiglas® cavities and on a sheet of ice showed agreeable penetration data. This motivated Chappelow et al. (1992) to develop a test method for ice penetration of deicers confined in Plexiglas cavities.

The SHRP Ice Penetration Test measures the depth a particle of solid deicer or 30 µL of liquid deicer penetrates a vertical cavity of ice at 3, 5, 10, 15, 20, 30, 45 and 60 minutes after application . The test apparatus is made from Plexiglas with holes drilled 35 mm deep using a 5/32-in. drill bit. The upper 5 mm is drilled again with a countersink bit to form an opening 10-mm in diameter. De-aerated water is frozen in a conventional freezer to form ice, but the surface must undergo further preparation to increase test uniformity and provide a good surface for deicer application. The ice surface is melted with an aluminum iron and the apparatus placed in the test chamber overnight at the testing temperature. The test chamber is the same type of cold dry box used in the SHRP Ice Melting Test. A few hours before the test begins, the surface is again melted and wiped. For testing liquid deicers, slightly more water is wiped so that the ice forms just below the rim. Dye aids in the visual sampling during the testing. For testing solid deicers a couple of pinhead-sized drops of dye are frozen on the prepared ice surface. With liquid deicers, dye is mixed with the deicer. Five replicates are recommended. Additional details for the test method are available in the *Handbook* (Chappelow et al., 1992).

Nixon et al (2005) performed the SHRP Ice Penetration Test on the same seven liquid deicers as used in the SHRP Ice Melting Test. The research does not recommend using this test for quality control purposes until the actual processes involved in ice penetration are further understood. There are two primary and conflicting roles played by traffic in which deicing chemicals can be forced into the ice or dispersed from the road. The spread of data for the replicates is not presented, and the primary motivation for not recommending the test is its inability to accurately simulate field conditions.

2.3. Ice Undercutting Tests

The third deicer performance test developed by Chappelow et al. (1992) is the SHRP Ice Undercutting Test (H-205.5 and H-205.6). The test method incorporates a pavement-like substrate and is probably the most representative of actual field performance of deicers, while still maintaining several benefits of a standard laboratory test. The specimen preparation for this test is more complicated, but probably produces more uniform ice samples than those used in the melting and penetration tests. First, a mortar substrate is prepared in accordance with ASTM C 109 with the bottom of the mold sandblasted to create a textured surface when the specimen is removed. After 28 days, the ice is prepared on the textured surface by adding 96 to 98 mL of 35°F water. The ice is frozen slowly from the bottom to the top by placing the mortar sample on a plate maintained at 14°F, whereas the surrounding air temperature is 33 to 35°F. If the surface does not appear level and smooth, it is melted with an aluminum plate and refrozen.

For testing solid deicers, two drops of dye are added to the surface about 1 in. apart using a felt tip marker filled with the dye solution. Each dyed area is intended for one deicer particle and at least five replicates for each material are recommended. The deicer particle is weighed before being transferred to the ice. Photographs are taken at 5, 10, 15, 20, 25, 30, 45, and 60 minutes with a camera mounted above the specimen. Undercut areas are measured using a length marking recorded in each photograph. Photos are projected on onion skin paper and the undercut areas calculated (using diameters) or measured.

With liquid deicers, small cavities are formed by a warmed aluminum rod and melted water extracted with a syringe. Five (5) mL of deicer solution is prepared by adding dye before 30 µL is placed into each cavity with a pipette. Photographs are taken at 5, 10, 15, 20, 30, 45, and 60 minutes for undercut area calculations. Provisions for using other substrates are discussed and available in the SHRP *Handbook*, along with other details of the standardized ice undercutting test.

Mauritis et al. (1995) developed a laboratory test of ice undercutting that could be used to screen the effectiveness of solid deicer chemicals. This test is different from the SHRP tests in that the test utilizes Pyrex test tubes and does not incorporate dye. Instead, ice undercutting is detected by the break in an electrical circuit caused by a wire detaching from the test tube coinciding with deicer penetration and undercutting. The test tube was 15 mm x 85 mm with 0.5 mL of water frozen. The deicer applications were single particles weighing 0.25 g. This test is probably suitable only for screening purposes because the absence of roadway substrates (i.e., concrete and asphalt) will limit the ability of using the test results to predict actual performance of deicers.

2.4. Ice Disbondment and Shear Tests

A disbondment test was reported by Kirchner (1992) and McElroy et al. (1990) in which ⅛-in. ice was frozen on mortar specimens from the bottom up in a controlled chamber (using the same methodology as the SHRP Ice Undercutting Test). The ice was exposed to solid deicer for 30 minutes and then pulled under a blade. The 1.5-in.-wide blade was stationary while the specimen was pulled by vertical and horizontal load cells. The data includes the deicer parameters (loading rate, number of pellets, weight of pellets), estimated percent undercut area prior to loading, the magnitude of the force generated (horizontal, vertical, and resultant with angle), and the estimated percent of ice removed. In most cases, the percent removed equaled the percent undercut.

The deicer application in the disbondment test was based on results of the ice undercutting test and the application rate increased with decreasing temperature. However, in all cases the pellets were applied to the surface with a dispenser that arranged the pellets in a "pool ball rack configuration (Kirchner, 1992 and McElroy et al., 1990)."

Each mortar/ice specimen accommodates two disbondment blade tests. Thus, all deicers and deicer combinations were tested twice with the following exceptions: NaCl three times at 25°F, four times at 15°F, and $CaCl_2$ pellets three times at 15°F (Kirchner, 1992 and McElroy et al., 1990). The resultant force per 1.5 in. (blade width) averaged 32.6 pounds, ranging from 5.3 to 61.9 pounds. The standard error ranged from 0 to 11 with an average of 4.4 pounds.

It is worth noting that the ice disbondment test was not standardized during the development of the SHRP *Handbook*. This is primarily because the disbondment test described above showed relatively easy removal in undercut areas and that excessive force was required in non-undercut areas. Thus, the simpler Ice Undercutting Test provides enough indication of the disbondment characteristics of deicers (Chappelow et al., 1992).

The Anti-Bonding Endurance Test (ABET) was developed by the Anti-Icing Materials International Laboratory for Transport Canada to measure the effectiveness of anti-icers on concrete surfaces (Bernardin et al., 1996 and Bernardin et al., 1998). Deicers are distributed onto the substrate when the substrate temperature is 23°F and the air is 26.6°F. The precipitation is considered to be freezing rain, with droplets measuring about 150 to 200 µm. The intensity was generally 2.5 mm/hr, but the duration is one of the experimental variables. Six specimens are prepared, three of which are used for verification of the icing intensity. After being subjected to specific precipitation duration, the ice is scraped and the friction is measured. The scraping apparatus was specially designed for the test procedure taking into consideration typical vertical plow loads. The precipitation duration times at which ice removal was successful make up the ABT (Anti-Bonding Times) range for a deicer. The selected substrate consists of aluminum plates coated with a proprietary Performance Friction Surface, commonly used on marine helipads. The non-porous high friction surface provided more reproducible and realistic results than concrete or aluminum substrates.

Ashworth et al. (1989) developed an interfacial shear test to compare the effectiveness of several different deicers when applied as anti-icers to Portland cement concrete (PCC) substrates. The effectiveness of the anti-icers was also compared with reference tests in which no anti-icers were applied. PCC substrates were prepared in accordance to ASTM C 192-76 (historical standard) and could be reused after a verifiable cleaning sequence. Four substrates are used for each test and each substrate accommodates two specimens; thus eight test specimens are prepared for each chemical/temperature combination. The entire substrate surface is brushed with the anti-icer, based on the desired application rate, and air dried. Teflon rings are placed on the substrate and the specimen is kept at -13°F overnight and until one hour after 32°F water is introduced in the rings.

The shearing apparatus consists of a Cal-Tester Model TH-5 (5000 pound tester) mounted just outside of a temperature-controlled chamber (regulated to within 0.2°F). The four substrates are placed in the chamber with one hooked up to the loader with two cables, allowing both specimens to be tested without opening the door. After four hours, the first substrate is tested. One hour is needed between testing each of the remaining three substrates so the chamber can return to the desired temperature (Ashworth et al., 1989).

The researchers noted that the chemical-treated substrates generally exhibit clean breaking during shear testing, whereas the reference specimens usually left about 1-mm-thick ice on about 10 percent of the area, especially at lower temperatures. Due to the variability of ice adhesion, comparisons were only made between the two specimens on a given substrate. For untreated substrates, the average standard deviation was reported as 9 percent, but decreased to 5 percent when comparing the same locations of a substrate (Ashworth et al., 1989).

Shear testing of compressed snow on treated and untreated pavement aggregate materials was published by Adams et al. (1992). Granite and limestone coupons (8.6 x 11.7 cm), two common types of aggregate in pavements, were first surface-grinded and then treated with 2.5 mL of concentrated brine (CMA or NaCl, or untreated to provide a baseline). Snow was applied to the coupon instead of ice, but to ensure uniformity the harvested snow was stored at -0.4°F until two days before testing at which point it was transferred to a 25°F cold room (the testing temperature). One hundred twenty (120) grams of snow sifted through a 2.0-mm sieve was applied to the substrate and compressed for 10 minutes at 31 psi (to simulate the compressive forces exerted by a car or light truck). Two samples measuring 5 cm x 5 cm were sawed to accommodate a rectangular shear band. The shear load was applied with a displacement rate of 3 mm/minute and the shear load at failure was recorded. To investigate the behavior of residual anti-icing material, the snow application, compression, and shear loading procedure was repeated up to 42 times.

Four total testing sequences were completed for each of the aggregate types. The average adhesive strength of snow for the four tests at each snow application was reported, but the amount of variation was not mentioned for the treated conditions. For the baseline (untreated), the average adhesive strength of snow was 7.1 psi with a standard deviation of 1.1 psi for granite. For limestone, the respective average and standard deviation was 13.7 and 2.9 psi (Adams et al., 1992).

Nixon and Wei (2003) compared the effectiveness of various deicers on three types of ice formed on concrete specimens prepared using an Iowa DOT concrete mix design. The three types of ice studied were refrozen ice, atmospheric ice, and compacted snow ice, all with a thickness of 10 mm. The refrozen ice was prepared on the concrete specimens in 1-mm lifts at 15–30 minute intervals until 10 mm of depth was achieved. Atmospheric ice formation was simulated at 23 and -4°F by spraying water in a fine mist onto samples until the desired thickness was achieved. The compacted snow ice was prepared by compressing sifted harvested snow for 10 minutes at 83 psi; cooled water was sprayed onto the snow ice prior to overnight storage. The average ice density of the three types was 0.056, 0.054, and 0.043 pound per cubic foot (pcf), respectively. Solid sodium chloride, solid calcium chloride, and 27.3 percent by weight liquid sodium chloride were tested. Four grams of chemical were needed to reduce variability of the results, even though this corresponds to field rates four to six times greater than normal.

Furthermore, the solid chemicals were ground for more even distribution. After 10, 20, 30, or 40 minutes of exposure, the ice was scraped at 23°F at 6 mph using a hydraulic ram scraping machine. Supposedly the cutting edge has "been shown to be particularly representative of field behavior, as determined in Nixon et al. (1996)" The cutting edge is instrumented with a three-dimensional load cell and provides the horizontal (scraping) and vertical (downward) forces generated during scraping. Tests on 108 ice samples without chemical treatment had 44 "successful" results in which ice bonding to the concrete was statistically significant (scraping and downward forces were both greater than zero with 95 percent level of confidence). With the chemical-treated specimens, zero-load samples due to poorly bonded ice were not distinguished from zero-load samples due to successful chemical performance.

2.5. Tests for Eutectic and Effective Temperatures

Eutectic temperature is the minimum temperature a deicer solution remains in liquid form, which depends on the concentration of the deicer, usually expressed as percent weight of the solution. During the process of melting snow or ice, additional water is produced and the deicer is diluted, which may cause the solution to re-freeze. Thus, the eutectic temperature can be significantly different from the effective temperature for a deicer (Table 1).

Table 1. Comparison of Eutectic and Effective Temperature for Several Deicers

	Eutectic Concentration	Eutectic Temperature, T_{eut}		Minimum Effective Temperature, T_{eff}		
Deicer	%	°C	°F	°C	°F	Source
$CaCl_2$	29.8	-51.6	-60.9	-35.0	-31.0	1
$CaCl_2$	*not provided*	-51.1	-60	-28.9	-20	2
$MgCl_2$	21.6	-33.3	-27.9	-20.0	-4.0	1
$MgCl_2$	*not provided*	-33.3	-28	-15.0	5	2
Urea	32.6	-11.7	10.9	-9.0	15.8	1
Urea	*not provided*	-12.2	10	-3.9	25	2
Formamide	60.0	-45.0	-49.0	-18.0	-0.4	1
NaCl	*not provided*	-21.1	-6	-9.4	15	2
Potassium acetate	*not provided*	-60.0	-76	-26.1	-15	2
CMA	*not provided*	-27.2	-17	-6.1	21	2
CMA	*not provided*	-10	14.0	-10	14.0	1
$C_2H_6O_2$ (ethylene glycol)	60.0	-51	-59.8	-23.3	-9.9	1

[1] Resource Concepts Inc (1992)
[2] Anonymous (2003)

Eutectic temperature and concentration can be determined using the materials and description in ASTM D 1177 (Chappelow et al., 1992). This method is intended for engine coolants, but is generally accepted by the snow and ice community as a method to determine eutectic curves of deicers. Liquid deicing products from manufacturers can contain trace proprietary compounds; thus, the eutectic curve for one product could be different from a similar product from a different manufacturer (Personal Communication, Ron Wright, February 23, 2010). Specific tests for effective temperature were not found in the literature search, although effective temperatures may theoretically be deduced from a modified SHRP Ice Undercutting Test using various substrates, test temperatures, and application rates. Usually the effective temperature of deicers is determined by a consensus of field experience and not a laboratory test. Factors that contribute to "effective temperature" include dilution and relative temperatures of pavement versus snow (Resource Concepts Inc, 1992). As mentioned in the Snow and Ice Fact Sheet #20 (Anonymous, 2003), the minimum effective temperature is the lowest temperature a deicer should probably be used, for practical purposes, because the amount of deicer needed at colder temperatures may be so much that it may be "unreasonable."

2.6. Other Performance-Based Tests

The International Standards Organization has a specification for aircraft deicing and anti-icing fluids, ISO 11078. Dietl and Stankowiak (2005) used a test analogous to this method by incorporating concrete material instead of aluminum to compare temperature and application rate to icing prevention.

The potential for differential scanning calorimetry (DSC) thermogram to quantify deicer performance was proposed by Shi et al. (2007). This suggestion was developed based on freezing/thawing of salt brine in biological systems by Han and Bischof (2004). The methodology can provide information on the characteristic temperature and the heat flow during the liquid/solid phase transition of a given deicer, which are more useful than a deicer's eutectic temperature. Conceptually, it may be possible to establish the characteristic temperature of a deicer product as a function of its concentration. The laboratory investigation in this project preliminarily explored this possibility, but run into difficulty when characterizing the DSC thermogram of very concentrated deicer solutions. This is an issue that may be addressed with enhanced DSC instrumentation. Future research may enable the establishment of such a characteristic temperature curve, which would replace the widely-used eutectic curve and provide more guidance on the complex dynamics of ice melting process, the role of deicer, and the appropriate application rate of deicer relative to the amount of accumulated snow and ice.

As discussed above, a variety of tests designed to measure deicer performance have been identified in the literature. Nonetheless, the application of these tests is important in understanding their benefit to the winter maintenance community. The website for the Keweenaw Research Center of Michigan Technological University indicates researchers there use the SHRP deicer performance tests, as well as laboratory tests for friction, frost formation, and bond strength and reduction (KRC, 2006). Even a brief look at patents associated with deicers often turns up significant use of deicer performance tests, especially the tests presented in the SHRP *Handbook of Test Methods for Evaluating Chemical Deicers*:

- Patent by Berglund et al. (2001), *Deicing Compositions and Methods of Use,* reported using a **modified SHRP Ice Penetration Test** for solid deicers (modified by using room temperature deicer instead of chilled deicer, triplicates performed instead of five total replicates, and only five time points measured instead of eight).
- Patent by Berglund et al. (2003), *Water-Activated, Exothermic Chemical Deicing Formulations,* reported using both **ASTM D1177** for freezing point determination and a **modified SHRP Ice Melting Test** for liquid deicers (modified by using 88 mm ×13 mm Petri dish instead of standardized Plexiglas dish, 20 g of water to make ice instead of 130 mL, using aluminum blade instead of aluminum plate to melt/re-freeze ice, applying 10 g of aqueous "solid" deicer to ice instead of standard solution, and performing the test in duplicate instead of triplicate).
- Patent by Chauhan et al. (2006), *Process for Producing a Deicing/Anti-Icing Fluid,* reported using the **SHRP Ice Penetration Test** for solid deicers.
- Patent by Hartley and Wood (2007), *Deicing Solution,* reported using the **SHRP Ice Melting test** for liquid deicers.
- Patent by Klyosov et al. (2000), *Liquid and Solid De-icing and Anti-icing Compositions and Methods for Making Same,* reported using both the **SHRP Ice Melting and Ice Penetration Tests** for solid and liquid deicers.
- Patent by Koefod (1996), *Corrosion-Inhibiting Salt Deicers,* reported using the **SHRP Ice Melting Test** for solid deicers.
- Patent by Mathews (1996), *Process for the Production of Road Deicers from Water Plant Residuals,* reported using the **SHRP the Ice Melting Test** for solid deicers.
- Patent by Rynbrandt and Hoenke (1993), *Method to Increase the Rate of Ice Melting by CMA Deicing Chemicals with Potassium Acetate,* reported using a **modified ice melting test** performed at 25°F in which 400 g of distilled water created ice in a 10 in. x 15 in. x 2 in. pan. Deicer was applied (10.8 g) and the melted portion was poured out and weighed after 60 minutes.

2.7. Summary of Literature Review

The literature review identified many possible test methods for deicer performance that could be used to screen potential deicer products and blends. Some of the test methods seem to be more widely used, while others have inherent limitations. A comparison of deicers in a laboratory setting is only helpful if field applications of the same deicers results in similar trends of effectiveness. Otherwise, the acceptance of a deicer based solely on laboratory tests is a futile endeavor. However, measures of the relationship between laboratory tests that measure deicer performance to potential field performance of those deicers was notably absent from the literature. Furthermore, most of the laboratory test methods neglected several parameters that likely play a role in the field performance of deicers, including, traffic, humidity, wind, active precipitation, and pavement. It is the understanding of this research team that the development of a laboratory test that effectively predicts field deicer performance is a topic of interest for the Clear Roads group. Given that the focus of this project was to develop laboratory test methods that could be used to screen potential deicing products and blends, and the desire for relatively simple and straightforward test methods, a more realistic laboratory method that incorporates pertinent field parameters is highly recommended. With that in mind, a summary of the more popular and promising test methods to assess deicer performance is presented in Table 2. The table provides the advantages, disadvantages, and value ranges for several deicers.

Table 2. Summary of promising and common laboratory test methods for deicers

Test Method	Advantages	Disadvantages	Sample of Results within the Literature
Ice Melting Test, SHRP H-205.1 and H-205.2 (Chappelow et al., 1992)	• simple procedure • simple equipment	• variations in ice across specimens and labs • prone to modifications, this can complicate comparisons	Ice melting over time should be reported, but at 60 minutes the following results were obtained (mL of brine per g of solid deicer): • NaCl at 25°F, 7.12 • NaCl at 15°F, 3.76 • NaCl at 5°F, 1.25 • CaCl2 at 25°F, 6.91 • $CaCl_2$ at 15°F, 4.01 • $CaCl_2$ at 5°F, 3.14
Ice Penetration Test, SHRP H-205.3 and H-205.4 (Chappelow et al., 1992)	• simple procedure • simple equipment	• according to the literature, only recommended for solid deicers	Ice penetration over time should be reported, but at 60 minutes the following results were obtained (average depth for solid deicers, mm): • NaCl at 20°F, 13.4 • NaCl at 15°F, 10.4 • $CaCl_2$ at 5°F, 9.5
Ice Undercutting Test, SHRP H-205.5 and H-205.6 (Chappelow et al., 1992)	• provides a substrate	• complicated procedure, more complicated equipment • need to control substrate and air temperature independently • recommended substrate is a mortar, which is barely realistic	Ice undercutting over time should be reported, but at 60 minutes the following results were obtained (area undercut in cm^2 per g of solid deicer) • NaCl at 25°F, 86.5 • NaCl at 5°F, 10.7 • $CaCl_2$ at 25°F, 77.3 • $CaCl_2$ at 5°F, 28.7
Ice Undercutting Test (Mauritis et al., 1995)	• simple procedure • better indicator of penetration than SHRP Ice Penetration Test	• standardization of ice volume and deicer application not yet investigated	Results read from a chart, interpolation error is present (minutes required to undercut) • NaCl at 28°F, 10 • NaCl at 2°F, 95 • $CaCl_2$ at 2°F, 25 • $MgCl_2$ at 2°F, 30
DSC Thermogram (Shi et al., 2007)	• method can potentially indicate effective temperature and ice melting capacity	• standardization of temperature range, heating/cooling rate, deicer concentration not yet investigated	None available at time of literature search.

3. SURVEY ANALYSIS

A five-question survey was developed to gauge the usefulness of knowing various performance aspects of deicers, as well as to measure the degree of implementation of the standardized tests identified during the literature review. Although the focus of the survey was primarily on the performance aspects of deicers, it provided a good opportunity to seek input regarding other deicer effects that also may be of interest. Thus two questions focused on the performance aspects of deicers, two questions inquired about the use and perception of standard tests, and one question asked about impacts of deicers. The survey instrument is included in Appendix A of this report.

The survey was distributed to members of the Clear Roads technical advisory committee as well as members of other relevant programs: the Pacific Northwest Snowfighters Association, the Aurora Program, and the Winter Maintenance Technical Service Program, in addition to participants of the 1st National Winter Maintenance Peer Exchange (August 2007, Columbus, OH). Finally, the survey was also posted on the Snow and Ice List-Serve, a subscriber based mailing list linking individuals worldwide in fields related to winter maintenance. The List-Serve is commonly used as an interactive venue to post questions and share responses related to winter maintenance materials, equipment, or practices.

A total of 49 responses were received from the 28 states shown in Figure 1, in addition to the following entities: AASHTO; Region of Waterloo, Ontario; Region of Peel, Ontario; New York City, New York; New York State Thruway Authority; nine Wisconsin counties (Clark, Eau Claire, Fond du Lac, Jackson, La Crosse, Manitowoc, Polk, Portage, and Vilas); Western Transportation Institute (by former Montana DOT employee), Cargill Deicing Technology; Dow Chemical Company; EnviroTech Services; Paradigm Chemicals; and Redmond Minerals. Twenty-six responses are attributed to states (and cities/counties within states) that are members of the Clear Roads program.

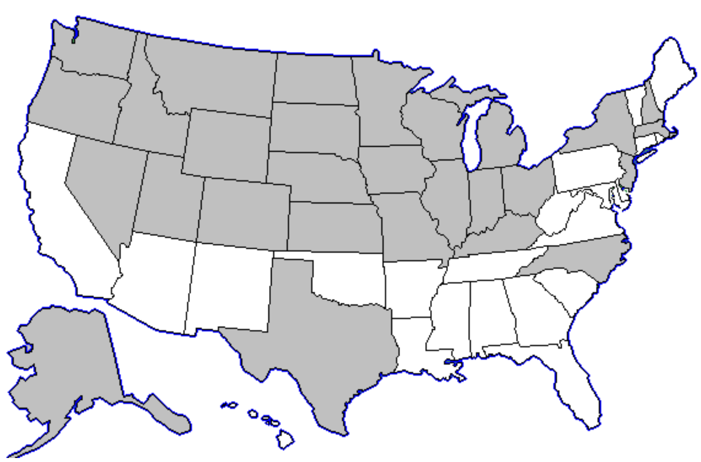

Figure 1: States that responded to survey (grey)

3.1. Performance Aspects of Deicers

Questions 1 and 2 inquired about the usefulness of various performance characteristics of deicers. A list was supplied and participants were asked to rate the usefulness of each aspect of deicers, from "very useful" to "not useful at all." The performance characteristics listed were:

- Melting ability or capacity
- Penetration ability on ice
- Penetration ability on compacted snow
- Ability to undercut or break the bond between ice/snow and the pavement
- Ability to prevent bonding between ice/snow and the pavement
- Effective temperature range
- Eutectic temperature (and concentration)
- Residual characteristics

Effective temperature and melting capacity received the highest average response, followed by the ability to prevent or undercut a bond between snow/ice and the pavement (Figure 2 and Table 3). The four responses that selected "Not useful at all" were submitted by manufacturers. The results from states (and counties within states) that are members of the Clear Roads program mirrored the overall results fairly closely, except penetration ability on snow ranked nearly as high as penetration ability on ice.

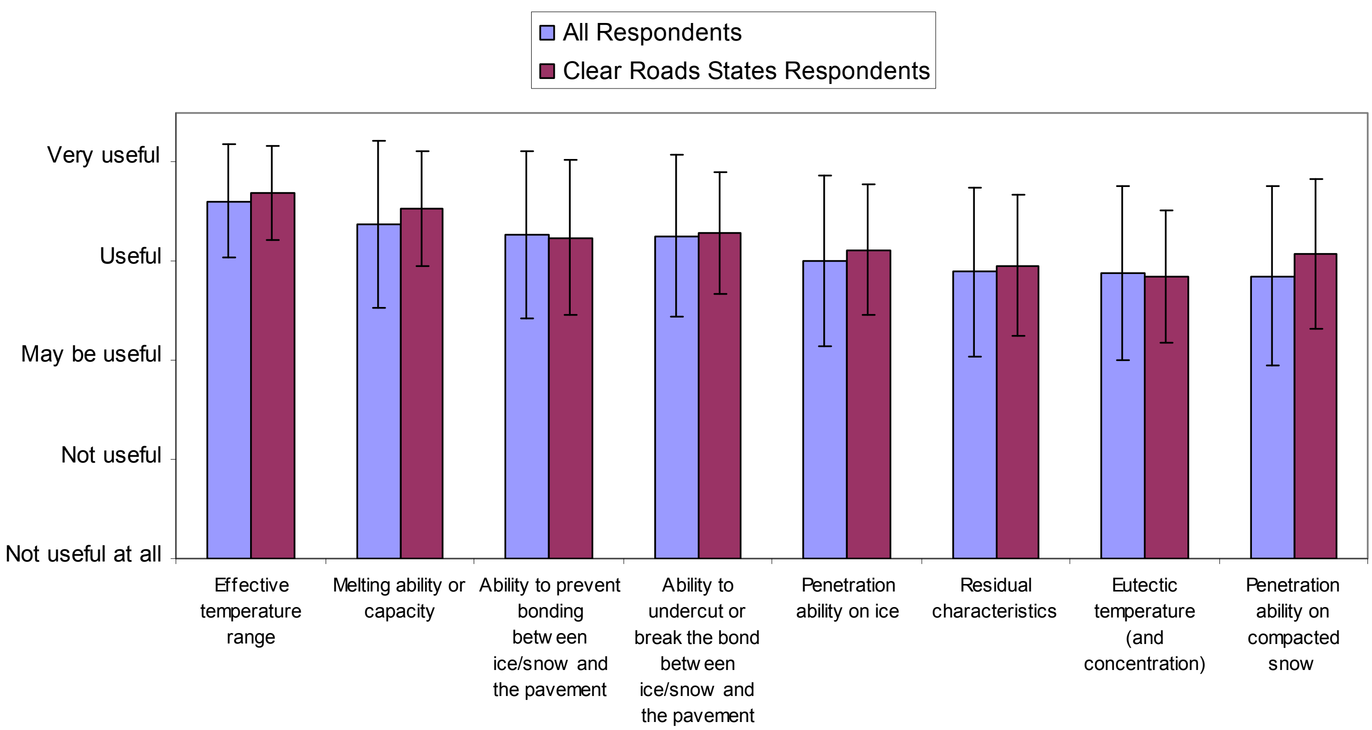

Figure 2: The average (± 1 standard deviation) ranking for the usefulness of various performance aspects of deicers

Table 3. The number of responses for each category for the performance aspects of deicers

All respondents:	Not useful at all	Not useful	May be useful	Useful	Very Useful
Effective temperature range	0	0	2	15	32
Melting ability or capacity	0	3	2	17	26
Ability to prevent bonding between ice/snow and the pavement	0	2	6	17	23
Ability to undercut or break the bond between ice/snow and the pavement	0	2	5	19	21
Penetration ability on ice	1	0	11	21	14
Penetration ability on compacted snow	1	1	14	19	12
Residual characteristics	1	0	14	21	12
Eutectic temperature (and concentration)	1	1	13	22	12

Participants were able to add to the list, but most strayed from performance aspects by writing in other properties, such as skid resistance, corrosiveness, corrosion-inhibiting characteristics, impact on the environment, handling ability in cold temperatures, etc. Several additions and comments about deicer performance were related to:

- Calculated Melting Capacity, to theoretically (mathematically) determine the volume of ice that will be melted—although without kinetics, there is no indication of when the ice will melt
- Time to penetrate versus temperature
- Bonding characteristics

There was also a detailed comment from one respondent advocating the view that ice melting capacity and effective temperature range are the most important parameters, suggesting that penetration and undercutting performance of deicers would probably follow the same trends as melting capacity. However, the respondent does caution that "the usefulness of any lab test ultimately depends upon its predictive power under field conditions." Thus, just as the SHRP Ice Melting Test is not a tool for determining the exact application rates required for specific temperatures because of the lack of many field factors, it is probably an appropriate tool for comparing deicer performances, especially relative to a very familiar deicer: salt.

In addition to the usefulness of the performance characteristic, participants were asked whether the results should be compared to pass/fail criteria or a scale. Almost overwhelmingly, the respondents indicated a preference for a scale (Table 4), with several comments advocating for a quantitative or numeric basis. One justification given for using a scale was that a scale could be more adaptable to regional needs. Of all the respondents who had selected pass/fail for at least one test characteristic, only one provided a reason: "In my opinion, interpretation of end result has to be easily understood by all levels of winter control staff. Using scale measurement can lead to subjective evaluation." A few respondents cautioned about the potential for test variability and showed concern over hard lines, both for pass/fail and scale metrics.

Table 4. Number and percentage of responses for the type of reporting: pass/fail, scale, or other

All respondents:	Number of responses	Percentage Indicating: Pass/Fail	Scale	Other
Effective temperature range	45	16	78	7
Melting ability or capacity	44	11	89	0
Ability to prevent bonding between ice/snow and the pavement	45	31	69	0
Ability to undercut or break the bond between ice/snow and the pavement	44	32	68	0
Penetration ability on ice	44	18	82	0
Penetration ability on compacted snow	44	23	77	0
Residual characteristics	44	27	66	7
Eutectic temperature (and concentration)	45	11	84	4

3.2. Implementation of Standard Deicer Performance-Based Tests

As identified in the literature review, several standardized test methods exist for quantifying various performance aspects of deicers. While the review also identified many experimental procedures developed by researchers, these tests were not included in the survey as it was assumed that they would not be familiar to practitioners. Thus, while only the performance-related SHRP tests (ice melting, ice penetration, ice undercutting), ASTM (eutectic temperature) and ABET (Anti-Bonding Endurance Test) tests were listed in the survey, participants were given the opportunity to contribute to the list. Question 3 specifically sought the degree of implementation of the listed test methods, with participants given the option to respond as "Have Used," "Currently Use," "Modified Procedure," "Don't Use," and "Never Heard Of." About 15 percent of participants skipped this question while approximately half indicated that they did not use any of the listed tests (Table 5). Thus, a follow-up question to obtain users' perceptions of the usefulness, reliability, and ease of use of the various tests applied to only 6 to 22 percent of the respondents, depending on the particular test method. The number of respondents for this portion was fairly limited, and none of the tests scored particularly high (Figure 3). Although not shown on the figure for clarity reasons, the standard deviation was approximately an entire ranking for nearly every test and judgment, with the main exception being the undercutting tests with a standard deviation near half a ranking for reliability and ease of implementation.

Table 5. Number of respondents for each test method, indicating limited implementation of the standard performance-based tests; the number on the left is for all respondents, the number on the right (in parentheses) is only for Clear Roads states respondents

Test Method	Skipped this one	Have used	Currently use	Modified Procedure	Don't use	Never Heard Of
SHRP H-205.1 Test Method for Ice Melting of Solid Deicing Chemicals	7 (4)	8 (3)	2 (1)	2 (0)	21 (11)	12 (8)
SHRP H-205.2 Test Method for Ice Melting of Liquid Deicing Chemicals	7 (4)	7 (2)	2 (1)	1 (0)	20 (11)	13 (8)
SHRP H-205.3 Test Method for Ice Penetration of Solid Deicing Chemicals	7 (4)	5 (1)	1 (0)	1 (0)	23 (13)	13 (8)
SHRP H-205.4 Test Method for Ice Penetration of Liquid Deicing Chemicals	7 (4)	6 (1)	0 (0)	1 (0)	23 (13)	13 (8)
SHRP H-205.5 Test Method for Ice Undercutting by Solid Deicing Chemicals	8 (5)	4 (0)	0 (0)	1 (0)	23 (12)	14 (9)
SHRP H-205.6 Test Method for Ice Undercutting by Liquid Deicing Chemicals	8 (5)	3 (0)	0 (0)	1 (0)	24 (12)	14 (9)
Anti-Bonding Endurance Test (Transport Canada, Airports Group)	8 (5)	0 (0)	0 (0)	0 (0)	20 (9)	21 (12)
ASTM D 1177 Standard Test Method for Freezing Point of Aqueous Engine Coolants	7 (4)	6 (2)	5 (3)	0 (0)	19 (8)	14 (10)

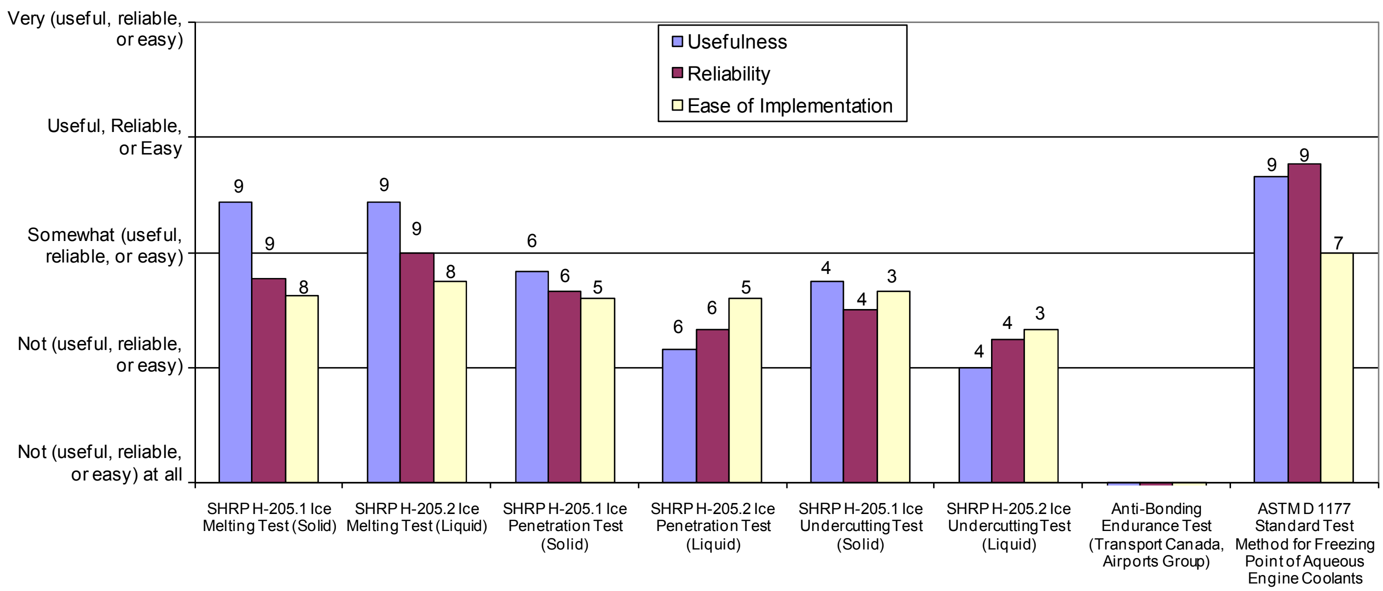

Figure 3: The average ranking for usefulness, reliability, and ease of implementation of various deicer performance tests, with number of responses shown above each bar

The SHRP test that has been used by the greatest number of respondents is the SHRP Ice Melting Test. Ten separate entities have or currently use the test for solid or liquid deicers. Of these, five are manufacturers and five are DOTs. The state DOTs rated the SHRP Ice Melting

Test between somewhat useful and very useful, whereas the manufacturers rated the test between not useful and very useful. One manufacturer indicated it currently uses the test for solid and liquid deicers and two states indicated they use the test for solid (Utah) and liquid (Minnesota) deicers. The Minnesota DOT (MnDOT) only uses the SHRP Ice Melting Test for liquids, but it is performed every time a bid sample is received or when it wants to evaluate deicers. MnDOT also added the Mauritis ice undercutting test (described in the literature review, Mauritis et al., 1995) to the list and indicated it developed this test and have used it, but it has been a couple of years since this test was last performed. The survey responses regarding this test's implementation were: Useful, Reliable but Not Easy (Personal Communication, Jim McGraw, May 9, 2008).

There were a few comments from respondents (mostly manufacturers, but also two detailed state responses) for Questions 3 and 4, particularly regarding the SHRP tests, that were taken into consideration before developing the laboratory protocols:

- "Not a big supporter of the SHRP methods due to accuracy and repeatability. Better methods are needed." (Manufacturer)
- "Tests are pretty subjectable from all the modifications that each lab uses because of the preparation of ice trays, cold temperature rooms or freezers, air flow, induction of materials, measurement methods, and subjective interpretation of results. Same comment as above for solids." (State response – Idaho)
- "While we have used some of these methods in the past, we feel they do nothing from a practical point of view towards effective evaluations. They are not useful." (Manufacturer)
- "Melt capacity, penetration and undercutting testing are relatively meaningless for liquid deicers, since these products are not intended for application directly onto ice or hardpack snow. They are intended to prevent a bond formation, not to do a significant amount of melting. Freeze point testing is very tricky and I'm not sure ASTM D 1177 fully addresses the possibility of supercooling resulting in artificially low freeze points, especially in salt solutions containing long chain carbohydrates as is the case agricultural by-product additives. It has been my experience that these additives slow down the kinetics of freezing, but not necessarily the equilibrium freeze point. This has resulted in performance claims of very cold freeze points, yet real world experience shows that freezing still occurs at temperatures much higher than the claim." (Manufacturer)
- "Right now the information is somewhat useful because agencies apply what it takes to get the performance. I would like to see how the relationship of the lab test will be employed to actual field applications. There is the problem as maintenance folks just apply what it takes to get the job done, not always what the right amounts should have been. Simply stated more will get the job done." (State response - Idaho)
- "We have routinely used the SHRP solid and liquid ice melting capacity tests for years as it is the only industry standard method at the moment. It is relatively easy to use provided one has a controlled temperature chamber. It is not highly precise, particularly with solid deicers, and without running very large numbers of replicates it is difficult to measure

differences in ice melting capacity that are much less than about 30%. That may be good enough since variation in the field is probably going to be even higher, but it also appears that the SHRP test may underestimate ice melting capacity in the field. We are currently investigating this and it may be that additional factors present in the field such as traffic action and sunlight have significant effects on ice melting action that are not captured by the SHRP test. We have also often used the ASTM freezing point test as that is commonly required by customers. However the data from this test is widely misunderstood and misapplied as well as being subject to inaccuracies in many formulas that tend to form amorphous glasses rather than well defined freezing points. It is a reasonably reliable direct measurement of a liquid’s freezing point for determination of stable storage conditions, but it is a very unreliable predictor of deicing ability, as it is often used for. It is also an unreliable predictor of true freezing point as more complex formulations often have complex phase behavior and do not exhibit well defined freezing points. To obtain precise phase diagram measurements, it is better to use a technique such as differential scanning calorimetry.” (Manufacturer)

- “Undercutting depends largely on the type of surface. There is a false perception that relative performance in the lab will always translate to the same relative performance in the field, even if the field conditions are different. This is a poor assumption unless validated with actual field data. There are numerous studies that demonstrate this fact.” (Manufacturer)

3.3. Effects of Deicers

Once a deicer has been found to meet performance requirements, it is often desirable to test its potential detrimental effects before widespread implementation. Because this project focuses on the performance characteristics of deicers, an exhaustive list of the standard test methods for deicer effects was not included in the survey. Instead, in an effort to keep the survey short, possible effects were listed and participants were asked to rate their importance from “Very Important” to “Not important at all.” *All responses to this question by manufacturers/producers were disregarded.*

The deicer effects associated with safety issues were found to be more important than infrastructure or environmental issues, with most respondents indicating “very important” or “important” for safety issues and “important” or “may be important” for other issues (Figure 4 and Table 6). The results from states (and counties within states) that are members of the Clear Roads program mirrored the overall results fairly closely. No respondent chose “not important at all” for any of the listed effects. This nationwide input may be helpful for consortiums in determining if possible effects of deicers should be tested. Appendix A can provide a guideline of existing tests for many of the effects listed in the survey.

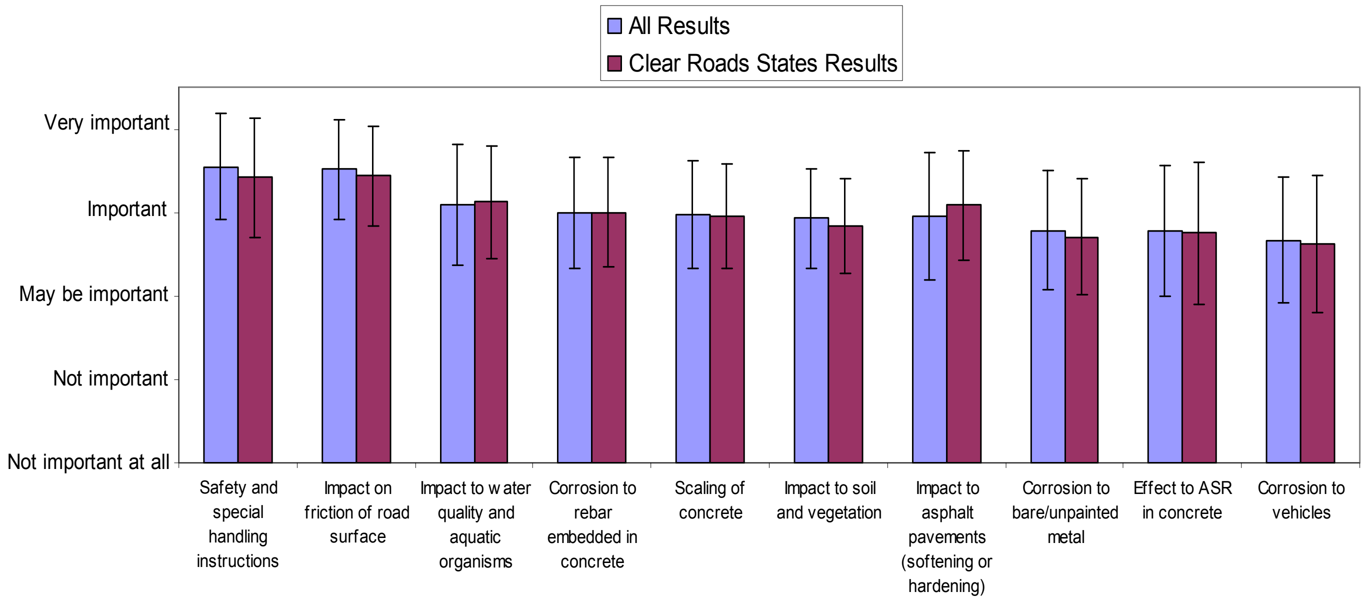

Figure 4: The average (± 1 standard deviation) ranking for the importance of various possible effects of deicers

Table 6. The number of responses for each available category for the effects of deicers

Impact	Not important at all	Not important	May be important	Important	Very Important
Impact on friction of road surface	0	0	2	16	23
Safety and special handling instructions	0	0	3	13	26
Corrosion to rebar embedded in concrete	0	0	9	24	9
Scaling of concrete	0	0	9	25	8
Effect to ASR in concrete	0	1	15	18	8
Corrosion to bare/unpainted metal	0	1	13	22	6
Corrosion to vehicles	0	2	15	20	5
Impact to asphalt pavements (softening or hardening)	0	1	10	21	10
Impact to soil and vegetation	0	0	9	27	6
Impact to water quality and aquatic organisms	0	1	6	23	12

3.4. Summary of Survey Analysis

The results of the survey indicate a relatively modest level of implementation of the SHRP deicer performance tests and ASTM freezing point test and no use of the Anti-Bonding Endurance Test (ABET). The comments elicited from Questions 3 and 4 show state DOTs rate the usefulness of the tests slightly higher than ratings attributable to manufacturers.

4. DEVELOPMENT OF STANDARD PERFORMANCE TESTS

4.1. Introduction

On the basis of findings from the literature review and survey and in consultation with the project technical advisory subcommittee, the research team focused on the following test methods for experimentation and refined development:

- Differential Scanning Calorimetry (DSC) thermogram test for liquid deicers
- Modified SHRP Ice Melting Test for solid and liquid deicers
- Modified SHRP Ice Penetration Test for solid and liquid deicers
- Modified ice undercutting test (designed by Mauritis et al., 1995) for solid deicers and liquid deicers

The tests were developed with the expectation that they will be performed by independent testing laboratories on any deicing chemical, additive or mixture. Ideally the test methods would not require any specialized equipment. However, the literature review indicated an environmental chamber or freezer is generally needed to test products used on roadways during the winter. One study conducted tests outdoors, but this is not practical during most of the year and includes too many uncontrollable factors. Even the tests selected for study provide only general trends or an assessment of relative performance and are not used to estimate application rates for field operations.

Each of the methods involved in the testing program existed in some form prior to their inclusion in this research. In the case of DSC, it had not previously been used on deicer solutions, and hence warrants some background information. The SHRP Ice Melting and Ice Penetration tests and Mauritis Ice Undercutting test were presented in Chapter 2; the variations considered for modification and possible improvement are described.

The DSC tests were performed at the Corrosion and Sustainable Infrastructure Laboratory at the Western Transportation Institute. The ice melting, penetration and undercutting tests were performed at the Subzero Science and Engineering Research Facility in the Civil Engineering Department of Montana State University.

The recommended test procedures are described in Appendix C.

4.2. Deicers

Reagent-grade solid sodium chloride, magnesium chloride, and calcium chloride with minimum purity of 99.0% were tested (Table 7). Reagent-grade chemicals are suitable for general laboratory use and can differ from commercial deicers in gradation and purity.

Table 7. Specifications of solid deicers

Formula	*Molecular Weight*	*CAS #*	*Brand*
NaCl	58.44	7647-14-5	Fisher Scientific
$MgCl_2 \cdot 6H_20$	203.31	7791-18-6	Sigma-Aldrich
$CaCl_2 \cdot 2H_20$	147.02	10035-04-8	Acros Organics

Commercial liquid deicers were donated by two DOTs. Illinois DOT provided 23% NaCl, 32% $CaCl_2$, and AGBP (an agricultural by-product based anti-icing product, presented anonymously in this report). Minnesota DOT provided a 30% $MgCl_2$–based deicer. Thus, all liquid deicers tested were commercial products, whereas all solid deicers were reagent-grade chemicals featuring high purity and little contaminants or additives.

4.3. DSC Thermogram Test

Development

The DSC thermogram may be a better method than the eutectic curve to rapidly quantify deicer performance. DSC is an experimental technique that measures the energy necessary to maintain a near-zero temperature difference between the test substance and an inert reference material, with the two subjected to an identical temperature program (Figure 5). The heat flow measurements indicate phase transitions, energy changes, and kinetics. DSC measurements typically require only a few milligrams of the sample, which is sealed in an aluminum capsule. The equipment needed for DSC measurements typically costs between $40,000 and $80,000, depending on the vendor and model; it is commonly available in materials testing laboratories.

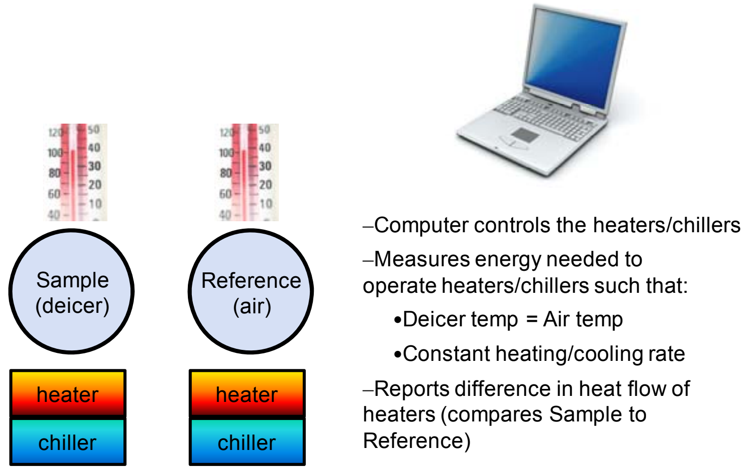

Figure 5: Concept of Differential Scanning Calorimetry (DSC)

A DSC thermogram for deionized water is shown in Figure 6. Note that this work only shows the warming cycle thermogram (the upper part in Fig. 7a) as it is more reproducible than the cooling cycle one (the lower part of Fig. 7a). At around 32°F a drop in heat flow between the water (sample) and air (reference) occurs, corresponding to the phase transition from ice to water. Two significant temperatures are noted by the DSC: 1) temperature associated with the lowest (peak) heat flow (34.45°F) and 2) the temperature associated with the frozen side of the peak (30.37°F). The area within the peak (shaded blue) is the integrated heat flow in Joules per gram (345.1), i.e., the amount of thermal energy needed to turn the water from solid phase to liquid phase.

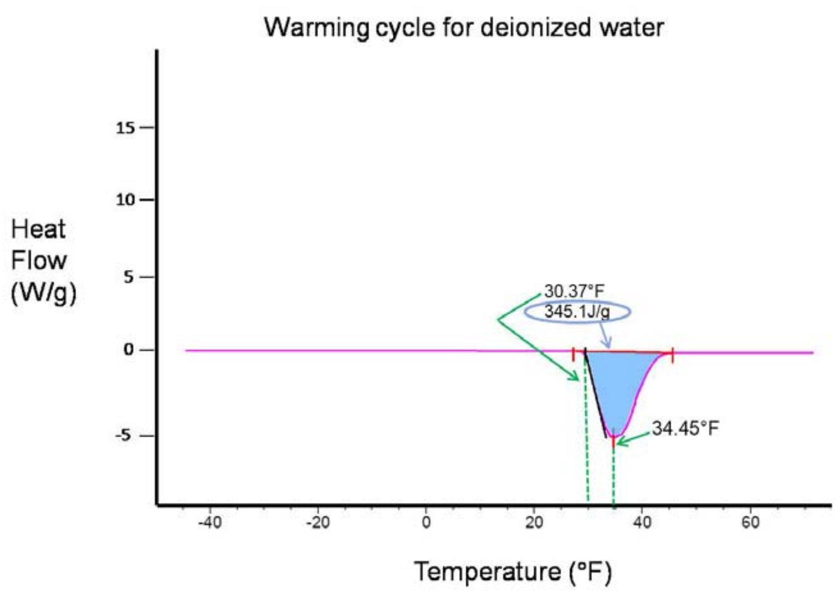

Figure 6: DSC thermogram of deionized water, warming cycle, 3.6°F/minute.

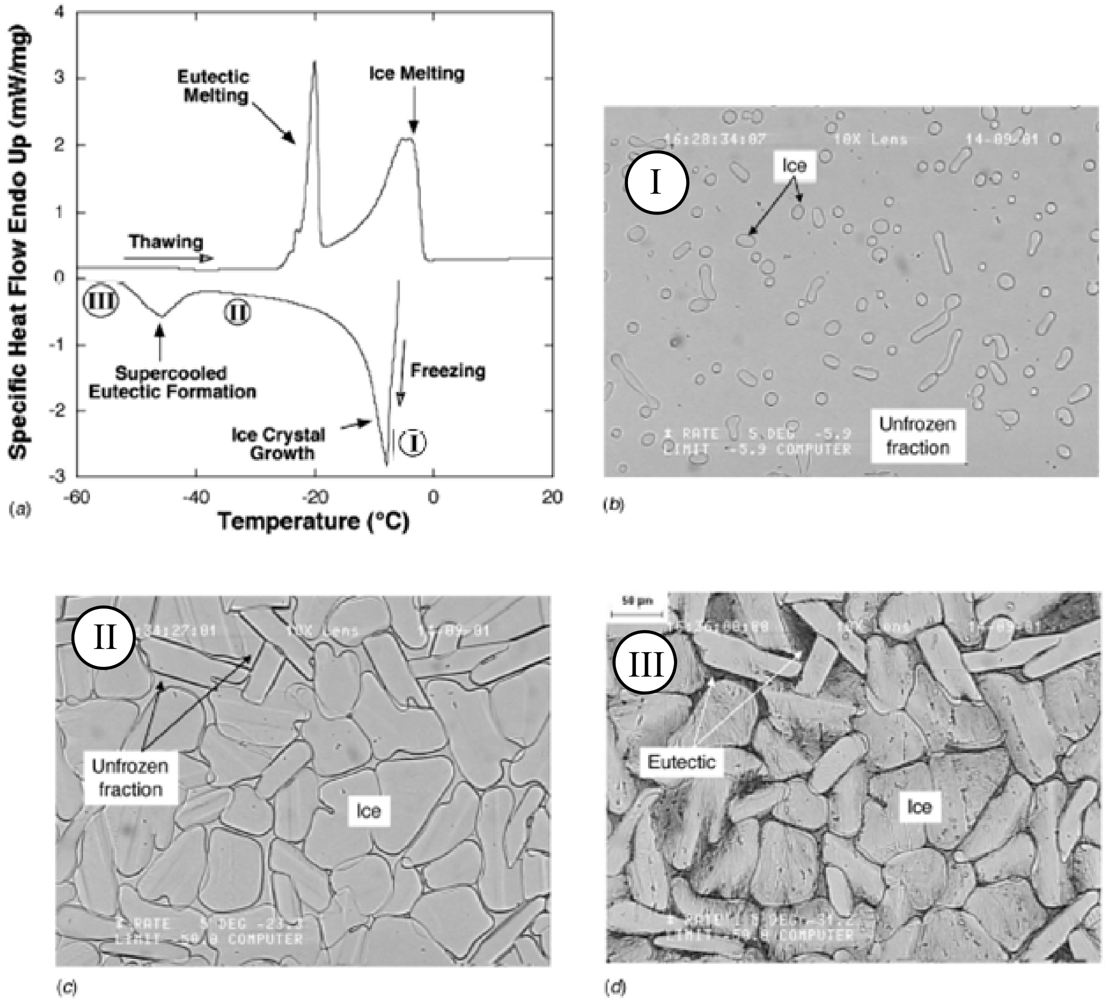

Figure 7: DSC thermogram and cryomicroscopy images during freezing/thawing of a simulated salt brine (adapted from Han and Bischof, 2004)

To understand the potential applicability of DSC to the winter maintenance applications, it helps to compare a DSC thermogram for deionized water and one for a simulated salt brine published by Han and Bischof (2004). The DSC thermogram of the simulated salt brine shows some interesting peaks (Figure 7). First, let us examine the cooling cycle thermogram (the lower part in Fig. 7a). As temperature decreases and approaches near Point I (-9°C, 16°F), the first peak shows up indicating the initiation and growth of ice crystals in the salt brine. As the temperature further drops near Point II, the second peak shows up, indicating the complete freezing of the salt brine (eutectic formation). The surface area under these peaks corresponds to the amount of thermal energy released in the two phase-transitions respectively. Next, let us examine the warming cycle thermogram (the upper part in Fig. 7b), which consists of eutectic melting and ice melting peaks corresponding the two peaks in the warming cycle respectively, even though the exact peak temperatures differ from those in the cooling cycle due to mechanisms related to the kinetics of ice crystal formation, growth and melting.

It should be noted that different chemical solutions would feature thermograms with different peaks in terms of peak temperature, temperature spread and surface area. This is the basis for using DSC thermogram as "fingerpoint" of the chemical solutions being tested. The freezing temperature near Point I (-9°C, 16°F) in Figure 7(a), is a much more reliable indicator of the start point of ice crystal growth than the eutectic temperature; this characteristic temperature (-9°C, 16°F) coincides with the "effective temperature" of this brine as a deicer or anti-icer, where ice crystals start to form and the pavement becomes icy. Furthermore, the specific heat flow at the exothermic peak may be used along with the characteristic temperature to estimate the ice-melting capacity of the chemical, as detailed later in this chapter.

In this study, to develop a DSC-based standard test protocol for deicer performance, DSC thermograms were measured for selected deicers at their optimal (eutectic) concentration and concentrations representing various dilution rates. The appropriate temperature range, heating and/or cooling rate, and sample size were also determined. Finally, the key parameters to be used for comparison purposes were chosen.

To determine the optimal DSC test protocol, a 23% NaCl solution made of deionized water and reagent-grade NaCl was used for protocol development. Initially, the full concentration (23% NaCl solution) was used; however the resulting thermograms merely hinted at characteristic phenomena occurring in certain regions of the temperature cycle that became more apparent once diluted deicers were tested. Dilution rates of 11:1, 6:1, 4:1, 3:1, and 1:1 (i.e., no dilution) were then used to determine the optimal dilution rate. Deicers of other formulations (including $MgCl_2$, sodium formate, and sodium acetate) were also used to select an appropriate dilution rate. A dilution rate of 3:1 (e.g., 10 mL added to 5 mL of 23% NaCl deicer) was chosen based on the criterion of lowest dilution that gave reproducible results of all deicer formulations tested to this point. Too high or too low a dilution rate caused poor reproducibility of DSC thermograms.

Cooling and warming rates were varied to determine optimal rates. Deicer samples were cooled and heated at rates of 18, 9, and 3.6ºF/min. A cooling and warming rate of 3.6ºF/min was preferred because the higher rates did not adequately reflect energy changes (whereas lower rates led to longer test duration for the same temperature range). While the DSC instrument has the capability of cooling down to -130ºF, a range of 77 to -76°F was chosen because it would still capture all phenomena relevant to field conditions for winter road maintenance and it reduced the test duration.

In determining the appropriate sample size, it was found that quantity by mass of the deicer could not be consistently sampled, therefore potentially affecting the reproducibility of results. It was decided to test samples based on mass of a particular volume rather than mass alone. The volume chosen was 10 µL measured with a micropipette. Volumes less than 10 µL were too small to give reproducible results, and volumes greater than 10 µL could exceed the volume of the sample pans (especially when heated).

Results

The optimal DSC test protocol consists of a 10 µL deicer sample diluted 3:1 with deionized water. The temperature range of the DSC test is 77 to -76 °F carried out at a rate of 3.6°F per minute; the sample is subject to a cooling then warming cycle. Different deicers developed unique characteristic peaks along both cycles, but the warming cycle was preferred for data analysis since the cooling cycle data were sometimes interfered by the supercooling effect. Most deicers produced one peak during the warming cycle, but sodium chloride solutions showed two peaks. The characteristic temperature and heat flow for the warmer peak provides information relevant to deicing on roads. The warmer temperature peak corresponds to the field scenario when the temperature drops and the pavement gets icy. Figure 8 provides a comparison of the 23% NaCl, 32% $CaCl_2$, and 30% $MgCl_2$ deicers. The DSC test provides the characteristic temperature (T) and heat flow (H) associated with the peaks.

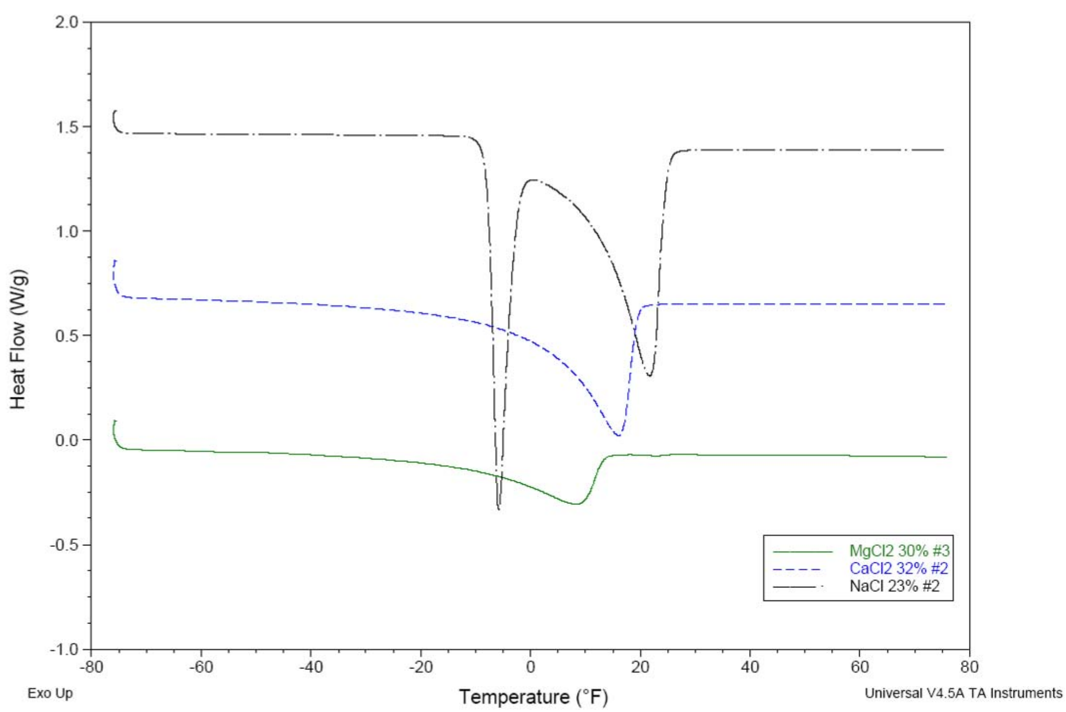

Figure 8: DSC thermograms of 23% NaCl, 32% $CaCl_2$, and 30% $MgCl_2$, dilution 3:1, warming cycle, 3.6°F/minute

The test should be performed a minimum of three times. Overall, the DSC test was found to be very repeatable, particularly for 23% NaCl (Table 8). However, more than three replicate tests should be conducted if the variation is too large. The average and standard deviation of the characteristic temperature (°F) and integrated heat flow (J/g) should be calculated for the first three tests. If more than one peak is present, the temperature and heat flow associated with the warmer peak should be reported. The coefficient of variation (CoV) should also be reported for the heat flow. The CoV is a measure of data dispersion and is equal to the ratio of the standard deviation to the mean. A low CoV—i.e., close to zero—indicates the three test samples had similar peak heat flows. A high CoV (closer to 100 percent) indicates greater variability in the measurements. On the basis of experimental trials, we determined the following criteria for data acceptance: if the CoV for the heat flow is greater than 10 percent or the standard deviation for the characteristic temperature is greater than 0.5°F, then additional tests should be performed. The computations for average, standard deviation, and CoV should be based on the results of a minimum of three tests. The computations for the 23% NaCl, 32% $CaCl_2$, and 30% $MgCl_2$ for various combinations of test runs is presented in Table 9. The 32% $CaCl_2$ deicer needed to be tested four times to meet the criteria for acceptable variation. The 30% $MgCl_2$ deicer needed to be tested five times, whereas 23% NaCl only needed three tests to be conducted.

Table 8. DSC test results for individual tests of 23% NaCl, 32% $CaCl_2$, and 30% $MgCl_2$

Deicer and Run #	Heat Flow (J/g)	Peak Temperature (°F)
23% NaCl, run 1	164.6	21.72
23% NaCl, run 2	163.2	21.85
23% NaCl, run 3	166.8	21.86
32% $CaCl_2$, run 1	125.3	16.56
32% $CaCl_2$, run 2	129.6	16.20
32% $CaCl_2$, run 3	80.42	15.49
32% $CaCl_2$, run 4	107.9	15.74
30% $MgCl_2$, run 1	83.46	12.00
30% $MgCl_2$, run 2	69.26	7.70
30% $MgCl_2$, run 3	71.58	8.53
30% $MgCl_2$, run 4	77.70	8.82
30% $MgCl_2$, run 5	72.16	8.02

Table 9. Variation of DSC testing for liquid deicers

Deicer	Run #s used in calculations	Heat Flow Average (J/g)	Heat Flow Standard Deviation (J/g)	Heat Flow Coefficient of Variation (%)	Peak Temperature Average (°F)	Peak Temperature Standard Deviation (°F)
23% NaCl	1, 2, 3	165	1.8	1.1	21.8	0.078
32% $CaCl_2$	1, 2, 3	112	27	24	16.1	0.54
32% $CaCl_2$	1, 2, 3, 4	111	22	20	16.0	0.48
32% $CaCl_2$	1, 2, 4	121	11	9.5	16.2	0.41
30% $MgCl_2$	1, 2, 3	74.8	7.6	10	9.41	2.3
30% $MgCl_2$	2, 3, 4	72.8	4.4	6.0	8.35	0.58
30% $MgCl_2$	2, 3, 4, 5	72.7	3.6	4.9	8.27	0.50
30% $MgCl_2$	3, 4, 5	73.8	3.4	4.6	8.46	0.40

DSC provides two opportunities for data interpretation and application that DOTs can utilize. Primarily, the first peak temperature at the high temperature end of the warming cycle is defined as the *characteristic temperature* of the deicer. The characteristic temperature for a deicer can be compared to that of sodium chloride and thus indicates its effective temperature range relative to sodium chloride. Furthermore, as will be shown later, a strong correlation between the DSC data (the characteristic temperature and the heat flow) and the Modified SHRP Ice Melting test data can be developed. This provides another opportunity to utilize the DSC test results, that is, to predict the performance of a chloride-based deicer in the ice melting test.

DSC tests were performed for another concurrent research project at the Western Transportation Institute that involved a larger variety of deicers, including acetate- and formate-based products. Figure 9 shows the DSC thermograms for the NaCl-based, $MgCl_2$-based, acetate- and formate-based, and agriculture by-product-based deicers. The reagent NaCl in Figure 9A compares well to the NaCl deicer provided by Illinois DOT. IceSlicer is a mined rock salt consisting of naturally occurring complex chlorides, though chiefly NaCl, with more than 40 trace minerals. Two $MgCl_2$ based deicers were tested; one is a 27–29% $MgCl_2$ liquid used by Colorado DOT and the other is Meltdown Apex, a 29–30% $MgCl_2$ commercial liquid deicer available from EnviroTech Services (Greeley, Colorado). Several acetate- and formate-based deicers were tested: CF7, Peak SF, NAAC, NAAC–Peak SF, and CMA. CF7 is a corrosion-inhibited 50% potassium-acetate-based liquid deicer available from Cryotech (Fort Madison, Iowa). Peak SF is a corrosion-inhibited granular sodium-formate-based deicer available from The Blackfoot Company (Toledo, Ohio). NAAC is a commercial anhydrous grade granular sodium-acetate-based deicer available from Cryotech. The sodium acetate–sodium formate blend was made from a mixture of half NAAC and half Peak SF. CMA is a commercial granular calcium-magnesium-acetate deicer available from Cryotech. The last group is deicers with agriculture by-products. Ice Ban is available from Earth Friendly Chemicals, but was given directly to WTI from Colorado DOT's stockpile; the deicer contains $MgCl_2$. Geomelt C is from America West (Pasco, Washington) and contains $CaCl_2$. Geomelt 55 is from SNI Solutions (Geneseo, Illinois).

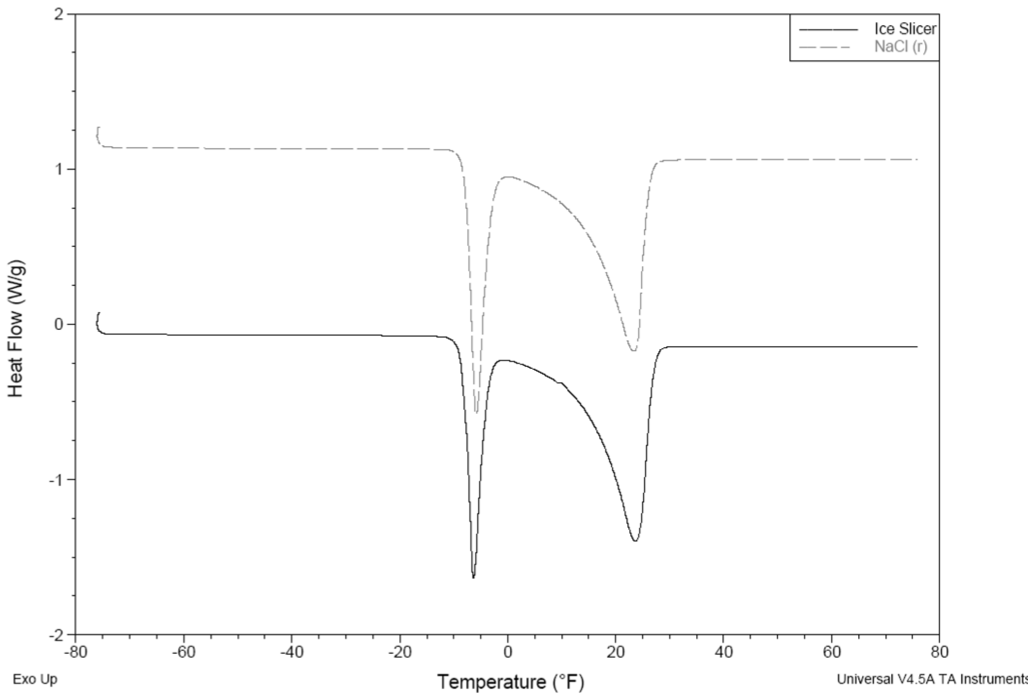

Figure 9A: Sodium-chloride-based deicers

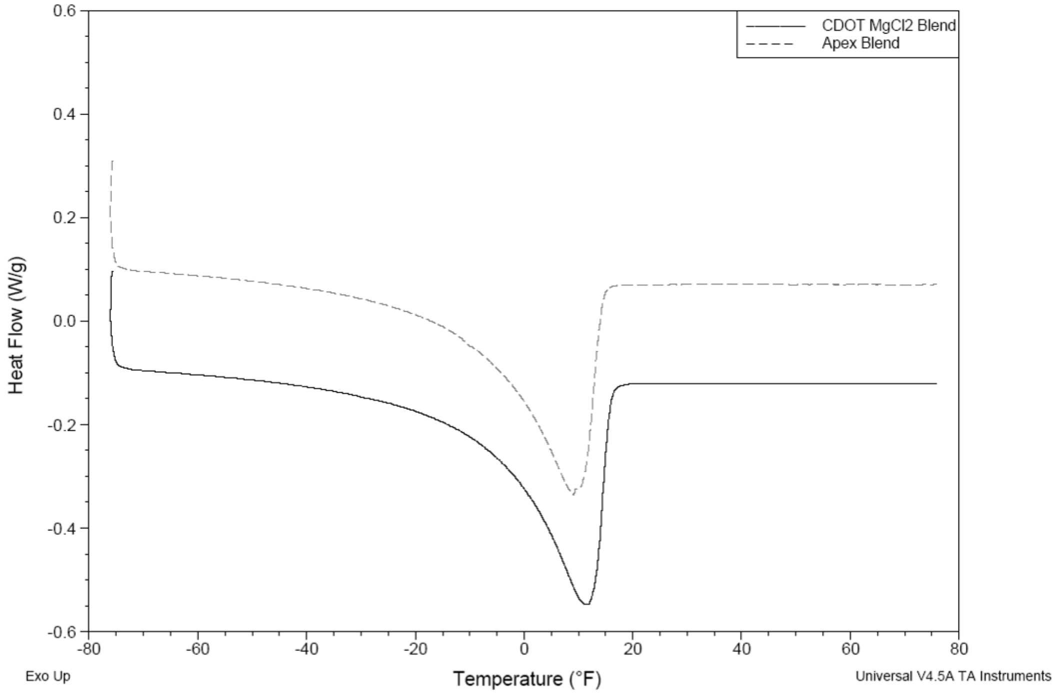

Figure 9B: Magnesium-chloride-based deicers

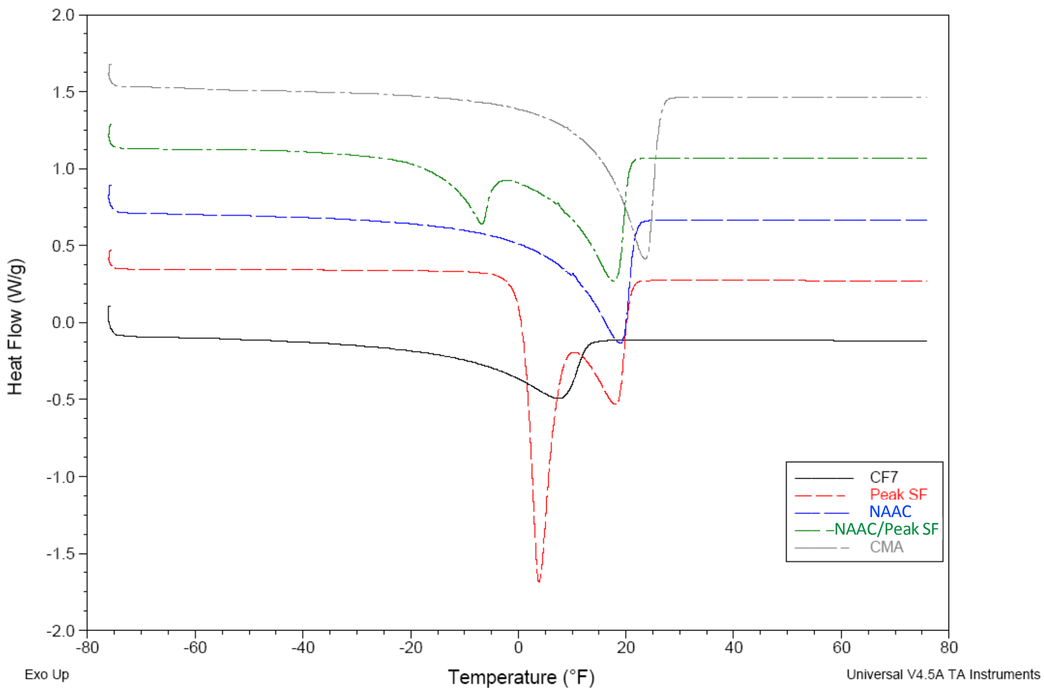

Figure 9C: Acetate- and formate-based deicers

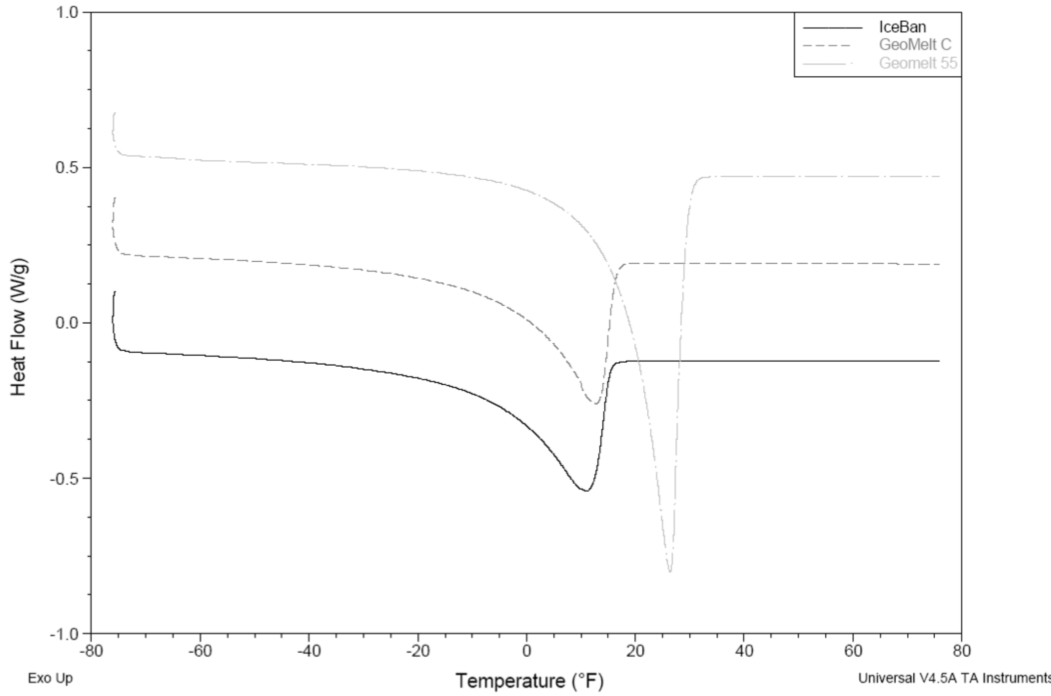

Figure 9D: Agriculture by-product based deicers

Figure 9: DSC thermograms grouped by deicer type

4.4. Modified SHRP Ice Melting Test

Development

The Ice Melting Test published in the SHRP *Handbook* requires a custom-built, 9-in.-diameter Plexiglas apparatus and, generally, two tests are conducted simultaneously. However, the SHRP protocol recommends three replicates be tested, which requires the process to be repeated. This can introduce undesirable error. It is preferable to conduct more replicates at one time to get a better average. Two fundamental changes to the SHRP Ice Melting Test were investigated: 1) using readily available, sterile, disposable laboratory Petri dishes with removable cover, and 2) conducting four simultaneous tests, of which three tests use the test deicer and one uses 23% NaCl solution as a control. Petri dishes with 3.356 in. diameter (standard 100 mm x 15 mm size) were purchased from Fisher Scientific (Figure 10). This change led to other changes in the test conditions, including ice dimensions and deicer application rate (Table 10). These changes ultimately reduce the volume of brine generated during the test and allow more tests to be conducted simultaneously. It was hoped that additional tests conducted at the same time would improve the repeatability. The control dish with 23% NaCl serves three purposes: 1) it allows the test deicer to be directly compared to a familiar product; 2) provides an indication of whether the test was successful—i.e., if the amount of brine collected in the control dish is not within a certain range, then the entire test needs to be repeated; and 3) if necessary, it can provide the ice melting capacity of a deicer in a relative (vs. absolute) term, which cancels out the possible interference of other uncontrolled experimental factors.

Table 10. Comparison of SHRP and Modified SHRP Ice Melting Test Conditions

	SHRP Ice Melting Test	Modified SHRP Ice Melting Test
Dish Diameter (in.)	9.0	3.356*
Water Volume (mL)	130	25
Ice Thickness (in.)	9/64 (0.14)	12/64 (0.19)
Solid Deicer		
Amount (g)	4.17	1.0
Equivalent Field Application (lb/lane·mile)	1320	2270
Liquid Deicer		
Amount (mL)	3.8	0.9
Equivalent Field Rate (gal/lane·mile)	144	245
Number of Concurrent Replicates	2	3
Number of "Control" Specimens	0	1

*while 3.356 in. may appear to be an odd size, it is the size of standard 100 mm x 15 mm Petri dishes

The application rate of the Modified SHRP Ice Melting Test is higher than typical field application rates. However, the test procedure does not incorporate traffic, mixing action, ultraviolet radiation and other parameters that likely improve the performance of deicers in the field. Additionally, even at warmer temperatures only a fraction of the ice melted in the presence of deicers—less than 6 mL of the 25 mL total water in the Petri dish.

All ice melting tests were conducted in a Plexiglas chamber in a 12 ft. x 14 ft. temperature-regulated chamber using deionized water. Ice did not readily form when the chamber was near 30°F, likely attributable to small vibrations in the table induced by the large cooling fans, slight temperature variations, and the purity of (and lack of nucleating agent in) deionized water. Once the water chilled to the test temperature, the addition of a small flake of ice caused the crystallization process to begin. This process was termed "seeding" and was not necessary at colder temperatures. As specified in the SHRP *Handbook*, the ice surface was melted with a metal plate and the dish was gently swirled to create a uniform and flat ice sample.

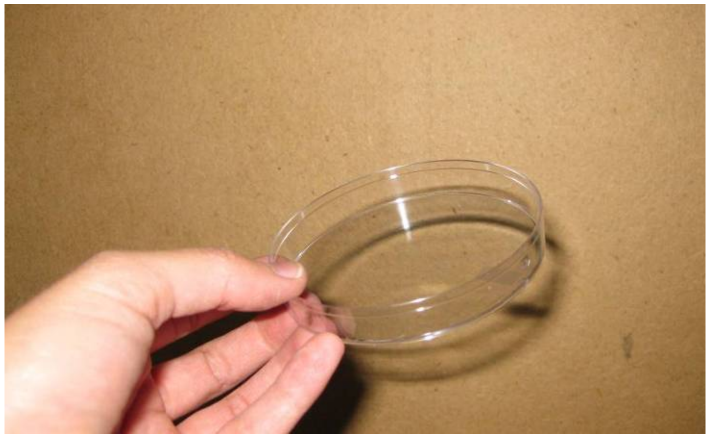

Figure 10: Petri dish used in Modified SHRP Ice Melting Test

Results

The Modified SHRP Ice Melting Test was conducted with fine particles of reagent-grade NaCl, $CaCl_2$, and $MgCl_2$ and liquid 23% NaCl, 32% $CaCl_2$, and 30% $MgCl_2$ deicers at 30°F, 15°F, and 0°F. Variability of the results of the test procedure was assessed both among the measurements collected within a test and between tests conducted on different days. At 10, 20, 30, 45 and 60 minutes after the deicer was applied to the ice samples, the liquid brine was collected by a syringe and the volume was recorded. After the brine volume was measured it was reapplied to the ice sample. Thus, the test provides ice melting over time for the test deicer and the control (a 23% NaCl solution—even when the test deicer is a solid). The test is considered successful if the brine volume collected in the control dish with 23% NaCl after 60 minutes is within the range specified in Table 11. The average brine volumes and CoV should be reported for the test deicer. However, low mean volumes of brine can artificially yield higher CoV values and the CoV is mathematically undefined when the sample mean is equal to zero. Thus, for all cases in which the average brine volume is less than 1.0 mL, the standard deviation should be reported instead of CoV.

Table 11. Acceptable Range of Control in Modified SHRP Ice Melting Test

Temperature (°F)	Volume of brine at 60 minutes (mL)
30	3.1 to 4.0
15	0.8 to 1.2
0	0.1 to 0.5

The average volume of brine collected using fine particles of reagent-grade NaCl, $CaCl_2$, and $MgCl_2$ at 30°F is shown in Table 12. The liquid $CaCl_2$ and $MgCl_2$ melted more ice than liquid NaCl during the test; this is partially attributable to the lower concentration of NaCl in the aqueous form. At 30°F, solid NaCl ultimately produced as much brine as solid $CaCl_2$ at 60 minutes, but showed lower brine volumes during earlier portions of the test. Our phone interview with a deicer manufacturer that conducts extensive SHRP Ice Melting tests each year revealed an interesting practice by the manufacturer. Specifically, the modified SHRP protocol implemented by the manufacturer only requires brine volumes be measured after 20 minutes of exposure to solid deicers and only after 60 minutes of exposure to liquid deicers. As shown in the highlighted section of Table 12, if we adopted this modification for the solids, NaCl would feature less ice melting capacity than CaCl2 and MgCl2. This illustrates that ice melting by deicers is a dynamic, time-sensitive process. To provide insights that could guide the field practice, we argue that both ice melting capacity at 20 and 60 minutes should be considered useful data to be collected. A graphical view of the volume of brine collected after 60 minutes at 30°F is shown in Figure 11.

Table 12. Modified SHRP Ice Melting Test Data at 30°F

Test Deicer	Average Volume of Brine Collected (mL)					Measurement of Variation: CoV (%) if average ≥ 1.0 mL Std Dev. (mL) if average < 1.0 mL				
	10	20	30	45	60	10	20	30	45	60
23% NaCl	1.9	2.4	2.8	3.2	3.6	5	0	4	3	3
23% NaCl	1.9	2.4	2.7	3.2	3.4	0	4	4	3	6
23% NaCl	2.1	2.7	3.1	3.4	3.5	5	4	6	3	0
32% $CaCl_2$	2.3	2.8	3.1	3.7	4.0	4	7	3	0	5
32% $CaCl_2$	2.4	2.9	3.3	3.7	4.0	0	3	3	5	5
32% $CaCl_2$	2.3	2.7	3.1	3.3	4.1	4	11	6	6	2
30% $MgCl_2$	2.6	3.2	3.7	4.2	4.7	8	3	14	2	6
30% $MgCl_2$	2.5	3.0	3.4	3.8	4.1	4	3	0	3	2
30% $MgCl_2$	2.5	3.0	3.4	3.9	4.3	0	3	3	3	2
NaCl (s)	1.0	1.8	2.6	3.7	5.3	20	14	13	16	15
$CaCl_2$ (s)	2.0	2.7	3.5	4.2	5.3	9	4	5	7	8
$MgCl_2$ (s)	2.7	3.5	4.0	4.5	4.9	4	4	6	7	4

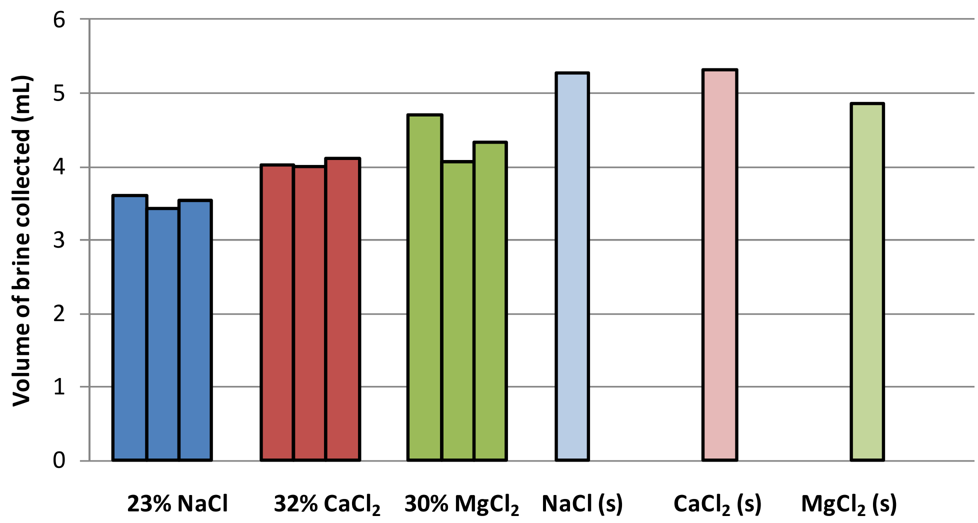

Figure 11: Modified SHRP Ice Melting Test results at 60 minutes at 30°F

The Modified SHRP Ice Melting Test was also conducted at 15°F; the data for the duration of the tests are shown in Table 13 and the 60-minute performance is shown in Figure 12. Similar to the scenario at 30°F, at 15°F the liquid $CaCl_2$ and $MgCl_2$ melted more ice than liquid NaCl during the test; this is partially attributable to the lower concentration of NaCl in the aqueous form.

Table 13. Modified SHRP Ice Melting Test Data at 15°F

Test Deicer	Average Volume of Brine Collected (mL)					Measurement of Variation: CoV (%) if average ≥ 1.0 mL Std Dev. (mL) if average < 1.0 mL				
	10	20	30	45	60	10	20	30	45	60
23% NaCl	1.0	1.1	1.1	1.1	1.1	10	9	9	9	9
23% NaCl	1.2	1.2	1.2	1.2	1.2	8	8	8	8	17
32% $CaCl_2$	1.5	1.5	1.6	1.6	1.6	7	13	13	13	6
32% $CaCl_2$	1.7	1.8	1.8	1.7	1.6	6	6	6	6	6
30% $MgCl_2$	1.7	1.9	2.0	2.0	2.0	12	11	10	10	10
30% $MgCl_2$	1.7	1.8	1.8	1.8	1.6	12	11	6	11	13
NaCl (s)	1.1	1.7	2.4	2.8	3.2	9	12	17	11	6
NaCl (s)	1.5	1.9	2.2	3.2	3.5	20	11	14	6	9
$CaCl_2$ (s)	2.2	2.5	2.7	2.9	3.0	9	8	4	7	3
$CaCl_2$ (s)	2.8	3.1	3.2	3.1	3.2	7	10	6	3	6
$MgCl_2$ (s)	2.2	2.4	2.4	2.5	2.5	9	0	8	4	4
$MgCl_2$ (s)	2.1	2.4	2.5	2.5	2.5	5	0	4	4	8

Note: for the same deicer the average volume of brine collected over time may remain the same or even decrease as a result of dilution and possibly refreezing.

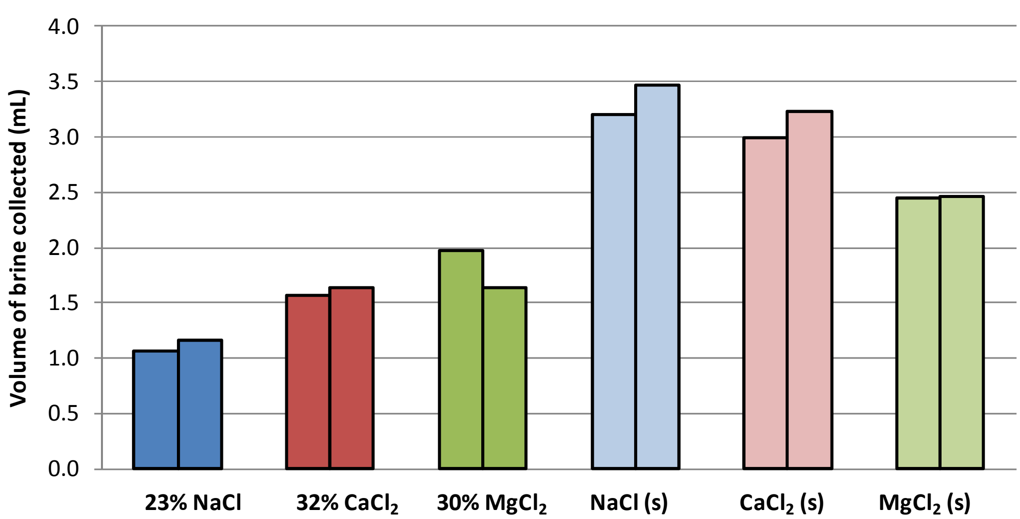

Figure 12: Modified SHRP Ice Melting Test results at 60 minutes at 15°F

It is interesting to note that solid NaCl melted more ice than solid $CaCl_2$ and $MgCl_2$ after 60 minutes, which was further experimentally confirmed. However, a comparison of brine volumes after 20 minutes shows solid NaCl melted less ice than $CaCl_2$ and MgCl2, which is more consistent with behavior in the field. The deicer particle gradation could be a contributing factor for this behavior. While the solid reagent-grade salts tested during this portion of the project had very similar gradations, they were considerably finer than commercial solid deicer products. Considering the critical role of deicer/ice interface in the ice melting process, the particle size of solid deicer can significantly affect how fast or slow the ice melts in the presence of the deicer. The practice followed by the manufacturer we interviewed is recommended for widespread application; that is, when the test is for the evaluation of commercial solid deicers, only the material that passes the Number 6 sieve and is retained on the Number 8 sieve should be used for the ice melting test, which corresponds to particle sizes greater than 0.09 inches (2.3 mm) and less than 0.13 inches (3.3 mm).

Table 14. Modified SHRP Ice Melting Test Data at 0°F

Test Deicer	Average Volume of Brine Collected (mL)					Measurement of Variation: CoV (%) if average ≥ 1.0 mL Std Dev. (mL) if average < 1.0 mL				
	10	20	30	45	60	10	20	30	45	60
23% NaCl	0.5	0.6	0.5	0.4	0.3	0.1	0.1	0.1	0.1	0.2
32% $CaCl_2$	1.0	0.9	0.8	0.8	0.8	10	0.1	0.1	0.1	0.2
30% $MgCl_2$	1.2	1.0	1.0	1.2	1.1	17	0.	20	25	18
NaCl (s)	0.0	0.1	0.3	0.3	0.6	0	0.1	0.2	0.2	0.2
$CaCl_2$ (s)	1.7	2.1	2.1	2.2	2.1	0	5	14	18	10
$MgCl_2$ (s)	1.6	1.6	1.7	1.6	1.7	0	13	6	13	6

Note: for the same deicer the average volume of brine collected over time may remain the same or even decrease as a result of dilution and possibly refreezing.

Finally, the Modified SHRP Ice Melting Test was also conducted at 0°F; the data are shown in Table 14. At 0°F, the liquid deicers melt very little ice. Recall, at the initiation of the test, 0.9 mL of liquid deicer is applied to the ice. Both 23% NaCl and 32% $CaCl_2$ tended to freeze or refreeze as the test progressed. This occurs because the freezing point of the solution is reduced as the concentration decreases. With 23% NaCl, the solution either started to freeze immediately, or it melted a small amount of ice but became too dilute to remain a liquid at 0°F. As the test progressed, the deicer continued to slowly freeze. The amounts of brine collected with the 30% $MgCl_2$ test were also small, but because they were greater than 0.9 mL some ice was melted. Solid $CaCl_2$ and solid $MgCl_2$ both melted significantly more ice than solid NaCl at this temperature.

Within-Test Variance The CoV or standard deviation should always be reported with the average brine volumes in order to assess within-test variance. The CoV and standard deviation values in Tables 12–14 show the variation among the three dishes with the test deicer during a particular test. Most CoV values were less than 15 percent. When standard deviation is reported instead of CoV (because the average brine volume is less than 1.0 mL), values less than 0.20 mL are generally attainable. Thus, to improve the level of satisfaction with the Modified SHRP Ice Melting Test, tests that do not meet these criteria for variation should be repeated.

Between-Test Variance Several respondents to the survey (Chapter 3) indicated the SHRP tests lacked repeatability. Often more than one test was conducted on separate days; this allows a comparison of between-test variance. Multiple tests on liquid deicers at 30°F had CoV values from 1.4 to 7.3 percent. This is within the same order of magnitude of CoV values within any particular test—thus, the Modified SHRP Ice Melting Test was repeatable with liquid deicers at 30°F. The between-test CoV values at 15°F were less than 15 percent with only three exceptions: solid NaCl at 10 minutes and solid $CaCl_2$ at 10 and 20 minutes. Thus, with few exceptions, the Modified SHRP Ice Melting Test was also repeatable at 15°F.

A Note of Caution We should take results of the Modified SHRP Ice Melting Test with "a grain of salt" when trying to predict the relative field performance of these deicers. The mixing action and fate/transport of deicers in the field is complicated by factors of traffic, UV absorption, gradation and angularity of deicer particles, moisture content and density of snow, pavement type and condition, wind, relative humidity, and possibly other factors. Additionally, the Modified SHRP Ice Melting Test mimics deicing practices more than anti-icing practices, i.e., test does not predict the ability to which liquid products prevent a bond between ice and pavement. The practice of prewetting solid deicers with liquid products could be incorporated by applying a 1.0 g sample of the prewet deicer to the ice specimen.

Recommended Implementation This report provides detailed results of ice melting over time for liquid and solid deicers, but this amount of detail is not likely needed in a specification test. Thus, the Modified SHRP Ice Melting Test should be implemented for liquid and solid deicers with brine volumes collected at only 20 and 60 minutes after application. Furthermore, brine volumes should only be reported to the nearest tenth mL, CoV to the nearest percent, and standard deviation to the nearest tenth mL to discourage inappropriate comparisons determined from this test method.

Relationship between DSC and Modified SHRP Ice Melting Test Data

DSC instruments are widely available in materials laboratories, but the equipment needed to perform the modified SHRP Ice Melting Test can be more difficult to acquire—requiring an expensive walk-in cold room or alterations to an upright freezer. Empirical relationships relating DSC data to performance as measured by Modified SHRP Ice Melting Tests were developed.

The DSC data used in the analyses were 1) the characteristic temperature (T_c) and 2) the heat flow (H) associated with the warming cycle. The heat flow (units J/g) was subtracted from the total heat of fusion of deionized water (345 J/g) to provide ΔH. The logarithmic values of ΔH were used in the correlations, since ΔH is an energy term. In all cases, the average T_c and average H from at least three tests were used. The Modified SHRP Ice Melting Test data were the volumes of brine collected throughout the test at the various temperatures ($IMC_{30°F}$, $IMC_{15°F}$, and $IMC_{0°F}$).

Tests conducted while developing the DSC protocol and the Modified SHRP Ice Melting Test protocol only involved pure solutions of NaCl, $CaCl_2$, and $MgCl_2$. However, more deicers are needed to establish a credible relationship. Thus, seven blends were created involving NaCl, $CaCl_2$, and AGBP (an agricultural by-product based anti-icing product, presented anonymously in this report). Several correlation equations were developed to investigate an appropriate relationship. The coefficient of determination (R^2 value) of a regression equation indicates the ability of the equation to predict the outcome of a given set of inputs. An R^2 value close to unity indicates the data fits the correlation equation very well.

The three correlation equations are presented below, one for each temperature. The equations for 30°F and 15°F use data from the tests on pure NaCl, $CaCl_2$, and $MgCl_2$ in addition to the seven blended deicers. The Modified SHRP Ice Melting Test was not performed at 0°F with the blended deicers. Therefore the third equation is based on fewer data points. The equations are valid for chloride-based deicers. Thus blends involving chlorides and an agriculture by-product additive are okay, but the equations should not be used for pure agriculture by-products without verification.

$$IMC_{30^\circ\mathrm{F}}\,(\text{mL brine}) = -0.02265T_c + 1.965\log(\Delta H) + 0.03285t - 2.1761 \quad (\mathrm{R}^2 = 0.94) \tag{1}$$

$$IMC_{15^\circ\mathrm{F}}\,(\text{mL brine}) = -0.08667T_c - 2.651\log(\Delta H) - 0.000716t + 9.114 \quad (\mathrm{R}^2 = 0.80) \tag{2}$$

$$IMC_{0^\circ\mathrm{F}}\,(\text{mL brine}) = 0.03869T_c + 6.494\log(\Delta H) - 0.00281t - 14.937 \quad (\mathrm{R}^2 = 0.93) \tag{3}$$

Where:

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

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

T_c = characteristic temperature on warming cycle from DSC (°F)

t = time between 10 and 60 (minutes)

4.5. Modified SHRP Ice Penetration Test

Development

The Ice Penetration Test published in the SHRP *Handbook* requires a custom-built Plexiglas apparatus with holes drilled to form cavities (Figure 13). An alternative off-the-shelf apparatus reasonably consistent with the apparatus specified in the SHRP *Handbook* was not identified. The dye specified in the SHRP *Handbook* was not readily available; thus food coloring (McCormick brand, red color) was tried. For liquid deicers, a dyed solution was prepared by mixing 25 mL of liquid deicer with two drops (~0.1 mL) of red food coloring. We conducted an ice penetration test using just the dye (standard 30µL application) and found penetration behavior to be similar to a 23% NaCl salt brine solution. However, for each ice penetration test using dyed deicers, 30µL is applied, of which only 0.12µL is dye—an amount assumed to be negligible. For solid deicers, three pinhead-size drops were placed on the ice surface of each cavity. Non-dyed ice was also tested to determine the potential ice-melting contribution introduced by the dye, which contains propylene glycol. Often the penetration depth of dyed solutions was difficult to visually assess. When this occurred a small metal probe was inserted in the cavity until it contacted the ice interface to determine penetration depth. The probe was maintained at the test temperature and did not contribute to any penetration or melting.

Figure 13: SHRP Ice Penetration Test apparatus

Results

The procedure for the Modified SHRP Ice Penetration Test is essentially the same as SHRP 205.3 and 205.4, except that dye is not added to the surface of the ice when testing solid deicers. Instead, penetration depth is determined by inserting a small, cold metal tool to determine penetration depth. The Modified SHRP Ice Penetration Test was assessed for variability both among the measurements collected within a single test involving five replicate specimens and between separate tests. The tests were conducted with solid NaCl, $CaCl_2$, and $MgCl_2$ deicers and dyed liquid 23% NaCl, 32% $CaCl_2$, and 30% $MgCl_2$ deicers at 30°F, 15°F, and 0°F. SHRP 205.3 specifies single deicer pellets weighing 22 to 27 mg should be used. The reagent chemicals tested for this project were smaller than commercial products and many grains were needed to maintain the same deicer mass. The SHRP-specified volume of 30µL was used to test liquid deicers. At 10, 20, 30, 45 and 60 minutes after the deicer was applied to the ice samples, the penetration depth was measured in millimeters. Thus, the test provides ice penetration over time for the deicer of interest and there is no control analogous to the 23% NaCl control used in the Modified SHRP Ice Melting Test.

Table 15. Modified SHRP Ice Penetration Test Data (with five replicates) at 30°F

Test Deicer	Average Depth of Penetration for 5 replicates (mm)					Coefficient of Variation of Penetration Depth for 5 replicates (%)				
	10	20	30	45	60	10	20	30	45	60
23% NaCl	2.2	3.9	5.3	8.0	9.7	47	17	18	9	12
23% NaCl	1.9	2.0	2.7	2.8	3.0	12	0	17	20	22
23% NaCl	2.1	2.6	2.8	3.7	4.3	26	32	37	37	29
32% $CaCl_2$	2.2	4.2	5.8	8.8	10.7	12	11	16	15	14
32% $CaCl_2$	2.0	3.3	4.8	6.7	7.9	27	45	38	27	22
32% $CaCl_2$	2.2	3.1	5.4	7.5	8.5	16	14	23	17	14
30% $MgCl_2$	1.5	2.1	3.0	3.2	3.8	39	21	31	21	25
30% $MgCl_2$	1.3	2.0	2.6	3.2	4.1	17	22	21	28	25
30% $MgCl_2$	1.7	5.0	6.2	8.2	9.9	16	43	38	28	16
NaCl (s)	6.6	11.3	13.5	15.8	19.1	8	22	20	15	20
NaCl (s)	5.9	8.6	11.2	17.4	19.5	7	10	16	11	9
$CaCl_2$ (s)	4.5	5.8	7.8	9.0	10.4	26	18	7	5	5
$CaCl_2$ (s)	5.1	6.5	7.3	8.5	9.6	14	12	9	11	10
$MgCl_2$ (s)	2.5	3.0	4.0	5.9	8.2	15	29	27	45	40
$MgCl_2$ (s)	3.6	4.9	5.8	7.0	8.0	23	15	18	20	23

The Modified SHRP Ice Penetration Test results for solid and liquid NaCl, $CaCl_2$, and $MgCl_2$ at 30°F are shown in Table 15. Overall, the CoV values for the Modified SHRP Ice Penetration Test are higher than the Modified SHRP Ice Melting Test. The maximum CoV value for the 30°F penetration tests is over twice as high as the highest CoV for the melting tests (47 compared to 19). Furthermore, the average CoV value for the penetration tests is nearly four times higher than the average CoV value for the melting tests. Because the penetration tests involve five replicate specimens conducted side-by-side during a test, the maximum and minimum penetration depths could be ignored and the average penetration depth could still be calculated with the remaining three values. Table 16 shows the average and CoV of the penetration depth data when the maximum and minimum values are ignored. By ignoring these two values, the within-test variability is greatly improved; the highest CoV value reduced from 47 percent to 36 percent and the average CoV dropped from 21 percent to 10 percent. This modification only affected the average of the average penetration depths by 0.01 mm. Thus, ignoring the maximum and minimum penetration depths improves the within-test variability without skewing the reported penetration depth.

Table 16. Modified SHRP Ice Penetration Test Data (without max and min values) at 30°F

Test Deicer	Modified Average Depth of Penetration for 5 replicates (mm)					Modified Coefficient of Variation of Penetration Depth for 5 replicates (%)				
	10	20	30	45	60	10	20	30	45	60
23% NaCl	1.8	4.0	5.0	8.0	9.5	16	13	0	0	5
23% NaCl	2.0	2.0	2.8	3.0	2.9	0	0	10	17	6
23% NaCl	2.0	2.3	2.5	3.3	4.0	0	12	20	9	0
32% $CaCl_2$	2.2	4.3	5.8	9.2	10.8	13	7	5	3	7
32% $CaCl_2$	2.2	2.9	4.6	6.5	7.9	7	11	14	6	7
32% $CaCl_2$	2.3	3.1	5.2	7.5	8.1	7	11	16	8	5
30% $MgCl_2$	1.5	2.1	2.8	3.2	4.0	33	11	12	2	13
30% $MgCl_2$	1.3	1.9	2.6	3.2	4.1	13	14	20	9	12
30% $MgCl_2$	1.7	5.4	6.5	9.0	9.8	17	31	30	8	16
NaCl (s)	6.4	11.9	14.1	15.7	18.8	3	10	6	6	15
NaCl (s)	5.8	8.3	11.3	17.5	19.8	5	7	13	9	5
$CaCl_2$ (s)	4.7	5.9	7.6	9.0	10.3	12	17	3	3	3
$CaCl_2$ (s)	5.1	6.5	7.2	8.6	9.6	11	12	5	2	1
$MgCl_2$ (s)	2.4	2.7	4.0	6.1	8.3	2	11	6	36	35
$MgCl_2$ (s)	3.3	4.8	5.5	6.8	7.8	9	6	9	11	16

Figure 14 shows the penetration depth after 60 minutes and illustrates the high variability between tests of liquid deicers. This is counter-intuitive in that liquid deicers were expected to show more consistent penetration depths because of the uniform distribution of the deicer on the small ice surface. However, ice crystallization is complex and the penetration depth was often not a distinct horizontal interface, rather, the deicer penetrated down indiscernible veins within the ice and the maximum depth was recorded. More tests would need to be conducted with liquid deicers to better assess the variability between tests.

Generally, more penetration was observed with the solid deicers than liquid products but the difference is not significant in the case of $CaCl_2$ and MgCl2. This is explained by at least two mechanisms at work. On the one hand, for the same type of deicers (NaCl, CaCl2, or MgCl2), relative to the liquid deicer, more chemical is present in the solid form and thus should provide more ice melting capability. On the other hand, while the liquid deicers had full contact with the ice layer, the solids had less contact area at the deicer/ice interface. The SHRP protocol calls for a single deicer pellet to be tested with a mass between 22 and 27 mg. However, because reagent-grade salts were used for the testing of solid products, a total mass between 22 and 27 mg was weighed, but required many fine particles instead of a single pellet. For the solid deicers at 30°F, NaCl penetrated significantly more than MgCl2 and CaCl2. It should be noted that the ice penetration test does not have any element to simulate the mixing action provided by the traffic in the field scenarios (which significantly improves the contact area between deicer and ice). As such, its value to provide any insight to guide field practice is very limited, let alone the inherently high variability of its test results.

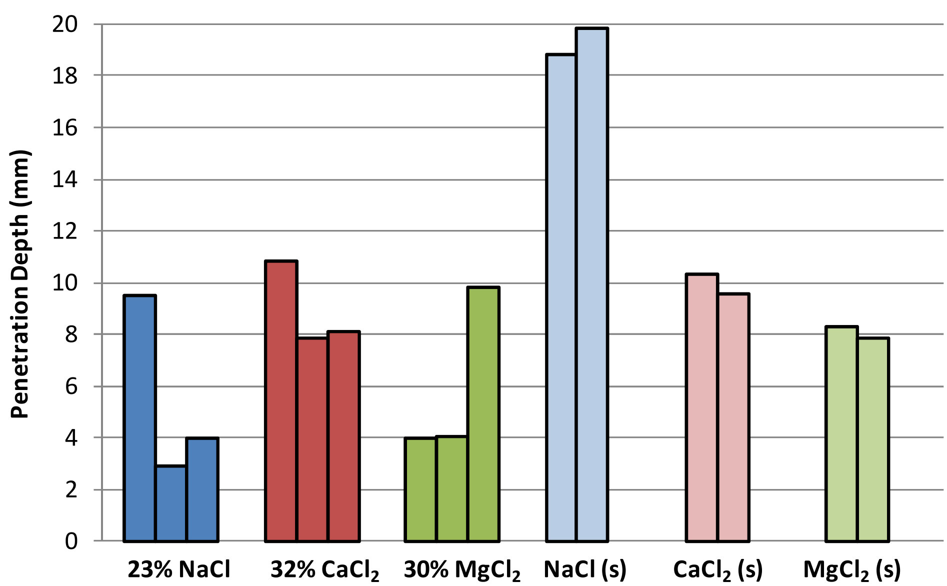

Figure 14: Modified SHRP Ice Penetration Test results at 60 minutes at 30˚F

The data for the Modified SHRP Ice Penetration Test conducted at 15°F with solid and liquid NaCl, $CaCl_2$, and $MgCl_2$ are presented in Table 17 with the modified data analysis method in which the maximum and minimum penetration depths are not used to calculate average penetration depth. Once again, the maximum and average CoV values are reduced when the average penetration depth is computed without including the maximum and minimum penetration depths. The maximum CoV value reduced from 52 percent to 39 percent and the average CoV value reduced from 22 percent to 12 percent. This modification only affected the average of the average penetration depths by 0.02 mm.

Table 17. Modified SHRP Ice Penetration Test Data (without max and min values) at 15°F

Test Deicer	Modified Average Depth of Penetration for 5 replicates (mm)					Modified Coefficient of Variation of Penetration Depth for 5 replicates (%)				
	10	20	30	45	60	10	20	30	45	60
23% NaCl	0.7	0.8	0.8	0.9	1.0	23	12	7	6	6
23% NaCl	0.4	0.5	0.6	0.6	0.6	35	11	10	10	24
32% $CaCl_2$	0.8	0.9	1.0	1.0	1.1	18	16	24	24	20
32% $CaCl_2$	0.5	0.8	0.9	1.0	1.0	0	0	13	6	6
30% $MgCl_2$	1.0	1.5	1.8	2.0	2.0	0	0	14	0	0
30% $MgCl_2$	1.0	1.0	1.5	1.8	1.7	39	0	33	16	17
30% $MgCl_2$	0.4	0.8	1.0	1.0	1.2	27	33	0	0	5
NaCl (s)	3.0	3.8	4.0	3.7	4.7	0	8	0	16	12
NaCl (s)	3.7	4.4	5.0	5.6	5.9	8	12	10	13	17
NaCl (s)	3.4	4.4	5.1	5.3	5.8	24	3	6	5	18
$CaCl_2$ (s)	1.2	1.8	2.0	2.0	2.0	25	16	0	0	0
$CaCl_2$ (s)	2.5	3.3	3.6	3.9	4.2	5	8	18	13	15
$CaCl_2$ (s)	2.7	2.8	2.9	3.3	3.6	25	20	26	20	18
$MgCl_2$ (s)	2.2	2.5	2.6	2.8	2.9	5	2	6	8	7
$MgCl_2$ (s)	2.5	2.8	3.1	3.2	3.4	12	10	3	5	3
$MgCl_2$ (s)	1.9	2.0	2.3	2.3	2.7	6	0	20	20	9

The penetration depths were very small for liquid deicers—less than 2 mm after 60 minutes of exposure to deicers—however, this is not surprising as liquid chemicals are not recommended for deicing applications, especially at low temperatures. Again, there was more variability in the penetration depth for liquid deicers than solids. In general, the Modified SHRP Ice Penetration Test was repeatable for solid deicers, although the CoV between tests with solid $CaCl_2$ was twice as high as for the NaCl and MgCl2 deicers.

Unexpectedly, the ice penetration depths of solid NaCl at 15°F were generally greater than that of solid $MgCl_2$ or solid CaCl2, as shown in Table 17. To confirm this trend, another round of ice penetration test of these solids (grounded to the same fine gradation) was conducted. The final average penetration depth (after 60 minutes of exposure at 15°F) for solid NaCl, CaCl2 and MgCl2 was 4.2 mm, 3.0 mm, and 2.5 mm respectively, which confirms the unusually outstanding performance of the fine particles of NaCl. We would expect different results if a single deicer pellet (vs. fine particles) was tested, although this could also be problematic. Shi et al. (2009) discovered that often a single pellet would become lodged in the ice penetration apparatus and penetration below the lodged particle would only occur if sufficient brine was generated to promote additional penetration (which was not the case at colder temperatures) and led to reproducibility issues regardless.

The Modified SHRP Ice Penetration Test was also conducted at 0°F with both solid and liquid deicers (Table 18). However, the liquid deicers exhibited very low penetrating ability and the low penetration depths contribute to the higher CoV values. For both liquids and solids at this lowest temperature, NaCl penetrated more ice than $MgCl_2$, which contradicts the field experience and the findings from the Modified SHRP Ice Melting Test. This observation, along with the inherently high variability in the test results, leads to the conclusion that the Modified SHRP Ice Penetration Test should not be recommended for evaluating deicing chemicals.

Table 18. Modified SHRP Ice Penetration Test Data (without max and min values) at 0°F

Test Deicer	Modified Average Depth of Penetration for 5 replicates (mm)					Modified Coefficient of Variation of Penetration Depth for 5 replicates (%)				
	10	20	30	45	60	10	20	30	45	60
23% NaCl	0.3	0.4	0.5	0.5	0.5	67	42	45	53	53
32% $CaCl_2$	0.5	0.5	0.5	0.5	0.5	12	12	12	12	12
30% $MgCl_2$	0.0	0.1	0.4	0.4	0.4	0	87	42	43	43
NaCl (s)	1.7	2.1	2.3	2.5	2.5	35	5	7	0	0
$CaCl_2$ (s)	2.1	2.8	3.1	3.1	3.1	5	10	13	13	13
$MgCl_2$ (s)	1.5	1.7	1.7	1.7	1.7	13	15	15	15	15

Based on the observations from this study and the findings of Nixon et al. (2005) and Shi et al. (2009), the Modified SHRP Ice Penetration Test is not recommended as a method for comparing the performance of deicers. First of all, the ice penetration performance should be highly related to the ice melting capacity of deicers, especially in the absence of traffic or mixing action. So the ice penetration test does not add much value if the ice melting test has already produced reliable results to indicate the relative performance of deicers. Secondly, the ice penetration results are highly variable, likely attributable to the inherent variability in the deicer/ice interface and the probabilistic nature of the brine generation and penetration processes. Finally, the gradation of solid deicers significantly affects the ice penetration test results and the test using single pellets of solid deicers has its own problem as well (e.g., the “lodging” phenomenon mentioned above).

4.6. Modified Ice Undercutting Test

Development

The ice undercutting test published in Mauritis et al. (1995) was used to compare the time needed for a 0.25 g particle of various deicers to undercut ice at different temperatures formed by freezing 0.5 mL of deionized water in a test tube. The repeatability of the test needed to be investigated in addition to determining the application rate to test liquid deicers. Also, glass test tubes are smooth and not representative of roads; thus, the bottom of some test tubes was roughened with sand paper. If the results of the scratched test tubes seemed more realistic, then a repeatable method of scratching the tubes would have been investigated, such as applying an acid etching solution for a certain duration. However, the test results for scratched and smooth test tubes were ultimately too variable.

The test apparatus requires freezing a wire or piece of string in ice at the bottom of a test tube. The wire allows the test tube to be suspended from a support beam (e.g., a wooden frame), and the test tubes falls down when the ice melts. A copper arch is also attached to the test tube and, when the water is frozen, the copper arch contacts two pieces of copper connected to the support beam. When the test tube falls it drops into a salt bath that prevents the tube from breaking. The salt bath also limits temperature fluctuations (Figure 15). The resistance between points A and B in Figure 15 are measured by a datalogger. If the resistance is low (less than 100 ohms) then the ice is still frozen and the wire arch on the test tube is still in contact with the wire on the support beam. If the resistance is infinitely high, then the ice melted and the test tube dropped. The purpose of the datalogger is to be able to identify the time at which the deicer undercut the ice and allowed the test tube to detach from the support beam without having to monitor the test. At colder temperatures, this could take over three hours (Mauritis et al., 1995).

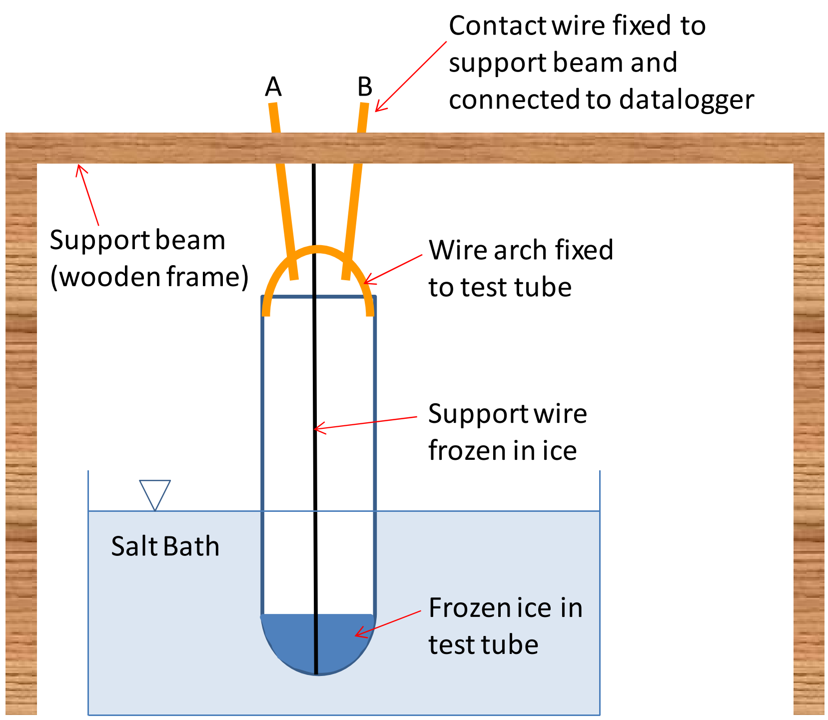

Figure 15. Mauritis Ice Undercutting Apparatus

Results

After testing various tube sizes and deicer application rates, an interim protocol was defined as a test involving 3.3 in. x 0.6 in. (85 mm x 15 mm) test tubes, 10 replicates, 0.5 mL of ice, and 100 µL liquid deicer. An example test result is shown in Figure 16. For this test, the undercutting times for the ten test tubes varied from 6 to 45.5 minutes, averaged 21.3 minutes, and had a standard deviation of 12.5 minutes. The test showed large variations between the 10 test tubes, despite well-controlled temperatures. The test was repeated three more times. The average and variance of the four tests indicate this test is not repeatable enough for further development (Table 19).

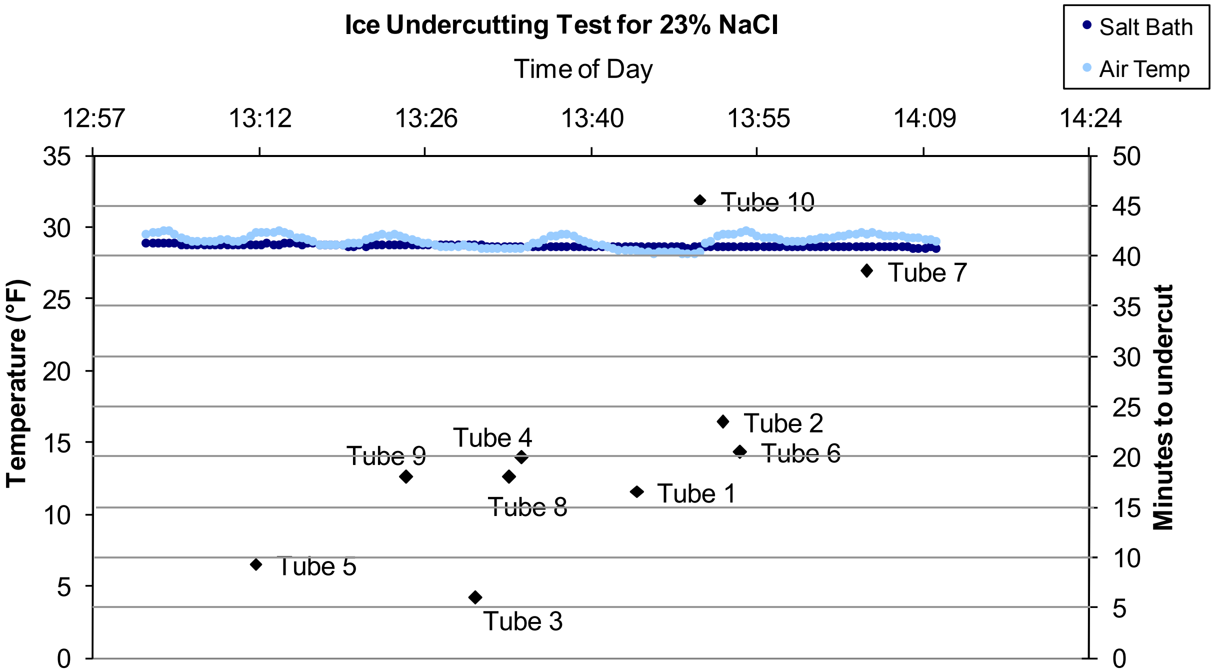

Figure 16: Sample result for ice undercutting test using 23% NaCl at 30°F

Table 19. Range of ice undercutting statistical data for 4 tests

Test No.	Minimum undercutting time (min.)	Maximum undercutting time (min.)	Average of undercutting times (min.)	Standard Deviation of undercutting times (min.)
Test 1	6	45.5	21.3	12.4
Test 2	8.5	70.5	38.7	21.0
Test 3	30.25	126.5	64.7	31.5
Test 4	0.5	128.0	64.5	38.2

4.7. Summary of Test Method Development

Four procedures were studied to quantify thermal properties and ice melting, ice penetration, and ice undercutting performance of deicers. Applying differential scanning calorimetry on deicer solutions is a relatively new technique to study the thermal properties of deicers. A DSC-based procedure was developed and standardized, which demonstrated to be a highly reproducible test for quality assurance of deicers. DSC thermogram can also provide an estimate of characteristic temperature and ice melting capacity for liquid deicers.

Two SHRP tests were modified to reduce the inherent variability within each test. The Modified SHRP Ice Melting Test involves more replicates of the test deicer and a 23% NaCl control used to accept or reject the test results. Based on the test results presented in this chapter, the volume of brine collected after 60 minutes of exposure to deicers at 30°F varied from 3.53 to 4.37 mL for liquid deicers and 4.87 to 5.32 for solid deicers. At 15°F, the volumes were reduced to 1.07 to 1.97 mL for liquid deicers and 2.45 to 3.2 mL for solid deicers. At 0˚F the volumes were even lower at 0.33 to 1.1 mL for liquid deicers and 0.5 to 2.1 for solid deicers.

The Modified SHRP Ice Penetration Test was studied with solid and liquid NaCl, $CaCl_2$, and $MgCl_2$. The original apparatus with five replicate ice samples was still used, but the data analysis was improved by computing the average and CoV of the penetration depths using only three data points at each time during the test. The maximum and minimum penetration depths were not included in the calculation of average penetration depth. Ultimately, however, the Modified SHRP Ice Penetration Test is not recommended for either solid or liquid deicers.

To develop the set of standardized test procedures, three common deicers—NaCl, $CaCl_2$, and $MgCl_2$ in solid and liquid form—were tested at three temperatures. However, blends and mixtures of deicers are increasingly common, in addition to additives produced from agriculture by-products. Thus, baseline tests are needed to ensure the three recommended test procedures are applicable to materials other than the ones used for developing the procedures. Chapter 5 provides baseline test results for NaCl, $CaCl_2$, $MgCl_2$, and deicer blends involving NaCl, $CaCl_2$, and an agriculture by-product.

5. BASELINE PERFORMANCE TEST RESULTS FOR DEICERS

Chapter 4 provides test results for common pure deicers using the test protocols developed during this research. This chapter reports the results of the standardized test protocols for DSC Thermogram and Modified SHRP Ice Melting Test conducted on the following deicers:

- Solid NaCl
- Solid $CaCl_2$
- Solid $MgCl_2$
- 23% NaCl
- 32% $CaCl_2$
- 30% $MgCl_2$
- AGBP
- The following blends of 23% NaCl, 32% $CaCl_2$, and AGBP:
    - Blend A: 95% NaCl + 5% $CaCl_2$
    - Blend B: 90% NaCl + 10% $CaCl_2$
    - Blend C: 85% NaCl + 15% $CaCl_2$
    - Blend D: 80% NaCl + 20% $CaCl_2$
    - Blend E: 90% NaCl + 5% $CaCl_2$ + 5% AGBP
    - Blend F: 85% NaCl + 5% $CaCl_2$ + 10% AGBP
    - Blend G: 80% NaCl + 5% $CaCl_2$ + 15% AGBP

AGBP is an agriculture by-product-based product that is marketed as a stand-alone anti-icing product or as an additive to salt brine for deicing roads, represented anonymously in this report. In particular, the product is a derivative of the sugar beet industry. Baseline tests were performed with AGBP alone in addition to blends with other salt solutions to ensure the test procedures could be used with these emerging materials.

5.1. DSC Thermogram Test Results

The DSC test results for baseline testing are presented in Table 20.

Table 20. Baseline Testing: DSC Thermogram test results for liquid deicers

Deicer	Heat Flow			Peak Temperature	
	Average (J/g)	Standard Deviation (J/g)	Coefficient of Variation (%)	Average (°F)	Standard Deviation (°F)
23% NaCl	165	1.8	1.1	21.8	0.078
32% $CaCl_2$	121	11	9.5	16.2	0.41
30% $MgCl_2$	73.8	3.4	4.6	8.46	0.40
AGBP	184	17	9.7	26.2	0.24
Blend A	158	7.3	4.6	21.9	0.41
Blend B	148	2.5	1.7	22.2	0.14
Blend C	145	4.0	2.8	22.3	0.35
Blend D	147	2.1	1.4	21.7	0.26
Blend E	141	6.0	4.3	23.0	0.25
Blend F	148	11	7.5	22.8	0.18
Blend G	147	12	8.1	22.3	0.36

5.2. Modified SHRP Ice Melting Test Results

The Modified SHRP Ice Melting Test was conducted at 30°F and 15°F for all the deicers (Table 21 and Table 22). AGBP and the mixed liquid deicers were not tested at 0˚F because previous testing indicated these liquids did not perform well at the coldest temperature; only the results for the solid deicers is reported for 0°F (Table 23). The solid deicers tested were reagent grade chemicals with a finer gradation than used by DOTs in field applications. Thus, baseline tests should still be conducted with commercial deicers (with particles retained on the No. 8 sieve after passing the No. 6 sieve).

Table 21. Baseline Testing: Modified SHRP Ice Melting Test (solid and liquid deicers) at 30°F

Test Deicer	Average Volume of Brine Collected (mL)		Measurement of Variation: CoV (%) if average ≥ 1.0 mL; Std Dev. (mL) if average < 1.0 mL	
	20 minutes	60 minutes	20 minutes	60 minutes
23% NaCl	2.7	3.5	4%	0%
32% $CaCl_2$	2.8	4.0	7%	5%
30% $MgCl_2$	3.0	4.3	3%	2%
AGBP	2.0	2.2	0%	5%
Blend A	2.6	3.8	8%	3%
Blend B	2.5	3.7	4%	3%
Blend C	2.6	3.8	4%	8%
Blend D	2.7	4.0	4%	5%
Blend E	2.5	3.8	4%	0%
Blend F	2.5	3.7	0%	3%
Blend G	2.4	3.3	8%	3%
NaCl (s)	1.8	5.3	14%	15%
$CaCl_2$ (s)	2.7	5.3	4%	8%
$MgCl_2$ (s)	3.5	4.9	4%	4%

Table 22. Baseline Testing: Modified SHRP Ice Melting Test (solid and liquid deicers) at 15°F

Test Deicer	Average Volume of Brine Collected (mL)		Measurement of Variation: CoV (%) if average ≥ 1.0 mL; Std Dev (mL) if average < 1.0 mL	
	20 minutes	60 minutes	20 minutes	60 minutes
23% NaCl	1.1	1.1	5%	5%
32% $CaCl_2$	1.8	1.6	8%	4%
30% $MgCl_2$	1.8	1.6	9%	9%
AGBP	0.7	0.6	0.2 mL	0.1 mL
Blend A	1.2	1.0	2%	6%
Blend B	1.2	1.2	0%	13%
Blend C	1.2	1.1	12%	11%
Blend D	1.3	1.1	5%	10%
Blend E	0.7	0.8	0.3 mL	0.3 mL
Blend F	1.1	1.0	7%	3%
Blend G	1.0	0.9	0%	0.1 mL
NaCl (s)	1.9	3.5	8%	9%
$CaCl_2$ (s)	3.1	3.2	8%	6%
$MgCl_2$ (s)	2.4	2.5	2%	9%

Table 23. Baseline Testing: Modified SHRP Ice Melting Test (solid deicers) at 0°F

Test Deicer	Average Volume of Brine Collected (mL)		Measurement of Variation: CoV (%) if average ≥ 1.0 mL; Std Dev (mL) if average < 1.0 mL	
	20 minutes	60 minutes	20 minutes	60 minutes
NaCl (s)	0.1	0.6	0.1 mL	0.3 mL
$CaCl_2$ (s)	2.1	2.1	5%	10%
$MgCl_2$ (s)	1.6	1.7	13%	7%

6. CONCLUSIONS AND RECOMMENDATIONS

Two test methods were identified, developed, and refined to screen potential deicers, additives, and blends. The tests should not be used to predict actual field performance or application rates because they lack consideration of traffic, humidity, active precipitation, ultraviolet radiation, and other elements. Instead, the tests provide only general trends or an assessment of relative performance. The tests were developed with the expectation that they will be performed by independent testing laboratories on any deicing chemical, additive or mixture. The two test protocols are:

- DSC Thermogram Test
- Modified SHRP Ice Melting Test

The DSC Thermogram Test provides the thermal properties of deicers in an aqueous state. Solid deicers can be tested by preparing an aqueous eutectic solution prior to the dilution required by the test protocol. The DSC-based test is highly reproducible and suitable for quality assurance of deicers, which can also provide an estimate of characteristic temperature and ice melting capacity for liquid deicers.

The Modified SHRP Ice Melting Test is an improved version of the SHRP Ice Melting Test because it incorporates two mechanisms to ensure acceptance of the test. One mechanism is a control in which 23% NaCl is tested side-by-side with the three test deicers. Acceptance bounds were determined for brine volumes collected in the control sample. If the test is acceptable based on the control, a separate mechanism is in place to ensure the variability is acceptable by checking the CoV values.

All tests were performed at the same facility. Two different operators were involved in conducting the Modified SHRP Ice Melting Test, while one operator conducted the DSC Thermogram Tests. While not essential, a round robin test is recommended to ascertain the variability between laboratories before full implementation of the test protocols. This is particularly important for the DSC thermogram test because its application in deicer evaluation is a novel use of this equipment commonly available in materials testing laboratories. The Modified SHRP Ice Melting Test should also be performed by other laboratories because the survey results suggested limited confidence in the repeatability of this test method.

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APPENDIX A: ADDITIONAL LITERATURE—TESTS FOR EFFECTS OF DEICERS

The focus of the literature review was to identify previous attempts to characterize performance of deicers in a laboratory setting. However, there is abundant information regarding tests that measure the effects of deicers on infrastructure and the environment. This appendix provides a review of standard laboratory test methods that characterize the effects of deicers on bare metal, coated and embedded metal, concrete, asphalt, and the environment.

A-1. Tests for Material Compatibility of Deicing Chemicals

Concerns of the compatibility of deicing chemicals with infrastructure materials are primarily centered on effects of deicers on pavements and highway infrastructure. The impacts of deicers to bare and coated metal, embedded metal, concrete and asphalt were identified in the literature review.

Bare and Coated Metal Tests

Corrosion is the primary concern regarding the impact of deicing chemicals to metal. Metal is found in the transportation environment in infrastructure (signs, guardrails, bridges), pavement (reinforced concrete, concrete expansion joints), and vehicles (passenger, commercial, DOT-operated vehicles). Epoxy-coated rebar can be found in concrete pavements, particularly in bridge decks. The epoxy coating is designed to protect rebar from corrosion, but any dings or scratches in the coating can invite local corrosion that can then proceed uninhibited along the rebar under the coating. Painted signs are another example of coated metals in the transportation environment.

Several possible types of test method for evaluating the corrosive effects of deicers or similar compounds were identified. Immersion testing usually involves submerging metal coupons in a solution and measuring weight loss after a certain period of time. The exposure can be cyclic as in NACE TM 0169-95, or constant as in ASTM F483. Spray tests are another method for exposing metal coupons to deicers. Electrochemical techniques, such as linear polarization, represent another category of testing. Most corrosion test methods utilize a standard corrosive solution designed to evaluate the performance of coatings. Modifications to these can provide a means of comparing deicers.

The NACE Standard TM0169-95 as Modified by the Pacific Northwest States is a gravimetric method that entails cyclic immersion of parallel coupon for 72 hours by alternating 10-minute immersion and 50-minute drying cycles using a custom designed machine. Each solution is tested in triplicate and there are two controls: distilled water and 3% NaCl. The weight loss result in MPY (milli-inch per year) is "corrected" by subtracting the corrosion due to distilled water (PNS, 2006). A corrosion-inhibited product must be 70% less corrosive than 3% NaCl to be approved for sale to member states of the Pacific Northwest Snowfighters Association (Washington, Oregon, Idaho, Montana and the province of British Columbia).

The SHRP H-205.7 immersion test with air aspiration was developed for evaluating corrosion of bare metal specimens in solutions of deicers in comparison to 3% NaCl. No standard metal is specified and the size of 1 in. x 2 in. x 0.125 in. is only suggested, although comparisons should only be made between substances tested on substrates of the same composition and geometry. Compositions should be tested in duplicates and inhibitor (if present) should be tested at three different concentrations. The suggested duration is up to six to eight weeks, although enough samples should be prepared to remove and weigh some before this time. Cleaning and calculations are in accordance to ASTM G1, although no guidelines for acceptance/failure are provided (Chappelow et al., 1992).

SAE J2334 is one of the few corrosion tests validated to simulate the corrosion of a vehicle with five years of exposure in the Snow Belt area. Several procedures are available to allow dip, fog, or spray applications. The standard solution contains NaCl, $CaCl_2$, and $NaHCO_3$ and the samples should be coated with automotive paint. After 15 minutes of exposure, the samples are dried for 17.75 hours and then put in a 100% humidity environment for 6 hours. In this way, 80 total cycles are completed, each lasting 24 hours with flexible options for weekend and holidays available (Levelton Consultants, 2007 and Xi and Xie, 2002). Xi and Xie (2002) modified SAE J2334 when they tested the deicers NaCl and $MgCl_2$ instead of using the standard solution. They also tested bare and coated specimens, but found the hygroscopic nature of some deicers to influence the corrosion results.

Several variants of salt-spray tests have been developed for "comparing the performance of materials and coatings (Levelton Consultants, 2007, p. 89)." The tests do not provide indications of field performance, but Levelton Consultants (2007) mention that the tests may be adapted to compare effects from various deicing chemicals. The testing conditions and type(s) of metals would need to be chosen through a comprehensive study. There are three ASTM standards for operating salt-spray equipment, but acceptance values or ranges, as well as the control(s), would need to be determined. The most commonly used practice is ASTM B117 for non-metallic coatings. This procedure is also amenable to testing scratched coatings.

Electrochemical techniques can be used to study most forms of corrosion in light of the fact that corrosion is an electrochemical process. Linear polarization resistance (LPR, within $E_{corr}\pm15$ mV) and Tafel polarization (beyond $E_{corr}\pm150$ mV) measurements were found capable of indicating the effect of inhibitor injection on the corrosion rate of carbon steel in natural seawater (Qiu and Chua, 1999). Levelton Consultants (2007) also utilized LPR to rapidly compare the corrosivity of 15 deicing chemicals at three concentrations on 5 substrates. The researchers also supplemented LPR data with weight loss measurements, finding better correlation when the LPR corrosion rate was low. Guidance for this technique is available from three ASTM standards: G3, G96 and G102. Levelton Consultants (2007) also provided the detailed operating procedure in Appendix A of Phase 2 of NCHRP Project 06-16. In many practical applications the use of LPR could be preferred due to its simplicity. However, there are concerns over its validity and reliability when LPR is used to quantify the corrosion rate, as it is prone to measuring errors of the test instrument and other variations. For Tafel polarization, the limitation is that the applied external perturbation may lead to significant change in the surface state of electrodes, in the solution composition, or in the controlling corrosion mechanism and kinetics.

Weak Polarization Curve is an experimental technique that measures the current-potential plot of a metal in an electrolyte when an external potential signal (perturbation) is applied within ±120mV range of its corrosion potential (E_{corr}). Such current-potential plot is termed a potentiodynamic polarization curve when the external potential signal is applied at a certain sweeping rate. By measuring the polarization curve, the instantaneous corrosion rate of the metal in the electrolyte can be calculated and the corrosivity of the electrolyte can thus be evaluated (Shi et al., 2007). This method requires more sophisticated software than LPR, but also reduces measurement error and dependency on “textbook” constants when calculating the corrosion rate.

Manufacturers sometimes include a corrosion inhibitor in deicing products to reduce the corrosiveness of deicers. There is no standard test method for the detection or measurement of the concentration of these inhibitors. The great variety of possible inhibitors and their proprietary nature has limited the development of such a test. However, the Western Transportation Institute is currently working on a project investigating the longevity of corrosion inhibitors in field conditions. Means of testing inhibitor presence and concentration are underway with a focus on using ultraviolet-visible spectroscopy. In the mean time, the PNS recommends that delivered batches of corrosion-inhibited deicers be tested using a method provided by the manufacturer (PNS, 2006).

Embedded Metal Tests

Several methods for evaluating corrosion of reinforcing bar embedded in concrete (hereafter simply referred to as rebar) have been standardized or developed during research projects. Some test methods were designed to specifically compare corrosivity of various deicing chemicals, while others use a standard solution to compare concrete or rebar coatings or mix designs.

The developmental work for the SHRP *Handbook* considered two methods for the corrosion of embedded reinforcing bar: the corrosion potential test and the macrocell test. The corrosion potential test method consists of a rebar/mortar specimen immersed in a mortar-filled bath with either simulated pore solution or deicer solution. The specimen is connected to a reference electrode immersed in a saturated KCl bath and the voltage is measured. The baths are connected via a salt bridge. A series of experiments identified several parameters concerning the mortar mix, curing time, curing conditions, rebar size, and specimen immersion depth. Relatively high consistency was obtained in less time (60 days total, 14 for casting/curing, 46 for testing) than the "time-to-corrosion accelerated laboratory test" which can take six to twelve months. The macrocell test setup is similar except each bath contains a rebar/mortar specimen; one bath has a mortar fill with simulated pore solution and the other bath has a mortar fill with deicer solution (Chappelow et al., 1993). Voltage is measured across a resistor and can be related to corrosion rate using Faraday's laws, as described by Balma et al. (2004). The macrocell test was found to be not as nearly consistent, but still promising to be more useful than the corrosion potential test method. Additional work is needed, particularly concerning the salt bridge, level of resistance, and the "reference electrode" specimen (Chappelow et al., 1993). Balma et al. (2004) indicate subsequent work has yielded improvements in consistency and reproducibility.

<u>ASTM G109</u> was essentially the selected corrosion test for embedded rebar in the SHRP *Handbook*, identified as <u>SHRP H-205.12</u>. A concrete specimen with 11 in. length x 6 in. height x 4.5 in width contains one "anode" No. 4 rebar placed 0.75 in. from the top and two "cathode" rebar placed 1.0 in. from the bottom. Edge effects are minimized by wrapping the 1.5 in. of each end of the rebar with electroplater's tape. The sides of the concrete are sealed with epoxy and the specimen is propped to allow air flow underneath. A dam is created on the top of the specimen to allow ponding of 3% NaCl. The two cathode rebars are grounded and connected by a resistor to the anode rebar. The voltage drop across the resistor is measured at predetermined times of alternating ponding and drying cycles. The test continues until there is a "clear difference" between reference and test specimens, or until corrosion is visible. Three specimens are needed for each deicer formulation/condition (Chappelow et al., 1992).

Levelton Consultants (2007) evaluated a variety of deicing chemicals by following ASTM G109 and ASTM C1556. <u>ASTM C1556</u> provides an indication of chloride ion diffusion. The standard indicates calculations are only applicable to a NaCl solution, whereas Levelton Consultants tested 23% NaCl, 29% $MgCl_2$, and 32% $CaCl_2$. The concrete samples had representative strength specifications by following an AASHTO specification (supplementary cementing materials were omitted). Fifteen deicers were tested at representative field concentrations (instead of three percent NaCl as specified by G109). After two years of exposure, corrosion had not initiated. According to C1556, the chloride ions had penetrated 0.7 in. below the surface after 19 months. Testing has continued, but results are not yet available.

The <u>Southern Exposure Test</u> specimens resemble G109 specimens except with six total No. 5 rebar (two upper, four lower) placed 1.0 in. from the top and bottom in 7.0 in. high concrete . The ponding solution is 15% NaCl with alternating 4-day ponding and 3-day drying cycles for

12 weeks. Continuous ponding then occurs for 12 weeks, followed by 12 weeks of cycling and finishing with another 12 weeks of continuous ponding. The method provides faster results than the G109 test, such that 15 to 20 years of tropical marine exposure are simulated in 48 weeks. As with G109, voltage across a resistor between the “anode” and “cathode” rebar systems is measured (Darwin et al., 2007).

The Cracked Beam Test uses three No. 5 rebar (one upper, two lower) placed 1.0 in. from the top and bottom in 7.0 in. high concrete. A thin (12 mil) stainless steel shim placed and removed during casting simulates a crack penetrating from the surface to the upper piece of rebar. The cycling/ponding of the Southern Exposure Test can continue for up to 96 weeks with 15% NaCl solution (Darwin et al., 2007).

Yang et al. (2003) measured the corrosion of 5 mm rebar in various types of concrete soaked for one day in 10% NaCl solution and dried for three days at 60°C. After 20 cycles, the rebar was removed from the specimen and the rust stripped adhering to the Chinese standard JTJ 228-87 by an acid wash and neutralization. Corrosion comparisons were based on percent weight loss of the specimens.

Concrete Scaling (Freeze-Thaw, Wet-Dry) Tests

Two categories of tests exist for the laboratory determination of the effects of deicers on concrete or mortar substances. Several tests have been designed to specifically examine the physical effects of freeze-thaw and/or wet-dry conditions, with or without the presence of a deicer. Generally these are scaling/spalling tests of which deicing salts have been shown to have exacerbating effects. The use of acetate/formate based deicers has been shown to increase the rate and/or occurrence of alkali-silica reactivity (ASR) in airfield concrete pavements. Thus several standard ASR-related tests have been modified during research projects to include deicers. The ASR tests will be discussed after the scaling tests.

ASTM C672, also called the ponding method, allows 6 mm of a four percent $CaCl_2$ solution (or other deicer solution should its effect be needed) to contact the top of a prepared and cured concrete specimen. Freezing and thawing cycles lasting 16 to 18 hours at 0°F and 6 to 8 hours at 73°F (with 45 to 55 percent relative humidity in the thawing environment) offers accelerated testing conditions. Visual examinations using a 0 to 5 scale occur every 5, 10, 15, 25, and 50 cycles. Usually only 50 cycles are completed, but more should be done in the absence of scaling, with visuals taken every 25 additional cycles (Ghafoori and Mathis, 1997 and ASTM, 1998).

The SHRP *Handbook* has two test methods for compatibility of deicers with concrete. The H-205.9 test is a modified version of ASTM C672. At least two specimens should be prepared for each condition tested (consistent with the ASTM C672 method). In SHRP H-205.9, the dam that holds the deicer solution is cast into the specimen using a stainless steel band, instead of fabricating a dike after finishing the concrete specimens of C672. This change necessitated a modification to smaller coarse aggregate, limiting maximum size from 1.0 in. to ⅜ in. Additionally, the provision for air-entrained concrete that is an option in C672 was removed. For evaluation, the visual rating is assessed every five freeze-thaw cycles as well as the weight of scaled material that is brushed from the concrete surface, filtered and dried (Chappelow et al., 1992 and Chappelow et al., 1993). Compressive strength testing can provide some assurances for comparisons between different concrete batches. The average difference should be less than 10.7 percent because this is the limit of acceptability for samples from the same batch tested on the same day (Chappelow et al., 1992).

The other SHRP concrete compatibility test is H-205.8 and provides some benefit over SHRP 205.9: smaller test specimens (1.5-in. diameter, 1.875-in. length), less labor-intensive and minimized loss of test solutions. These benefits may be at the cost of losing more realistic testing conditions. Again, non-air-entrained concrete is used and the evaluation is based on measured weights of either the specimen or the scaled particles. The samples are exposed to deicing chemicals by being pressed against a soaked sponge in a sealed container. The weighed material is dried for 24 hours at 73°F and 50 percent relative humidity. Four specimens are prepared for each condition tested and two controls are recommended: deionized water and a 3% NaCl solution (Chappelow et al., 1992 and Chappelow et al., 1993).

Levelton Consultants (2007) point out the limitations to both SHRP 205.8 and 205.9, which mainly lie in the use of non-air-entrained concrete. This, along with a relatively high water to cement ratio of 0.51 and the absence of supplementary cementitious material, likely causes the specimens to deteriorate from the physical effects of freeze-thaw instead of interactions with deicing chemicals. With long freezing periods at very cold temperatures and small specimens, the deicers are not likely to prevent freezing. They suggest more realistic concrete specimens with air-entrainment, shorter freezing periods at higher temperatures, longer thawing periods, and perhaps the addition of wet-dry cycles to allow chemical reactions and ion diffusion to play their part. These changes will, however, lengthen the testing duration.

AASHTO T 161 provides several procedures for determining the freeze-thaw resistance of concrete. The temperature range is 40°F to 0°F with cycles lasting from two to four hours. Options for testing the concrete specimens include A) freezing and thawing in water, B) freezing in air and thawing in water, and C) freezing while wrapped in moist cloth and thawing in air. A durability factor is calculated based on the specimen's relative dynamic modulus of elasticity. Usually up to 300 cycles are performed, but testing can be terminated early when the dynamic modulus of elasticity reduces to 60 percent of its initial value (WSDOT, 2007 and Meininger, 2000).

The Swedish Standard SS 13 72 44, called the Borås method, is similar (and some say improved) to the ponding method of ASTM C672 except the freezing is controlled in a top-down fashion by insulating the sides and bottom of the concrete specimens. For the freeze-thaw cycling, the salt solution on top of the specimen is cooled to 0°F within 16 hours and then raised to about 70°F within 8 hours; thus one cycle lasts 24 hours (Ghafoori and Mathis, 1997). The scaled particles are collected and weighed at 28, 56 and 112 days, providing mass scaling per unit area designated as m_{28}, m_{56}, and m_{112}. Acceptability is determined based on the scaling show in Table A-1 (sometimes the m_{112} is not necessary):

Table A-1. Acceptability criteria for Swedish Standard SS 13 72 44 (Jóźwiak-Niedźwiedzka, 2005)

Very Good	average m_{56} < 0.10 kg/m^2
Good	average m_{56} < 0.20 kg/m^2, or average m_{56} < 0.50 kg/m^2 and m_{56}/m_{28} < 2
Acceptable	average m_{56} < 1.00 kg/m^2 and m_{56}/m_{28} < 2, or average m_{112} < 1.00 kg/m^2
Unacceptable	none of the above satisfied

Scaling of pavers can be investigated using the Canadian standard CAN3-A231.2-M85 in which specimens are immersed in a NaCl solution. Freeze-thaw cycling occurs at 5°F for 15 hours (plus 1 hour for temperature reduction) and at 73°F for 8 hours. Scaled particles are collected after 10, 25 and 50 cycles (Ghafoori and Mathis, 1997).

The Ontario Ministry of Transportation test method MTO LS-412 for scaling resistance of concrete is also similar to ASTM C672. However, the standard deicing solution is three percent NaCl and the scaled particles are collected and weighed every five cycles. The failure limit is 0.80 kg/m^2 (cumulative) after 50 cycles (Panesar and Chidiac, 2007). The test method exaggerates typical field conditions and results cannot be used to predict field performance, as shown in Boyd and Hooton (2007) for research conducted using laboratory and field specimens. Variability was found by Boyd and Hooton (2007) even across only three different laboratories. The samples were air-entrained and all mixes except one included supplementary cementitious materials, although the samples with 100 percent ordinary Portland cement had the least variability.

The RILEM CDF test (Capillary suction of Deicing solution and Freeze thaw test) recommends five specimens be tested for each condition (usually concrete mix); the deicing solution is 3% NaCl. This procedure uses an ultrasonic bath to remove the scaled material. The bath water is then filtered and the mass of scaled material determined after a drying procedure. The freeze thaw cycling is preceded by a 7-day period of capillary suction in which one side of the prepared specimen is submersed 5 mm into the deicing solution at 20°C. The freeze-thaw cycle lasts 12 hours with a range from +68 to -4°F. Cooling occurs at a constant rate for four hours and then remains at -4°F for three hours. The temperature increase is also at a constant rate for four hours, but only remains at +68°F for one hour. Although the scaling after 28 cycles is required, additional measurements are recommended (RILEM, 1995). The CDF test was published as a recommendation in 1996 and as late as 2004 references have been made to the 1996 publication. A more recent publication or version of the CDF test was not identified.

Quanbing and Beirong (2005) modified the RILEM CDF test by increasing the NaCl solution to 4%, decreasing the cycle length to six hours (three hours freezing, three hours thawing), and relocating the temperature sensor. The researchers recommended this modified test as a Chinese standard because it provided more rapid evaluation of scaling. They claim it provides consistent results, but the proof is published in a Chinese journal.

Yang et al. (2002) tested concrete repair material using single-surface and whole soaking scaling methods with a three percent NaCl solution. The cycle consisted of freezing at -40°F for four hours and thawing at 68°F for four hours. Scaling was reported as mass of scaled material per unit surface area. Additional procedural information was not reported and the deicer scaling test method is described in Chinese. However, it is possible that the modified RILEM CDF test replaced this deicer scaling test.

The Turkish Standard TS 699 is a compilation of many tests for the physical properties of concrete, including freeze-thaw resistance (Eren and Bahali, 2005). Colak (2002) performed freeze-thaw testing according to TS 699 with four hours of freezing at -4°F and four hours of thawing in water at 68°F. Colak (2002) performed visual inspection and compressive strength testing on some samples every five cycles. Eren and Bahalia (2005) performed accelerated freeze-thaw testing on natural building cut stones using a sodium sulfate solution, in accordance to TS 699. Resistance is quantified by weight loss, but additional information was not provided about the methodology (the standard is published in Turkish).

Wang et al. (2006) performed freeze-thaw testing of five deicing compositions using air-entrained Portland cement concrete and paste specimens. Twelve specimens are needed for each chemical/material combination for replicate samples used in compressive testing. For freeze-thaw testing, the samples were immersed in water (the control) or deicing solution for 15 hours at -4°F. Thawing took place in a water bath for a total of nine hours, although the samples actually thawed within four hours. Sixty cycles were completed with weight, scaling and compressive strength sampling throughout. Samples were weighed every five cycles after gently removing scaled particles. Visual examination using a rating scale of 0 to 5 was done on eight samples (four paste, four concrete) every 20 cycles. Compressive strength testing of six samples (three paste, three concrete) was also done every 20 cycles. Mass measurements do not appear to be an adequate measure of scaling because of the potential for salt crystallization and increase in absorptive surface area with cracking – even samples exhibiting scaling could show mass increase instead of mass loss. The variability or standard deviation was not reported for mass, scaling, or compressive testing results.

Most research and test procedures relating the effects of deicers on concrete focus on freeze-thaw damage. However, wet-dry conditions were also investigated by Wang et al. (2006) using a 24 hour cycle time. Immersion of samples in water (the control) or deicing solution lasted 15 hours at 4.4°C. The drying period was nine hours at approximately 23°C and 50 percent relative humidity. Mass measurement (every 10 cycles), scaling rating (every 20 cycles), and compressive strength testing (every 20 cycles) were completed on paste and concrete specimens in a very similar manner to the freeze-thaw testing also done by the researchers.

Concrete ASR Tests

Scaling of concrete surfaces in the presence of deicing chemicals has been studied for a long time. More recently, however, the contribution of deicers to accelerated alkali-silica reaction (ASR) in airfield concrete pavements led to modifications of current standard ASR tests. One notable difference between winter maintenance of airfields versus highways is the lack of chloride-based deicers. Airfield anti-icing and deicing practices generally include potassium acetate, urea, sodium acetate, or sodium formate, with potassium acetate used by most airports. However, use of potassium acetate is not absent in highway winter maintenance, and can be found particularly in Fixed Automated Spray Technology (FAST) systems.

ASTM C1260, the mortar bar method, is a relatively short-lived ASR test for reactive aggregates, usually lasting about 16 days. After 48 hours of curing, samples measuring 25 mm x 25 mm x 285 mm are immersed in 1N NaOH solution. Determinations are based on percent expansions from length measurements during testing. Limitations for expansion can be based on ASTM guidance, while the Federal Aviation Administration and the U.S. Air Force each have their own version of acceptability, as well as provisions for longer testing periods.

Rangaraju and Olek (2007) modified ASTM C1260 by using deicers for the soak solution instead of sodium hydroxide. Until additional testing can be completed using a larger selection of aggregates and cements, the modified methodology is recommended in the interim. The liquid deicer options are either 50 percent by weight potassium acetate or potassium formate. The solid deicer options are saturated solutions of sodium acetate or sodium formate. Commercial deicers are preferred over reagent grade chemicals. Testing for 28 days after curing is recommended, although most expansion was seen within 14 days.

In some cases, expansions under ASTM C1260 do not conclusively indicate aggregate susceptibility and ASTM C 1293 is recommended as a follow-up test. However, this test lasts up to a year with specimens arranged vertically in a closed container at 100°F and nearly 100 percent relative humidity. Rangaraju and Olek (2007) also modified C1293 by using deicer soak solutions instead of the high-humidity environment. The researcher also experimented with the specimens positioned horizontally and found expansions under the same conditions/materials to be greater than their vertical counterparts.

Asphalt Tests

Effects of deicers on asphalt pavement have been less studied. Most notably, freeze-thaw testing is usually limited to concrete specimens for accelerated results concerning scaling. Nonetheless, Hassan et al. (2000 and 2002) performed freeze-thaw and wet-dry laboratory testing of asphalt core samples. The procedures deviated from some of the standardized conditions used for concrete specimens: samples were immersed in two percent deicer solutions and underwent a freezing cycle of 24 hours at -31°F and a thawing cycle of 24 hours at 86°F. The indirect tensile strength and elastic modulus of three replicate samples were measured after 25 and 50 cycles while mass measurements were taken every five cycles. Two controls were utilized: three dry virgin specimens not subject to freeze-thaw and six specimens subject to freeze-thaw with distilled water (Hassan et al., 2000). Chemical reactions were also thought to play some role in asphalt deterioration in the presence of deicers. However, chemical reactions can be very slow during winter months, so the researchers added warm wet-dry conditions after freeze-thaw cycling in a follow-up project to simulate potential summer reactions. This project also used asphalt cores, but limited the freeze-thaw exposure to 15 cycles. Some specimens were removed for indirect tensile strength measurements while the remaining underwent 40 wet-dry cycles at 104°F. The wetting cycle lasted two days using distilled water (for a control) or two percent deicer solution; the drying cycle lasted one day. Mass measurements were taken every 10 wet-dry cycles and indirect tensile strength was determined at the end of the 40 wet-dry cycles.

The standard boiling water test of ASTM D3625 specifically investigates the effects of water on uncompacted bituminous-coated aggregates. Pan et al. (2008) modified this test to use a commercial sodium acetate deicer with concentrations ranging from zero (as in the standard protocol) to 40 percent. The percentage of aggregates stripped of the bitumen coating at the end of the test ranged from 4 to 42 percent, coinciding with the increase in deicer concentration. Additional study, especially incorporating a greater variety of bitumen, aggregates, and deicers could suggest this as an applicable screening test for deicers or new aggregate/bitumen susceptibility.

Pan et al. (2008) developed an aqueous solution test to investigate the effects of sodium acetate and CMA deicers on asphalt binder. In the test 80 mL of deionized water is mixed with four grams of asphalt binder and enough deicer to create solutions of 0, 10, 20, 30, and 40 percent by weight. Magnetic stirring of 5 rotations per second ensures continuous mixing. A water bath at

32, 68, 104, 140 or 176°F is maintained for two hours during testing. The suspension mixture is separated from the floating asphalt, diluted and then again separated by centrifuge. At all temperatures the control with zero deicer exhibited no suspended or emulsified asphalt whereas emulsification increased with both deicer concentration and testing temperature. Thus, screening of deicers could include some form of this test, although additional study would be needed to investigate its applicability.

Use of Deicer Material Compatibility Tests

As discussed above, a variety of tests developed to quantify the impact of deicers to various materials have been identified in the literature. Nonetheless, the application of these tests is important in understanding their benefit to the winter maintenance community. Even a brief look at patents associated with deicers often turns up significant use of these tests:

- Patent by Barbour and Wiesenfel (1998) *Anti-Icing Composition Having Anti-Corrosion and Anti-Spalling Properties* reported using the **NACE TM0169** corrosion test method.
- Patent by Beazley et al. (1998) *Corrosion Inhibited Calcium Chloride Solids and Brine Solutions* reported testing the invention using **NACE TM0169** (or **SHRP 205.7**, not exactly specified) corrosion test method
- Patent by Berglund et al. (2001) *Deicing Compositions and Methods of Use* reported using the **SHRP H-205.7** and **ASTM F483** corrosion tests
- Patent by Berglund et al. (2003) *Water-Activated, Exothermic Chemical Deicing Formulations* reported using **ASTM F483** corrosion test using metal aircraft alloys
- Patent by Dietl and Stankowiak (2000) *Method of Melting Snow and/or Ice and a Deicer Comprising Sodium Formate and Sodium Chloride* reported using the **ASTM F483** corrosion test
- Patent by Ireland and Lucas (1993) *Dihydrogen Orthophosphate Deicing Composition* indicates apparent use of a **modified ASTM C672** or **SHRP H-205.9** scaling test.
- Patent by Klyosov et al. (2000) *Liquid and Solid De-icing and Anti-icing Compositions and Methods for Making Same* reported using the **SHRP H-205.7** corrosion test
- Patent by Koefod (1996) *Corrosion-Inhibiting Salt Deicers* reported using the **SHRP H-208.9** scaling test
- Patent by Vickers and McGonigle (2005) *Snow and Ice-Melting Granules and Method for Preparing Same* reported using the **PNS version of NACE TM0169**
- Patent by Zaid (1997) *Corrosion Inhibitor* reported using **SHRP H-205.7** corrosion test method.

A-2. Tests for Environmental Effects of Deicing Chemicals

In recent years, the environmental effects of deicing chemicals have increasingly gained attention and scrutiny. Environmental effects include toxicity to living organisms, air quality concerns, and water quality concerns.

The SHRP H-205.11 test is a suite of ASTM and EPA test methods to measure effects of deicers on terrestrial and aquatic plants and animals. The acute toxicity tests reference the EPA document EPA/600/4-85/013 and ASTM E729; the chronic toxicity tests reference the EPA document EPA/600/4-89/001, and the seed germination tests reference the EPA document EPA/560/6-82/002 (Chappelow et al., 1992).

The guide produced for NCHRP Project 6-16 and described in NCHRP Report 577 performed 9 tests on 42 deicing chemicals described in the 20th edition of *Standard Methods for the Examination of Water and Wastewater* published by the American Public Health Association. The tests measured Biochemical Oxygen Demand (method 5210 B), Chemical Oxygen Demand (method 5220 D), Nitrate and Nitrite (method 4500-NO3-H), Ammonia (method NH3-F), Total Kjeldahl Nitrogen (method NorgB), Total Phosphorus (method 4500-PB,E), Total Soluble Phosphorus (method 4500-PE), Cyanide (method 4500-CN-C), Arsenic, Cadmium, Chromium, Copper, Lead, Mercury, Nickel, Selenium, Silver, and Zinc (method 3125) (Levelton Consultants, 2007). Likewise, the PNS group requires testing on all of the above as well as Barium but with the exception of total soluble phosphorus, nickel, and silver (PNS, 2006). It is worth noting that occasionally the analytical method requires modification or samples need to be diluted (Levelton Consultants, 2007)

Levelton Consultants (2007) also performed aquatic toxicity tests using 15 deicing chemicals based on three 1994 EPA standards for chronic toxicity to freshwater organisms (the Fathead Minnow, the water flea *Ceriodaphnia dubia*, and the green alga *Selenastrum capricornutum*). These standards have been modified and superseded as of 2002. The most susceptible organism tested was the water flea, followed by the green alga, and then the Fathead Minnow. Variations in toxicity were found among deicers even in the same class (e.g. NaCl), probably due to additives and contaminants.

A-3. Demonstrating Systematic, Multi-Criteria Approach to Deicer Selection

In the last decades, the growing use of deicers has raised concerns about their effects on motor vehicles, transportation infrastructure, and the environment. Transportation agencies are under increasing pressure to maintain high levels of safety and mobility on roadways even during the winter months, while working with limited financial and staffing resources and recognizing the corrosion and environmental challenges related to chemical and material usage. Too often, the selection of snow and ice control materials is focused solely on material cost and effectiveness (effective temperature and level-of-service impacts). Procurement decisions too often ignore costs of corrosion and environmental impacts. An asset management perspective should be utilized to strike the right balance in meeting multiple goals of each highway agency, including safety, mobility, environmental stewardship, infrastructure preservation, and economics.

While there is increasing amount of information available regarding various aspects of deicers in terms of performance and impacts, how to use the information is a challenge for winter maintenance decision-makers. Research is needed to establish a multi-criteria framework that would integrate the local priorities with the laboratory testing data in a quantitative manner and thus allow agencies to make more effective, defensible decisions in selecting, purchasing, or formulating deicers for snow and ice control.

In addition, there is conflicting information regarding the relative impact of NaCl, $MgCl_2$, $CaCl_2$ and other deicers to Portland cement concrete (PCC), since the evaluation of such impacts was often conducted using different brands and concentrations of deicers and followed different types of laboratory test protocols. There is a lack of accelerated laboratory tests of PCC durability in the presence of deicers, which would take into account of wet-dry cycles, freeze-thaw cycles, and mechanical stresses typically experienced by the DOT field concrete structures and components. Some deicers may pose detrimental effects on the DOT concrete infrastructure and thus reduce concrete integrity and strength. Research is needed to evaluate the risks of deicers that are of interest to DOTs and to identify/evaluate best practices that can be used to protect the roads and bridges from deicers.

One future research topic for Clear Roads to consider is to establish and demonstrate a quantitative multi-criteria approach to decision-making or optimization in selecting or formulating liquid deicers for snow and ice control, and to improve the knowledge of the performance characteristics of the blended liquid products and their impacts on the transportation infrastructure. To this end, this research will start with an agency survey in order to collect information on: what deicer products and their concentrations to test in this research, what deicer attributes to quantify or characterize, what laboratory tests to use (including the wet/dry and temperature cycles as well as mechanical stresses to simulate), the priority of various deicer attributes in the deicer selection process, etc. This research will establish standard laboratory test protocols to evaluate PCC durability in the presence of deicers, which will realistically simulate the field experience of DOT concrete structures and pavements in the highway environment. Based on the survey responses, a design of experiments will be conducted in order to minimize the number of experiments needed to illustrate the complex relationship between the composition of the blended liquid deicers and their performance and impacts. With the statistically sound experimental design, the data obtained from the various laboratory tests will be analyzed and modeled using artificial neural networks (ANNs) and response surface methodology (RSM). ANNs provide non-parametric, data-driven, self-adaptive approaches to information processing. They are powerful in tackling complex, non-linear problems and have been successfully used to model, predict, control and optimize non-linear systems.

In the context of multi-criteria decision making (MCDM), rational decision-making guidelines can be developed to help winter maintenance managers in selecting the most suitable deicers for conditions in their agency or local jurisdiction, taking into account the array of factors involved. The composition and value of the deicer composite index could change with the changes in user priorities and objectives. As such, this research will also conduct *"what-if"* analysis to illustrate how the optimum deicer formulation may change depending on the specific user scenario, and how under each user scenario the formulation can be optimized to allow the most applicable deicer to be selected based on its relative ranking.

APPENDIX B: BLANK SURVEY

The survey was distributed as a Microsoft Word file with interactive buttons for selecting the desired response from a set of possible responses for each question.

CLEAR ROADS
research for winter highway maintenance

Clear Roads Survey: Evaluation of Deicing/Anti-icing Chemicals

The Clear Roads pooled-fund project is a collaborative effort of 14 member states initially formed because of the need for real-world testing in the field of winter highway operations. Please visit our website at http://www.clearroads.org/ to see our research projects, meeting minutes, and much more.

One research project currently underway is titled "*Development of Standardized Test Procedures for Evaluating Deicing Chemicals*." The objective of this research is to develop and/or identify a series of standard laboratory testing procedures and ranges that can be used to evaluate the performance of deicing chemicals, additives and mixtures used on roadways and other transportation facilities. We need your help in moving this forward.

There are many aspects of winter maintenance products that can be tested, such as performance, effective temperatures, safety, impacts to infrastructure, and so on. We have identified several existing standard tests and would like to hear about your experience with any of these. In addition to the performance of winter maintenance chemicals, we are also interested in knowing what additional aspects you'd like to know more about before using them to treat the roads. We would really appreciate your participation in this survey.

Thanks!

1. What aspects regarding the *performance* of deicing and/or anti-icing chemicals need to be tested in the laboratory? Please rank all that apply, choosing from the following options (click on "Select"):
   "Not useful at all"
   "Not useful"
   "May be useful"
   "Useful" or
   "Very useful"

   Select Melting ability or capacity
   Select Penetration ability on ice
   Select Penetration ability on compacted snow
   Select Ability to undercut or break the bond between ice/snow and the pavement
   Select Ability to prevent bonding between ice/snow and the pavement
   Select Effective temperature range
   Select Eutectic temperature (and concentration)
   Select Residual characteristics
   Select Other (write in):
   Select Other (write in):

   Comments:

2. For each of the performance attributes listed above, should a scale or pass-fail criterion be used for test results? For example, assume the melting ability for a chemical was tested and found to be 2.2 grams of ice melted per gram of chemical. Should this number be compared to a pass-fail relationship (such as pass if result exceeds 1.5) or should the number be compared to a scale (such as "Great" if higher than 3, "Good" between 2 and 3, "Acceptable" between 1 and 2, and "Unacceptable" below 1)? Select your response below (Click on "Select").
   If something other than a scale or pass-fail should be used, please elaborate in the Comments section.

   Select Melting ability or capacity
   Select Penetration ability on ice
   Select Penetration ability on compacted snow
   Select Ability to undercut or break the bond between ice/snow and the pavement
   Select Ability to prevent bonding between ice/snow and the pavement
   Select Effective temperature range
   Select Eutectic temperature (and concentration)
   Select Residual characteristics
   Select Other (write in):
   Select Other (write in):

   Comments:

3. Which of the following laboratory tests has your agency performed (internally or with an outside contract)? If used, please indicate if the test procedure was modified. Otherwise, indicate if you have never heard of the test. Check all boxes that apply.

Test Method	Have used	Currently use	Modified Procedure	Don't use	Never Heard of
SHRP H-205.1 Test Method for Ice Melting of Solid Deicing Chemicals	☐	☐	☐	☐	☐
SHRP H-205.2 Test Method for Ice Melting of Liquid Deicing Chemicals	☐	☐	☐	☐	☐
SHRP H-205.3 Test Method for Ice Penetration of Solid Deicing Chemicals	☐	☐	☐	☐	☐
SHRP H-205.4 Test Method for Ice Penetration of Liquid Deicing Chemicals	☐	☐	☐	☐	☐
SHRP H-205.5 Test Method for Ice Undercutting by Solid Deicing Chemicals	☐	☐	☐	☐	☐
SHRP H-205.6 Test Method for Ice Undercutting by Liquid Deicing Chemicals	☐	☐	☐	☐	☐
Anti-Bonding Endurance Test (Transport Canada, Airports Group)	☐	☐	☐	☐	☐
ASTM D 1177 Standard Test Method for Freezing Point of Aqueous Engine Coolants	☐	☐	☐	☐	☐
Other (please specify)	☐	☐	☐	☐	☐
Other (please specify)	☐	☐	☐	☐	☐

Comments:

4. For each of the tests indicated in Question 3 that you have used or currently use, please rate in terms of the test's usefulness, reliability, and ease of implementation for measuring and comparing the performance of deicing and anti-icing chemicals. Select your response below from the following options (Click on "Select").

"Not useful at all"	"Not reliable at all"	"Not easy at all"
"Not useful"	"Not reliable"	"Not easy"
"Somewhat useful"	"Somewhat reliable"	"Somewhat easy"
"Useful"	"Reliable"	"Easy"
"Very Useful"	"Very Reliable"	"Very easy"

Test Method	Usefulness	Reliability	Ease of implementation
SHRP H-205.1 (Ice Melting, solid)	Select	Select	Select
SHRP H-205.2 (Ice Melting, liquid)	Select	Select	Select
SHRP H-205.3 (Ice Penetration, solid)	Select	Select	Select
SHRP H-205.4 (Ice Penetration, liquid)	Select	Select	Select
SHRP H-205.5 (Ice Undercutting, solid)	Select	Select	Select
SHRP H-205.6 (Ice Undercutting, liquid)	Select	Select	Select
Anti-Bonding Endurance Test (Transport Canada, Airports Group)	Select	Select	Select
ASTM D 1177 Standard Test Method for Freezing Point of Aqueous Engine Coolants	Select	Select	Select
Other (please specify)	Select	Select	Select
Other (please specify)	Select	Select	Select

Please provide additional comments, such as advantages or specific drawbacks of particular tests:

5. What effects of deicing and/or anti-icing chemicals would your agency most want to know before applying the chemical on roadways? Please rank all that apply, choosing from the following options (click on "Select"):
   "Not important at all"
   "Not important"
   "May be important"
   "Important" or
   "Very important"

Select	Impact on friction of road surface
Select	Safety and special handling instructions
Select	Corrosion to rebar embedded in concrete
Select	Scaling of concrete
Select	Effect to Alkali-Silica Reaction (ASR) in concrete
Select	Corrosion to bare/unpainted metal
Select	Corrosion to vehicles
Select	Impact to asphalt pavements (softening or hardening)
Select	Impact to soil and vegetation
Select	Impact to water quality and aquatic organisms
Select	Other (please specify):
Select	Other (please specify):

Comments:

Please provide your name, title, agency, phone number and e-mail address so that if we have further questions we may contact you. We are specifically interested in learning about why a test method may have been dropped if this was indicated in Question 3.

Name and Title:

Agency:

Phone:

E-mail:

Thank you for your time!

Please email the completed survey to Dr. Xianming Shi, P.E. at xianming_s@coe.montana.edu; or fax at 406-994-1697. Thanks!

APPENDIX C: TEST PROTOCOLS

DSC Thermogram Test Protocol

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 a laboratory 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, and useable results. The DSC machine used for test method development was a TA Instruments Q200.

Method

1. Deicer Preparation: To test liquid deicers, collect a sample of product 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 equal to the eutectic concentration of the deicer. Dilute the initial sample with deionized water at a ratio of 3:1 (i.e., water:deicer = 2:1 by volume). A convenient method is to combine 10 mL of deionized water with 5 mL of deicer.

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

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

4. Replication: Conduct the DSC test for at least three replicate samples of deicer. Based on the variation (in analysis portion), more tests may be needed.

Analysis

1. Integration: Isolate and integrate the peak in the warming cycle on the thermogram to determine heat flow (J/g) and peak temperature. Depending upon 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.

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

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

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

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

Where

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

T_i is peak temperature (°F) for test i

n is number of replicate tests

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

Interpretation

The DSC test provides two levels of interpretation:

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.

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:

$$IMC_{30^\circ \mathrm{F}}(\text{mL brine}) = -4.476 - 0.0288T + 3.83\log(\Delta H) \quad \left(\mathrm{R}^2 = 0.90\right)$$

$$IMC_{15^\circ \mathrm{F}}(\text{mL brine}) = 9.027 - 0.1009T - 2.54\log(\Delta H) \quad \left(\mathrm{R}^2 = 0.94\right)$$

Where:

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

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

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

Modified SHRP Ice Melting Test Protocol

The modified protocol is similar to the standards SHRP H205.1 “Test Method for Ice Melting of Solid Deicing Chemicals” and H205.2 “Test Method for Ice Melting of Liquid Deicing Chemicals” in the Strategic Highway Research Program’s *Handbook of Test Methods for Evaluating Chemical Deicers* (Chappelow et al., 1992). The primary modifications are:

- Smaller ice sample and deicer application
- Increased number of replicates conducted during one test
- A control to indicate success or failure of the experiment
- Reduced sampling frequency

The Modified SHRP Ice Melting Test needs to be conducted in a walk-in temperature-regulated environmental chamber or upright freezer modified with access portals. Specifications for these can be found in Annex 1 and Annex 2 of Appendix B in the *Handbook of Test Methods for Evaluating Chemical Deicers* (Chappelow et al., 1992).

Materials

1. Petri dishes: Four standard 100mm x 15mm (outer dimensions) sterile plastic (polystyrene) Petri dishes, with lids. The average inside diameter of the Petri dish should be 3.356 in.

2. Timers or stop watches: Four timers or stop watches

3. Deionized water

4. Syringe: Two clear plastic syringes with disposable metal tip

5. Graduated cylinders: Two 10-mL graduated cylinders, One 25-mL graduated cylinder

6. Pipette: Pipette capable of applying 0.90 mL of liquid

7. Scale: Scale capable of reading to the nearest 0.1 g

8. Blow torch

9. Metal tool for smoothing ice: A circular metal tool that fits in the Petri dish and can be heated

Method

1. Ice Preparation: Pour 25 mL of deionized water into each of the four Petri dishes and cover with lids. Freeze water at the testing temperature, 30°F, 15°F, or 0°F. Heat the metal tool with the blow torch and melt the ice surface. Swirl the dish to evenly distribute the melted water. Cover dish and re-freeze. This should produce a smooth ice surface. If it is still wavy or has ice protrusions, melt the surface again and re-freeze.

2. Deicer Preparation: If testing liquid deicers, use full-strength samples intended for field application. This could be solutions containing one solute, or blends of various liquid deicers, including blends incorporating agricultural by-products. Don't dilute the solutions beyond what is applied in the field. Isolate at least 10 mL of a representative sample and place in a sealed container with the ice samples to equilibrate to the testing temperature. Also place the pipette and disposable pipette tips in the testing area. If testing solid deicers, collect at least 10 g of a representative sample of sieved material that passed the No. 6 sieve and was retained on the No. 8 sieve. Measure 1.0 g of the deicer and place in a sealed container with the ice samples to equilibrate to the testing temperature.

3. Control sample Preparation: Prepare a solution of 23% NaCl by dissolving 23.0 g NaCl in about 60 mL of deionized water. Once dissolved, add deionized water until the total volume is 100 mL. This control batch can be used for many ice melting tests if it is in a sealed container and shaken prior to extracting each portion. Also place this sample adjacent to the ice specimens to equilibrate to the testing temperature.

4. Begin Test:

   a. Apply control deicer to ice: To begin the test, extract 0.90 mL of the control (23% NACl) and apply to the surface of an ice sample. Activate one timer when the control is applied. The Petri lid dish should be left off at this point.

   b. Apply test deicer to ice: When the first timer indicates 1–2 minutes have elapsed, activate a second timer when applying the test deicer to a different ice specimen. If testing liquid deicers, shake the sample, and extract 0.90 mL of deicer and apply to the ice. If testing solid deicers, distribute the 1.0 g sample as evenly as possible over the ice surface. When the second timer indicates 1–2 minutes have elapsed, apply the test deicer to another ice specimen. Continue until three ice specimens are exposed to the test deicer.

5. Measure 20-Minute Brine Volume: Use one syringe and 10-mL graduated cylinder for the control specimen and a different syringe and cylinder for the test deicer.

   a. Control: When the timer associated with the control reads 20 minutes, use the syringe to collect all the melted brine. The ice sample can be tipped to allow the brine to collect to one area to facilitate this process. Empty the contents of the syringe into a graduated cylinder and record the volume of brine to the nearest 0.05 mL. Pour the brine from the cylinder back onto the ice surface. This entire process should be completed within 1 minute.

   b. Test samples: When the timer associated with the first test sample reads 20 minutes, collect the melted brine (using a different syringe than was used for the control specimen). If testing solid deicers, cavities usually form in the ice; be sure to extract all the brine formed in each cavity. Again, empty the contents of the syringe into the graduated cylinder used for the test deicers and record the brine volume to the nearest 0.05 mL. Pour the brine from the cylinder back on the ice surface. For solid deicers in which cavities formed in the ice, distribute the brine into the cavities to match the distribution present prior to collecting the brine, as closely as possible. This entire process should be completed within 1 minute and should be performed with each ice sample exposed to the test deicer when the time indicates 20 minutes.

6. Measure 60-Minute Brine Volume: Repeat steps 5a and 5b when each timer indicates 60 minutes, except the brine doesn't need to be re-applied to the ice.

7. Clean Up: The Petri dishes, ice and deicer can be discarded. The graduated cylinders and syringes should be cleaned before using the items for another test

Analysis

1. Success/Failure Based on Control Specimen: Compare the brine volume collected after 60 minutes of exposure to the control deicer to the values in Table A-1. If the measured volume of brine is within the acceptable range, then continue the Analysis. If not, the test should be repeated.

Table A-1. Acceptable Range of Control in Modified SHRP Ice Melting Test

Temperature (°F)	Volume of brine at 60 minutes (mL)
30	3.1 to 4.0
15	0.8 to 1.2
0	0.1 to 0.5

2. Calculations: Calculate the average and standard deviation of the 20-minute and 60-minute brine volumes associated with the three test deicer specimens. If the average brine volume is at least 1.0 mL (≥1.0 mL), then also calculate the coefficient of variation. The average and standard deviation should be reported to the nearest 0.1 mL; and the coefficient of variation to the nearest percent.

$$V_{avg,\,20} = \frac{\sum_{i=1}^{3} V_{i,\,20}}{3} \qquad V_{avg,\,60} = \frac{\sum_{i=1}^{3} V_{i,\,60}}{3}$$

$$V_{stdev,\,20} = \sqrt{\frac{1}{2}\sum_{i=1}^{n}\left(V_{i,\,20} - V_{avg,\,20}\right)^2} \qquad V_{stdev,\,60} = \sqrt{\frac{1}{2}\sum_{i=1}^{n}\left(V_{i,\,20} - V_{avg,\,60}\right)^2}$$

$$V_{cov,\,20} = \frac{V_{stdev,\,20}}{V_{avg,\,20}} \times 100\% \qquad V_{cov,\,60} = \frac{V_{stdev,\,60}}{V_{avg,\,60}} \times 100\%$$

Where

$V_{i,\,20}$ is the volume (mL) of brine collected on ice specimen i after 20 minutes

$V_{i,\,60}$ is the volume (mL) of brine collected on ice specimen i after 60 minutes

3. Success/Failure Based on Variation of Test Deicer: The test needs to be repeated if the measures of variation are too high. If $V_{cov} \geq 15$ percent or if $T_{stdev} \geq 0.3$ mL for either the 20-minute or 60-minute measurements, then the test needs to be repeated. If the test meets the criteria for acceptable levels of variation, report the average and standard deviation or coefficient of variation (as appropriate) for the brine volumes at 20 and 60 minutes.

4. Reporting: If the test is considered successful, report the average brine volume and either the standard deviation or the coefficient of variation.

Supplement to Final Report

The Final Report states that the tests "should not be used to predict actual field performance," which runs counter to Clear Roads original stated goal of helping agencies to predict performance. How would you frame this to the snow and ice community to help them see the usefulness of these tests?

The tests can be used to predict relative field performance of a deicer and should be used in the context of a well-known product, such as sodium chloride. The tests do not provide the information needed to determine how much chemical to apply to a snow or ice covered road. This excerpt from the SHRP *Handbook*[1] is important to keep in mind:

> "The utility of most of the test methods [including the Ice Melting Test] will be enhanced when the test results are compared to the test results obtained for conventional deicing chemicals. Either sodium chloride or calcium chloride should be used as control or reference materials because they are the principal components of the most widely used chemical deicer formulations. Laboratory tests are designed to evaluate stated characteristics under controlled, specified conditions, and in most cases, to provide comparative data over an accelerated time interval. Although reasonable attempts have been made to reconcile these approaches with actual field materials and conditions, some differences remain. After initial evaluations in the laboratory, field testing is ultimately required to determine acceptable deicer performance and compatibility."

You have indicated that the lab tests are likely to have considerable variation between labs, which may present challenges to us in implementing these as "standard tests" that are considered valid by all parties. You have suggested Round Robin tests between labs, but how likely is that to convince a vendor or the rest of the Snow and Ice community of the repeatability? Are there additional comments you could add that might help those with less education in Chemistry to understand the value of these tests?

A Round Robin test would quantify the amount (or lack) of repeatability and to identify/address certain details currently not specified in the test procedures that may contribute to any inconsistency between different laboratories. We found good repeatability in our laboratory in terms of the DSC and modified SHRP ice melting tests. Nonetheless, ASTM standards are widely used in many industries and every standard requires a statement regarding the test method's Precision and Bias (new standards need the statement within five years). There is even a standard that describes how to conduct an interlaboratory study (these involve several labs) to determine the precision of the test method (ASTM E691). According to ASTM, at least six laboratories should be used, but fewer than six can participate because "the bottom line is that some precision information is preferable to no precision information[2]." Because of this, we feel a Round Robin test would help increase user acceptance and confidence of the snow and ice community in the repeatability and reproducibility of the test methods. Nonetheless, an alternative approach to Round Robin test would be to have the testing community peer exchange every a few years to compare notes and fine-tune the existing test method.

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[1] Chappelow, Cecil C., A. Dean McElroy, Robert R. Blackburn, David Darwin, Frank G. de Noyellas, and Carl E. Locke. Handbook of Test Methods for Evaluating Chemical Deicers. Strategic Highway Research Program Report No. SHRP-H-332, 1992.

[2] Picariello, Pat. "Fact vs. Fiction: The Truth about Precision and Bias." ASTM Standardization News, March 2000. Online http://www.astm.org/SNEWS/MARCH_2000/P&B_mar00.html

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