

Understanding the Salt Phase Diagram

Final Report

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Executive Summary

The objective of this project is to aid winter maintenance practitioners as they make informed decisions on the use of the road salt sodium chloride (NaCl), commonly known as rock salt, solar salt, or salt brine, by providing them with materials that outline what occurs in a NaCl solution at varying temperatures and concentrations. Key information was identified in a detailed literature review and a follow-up laboratory investigation monitored ice formation and salt precipitation for various concentrations of sodium chloride (NaCl) brines at varying temperatures, mimicking what may be observed at different points on the NaCl phase diagram. A one-page fact sheet and educational video were developed, using the results of the laboratory tests and literature review, with the intent that they inform winter maintenance practitioners on the use and application of salt phase diagrams.

Salt phase diagrams are a great source of information for understanding the chemistry of NaCl solutions (brines) and provide key information such as the eutectic point, which is the temperature at which a mixture may melt or freeze, and the solubility limit, or maximum concentration of a solute that can be completely dissolved in a solvent without forming a precipitate. Phase diagrams also help users identify which deicer type or deicer blend will meet their environmental needs (e.g., temperature). While the published domain contains information on NaCl phase diagrams and eutectic curves, much of it is targeted at the scientific and engineering communities and lacks sufficient explanation of the concepts in language that can be widely understood. The project's [one page fact sheet](#) and [educational video](#) were developed to fill this gap.

The educational video includes excellent footage of ice and salt crystal formation that was collected during the project's lab tests; however, insufficient ice crystal data and a variety of other issues prevented further analysis. Detailed ice crystal formation results could provide significantly more information on the use of NaCl brines and their use as road salt. This project will serve to provide lessons learned for future NaCl research.

Key findings

Images of ice crystals with bubbles, potentially filled with salt brine, indicates that the solid phase of ice crystals and salt crystals is not pure, implying that many phases can co-exist. This reinforces the concept that the ice formed in the presence of the salt brine is weaker than ice formed only in presence of pure water.

When measuring pavement friction following the application of salt brine at various concentrations, the results varied between pavement type, salt concentration, and friction measurement technique. There is value in further refining this, or another, performance test method to assess the influence of salt brine concentration on pavement friction.

Knowledge gaps and future research idea are presented. Specifically, the application of advance imaging techniques like Raman microscopy, scanning electron microscopy (SEM), x-ray fluorescence (XFR), and nuclear magnetic resonance (NMR) spectroscopy and reflection infrared spectroscopy to better ascertain the chemistry and physics, and specifically the kinetics, of water, ice, and salt/salt brine interactions.

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Introduction

The purpose of this project is to aid winter maintenance practitioners as they make informed decisions on the use of the road salt sodium chloride (NaCl) – commonly known as rock salt, solar salt, or salt brine, by providing them with materials that outline what occurs in a NaCl solution at varying temperatures and concentrations. These end products include a [one-page fact sheet](#) and [educational video](#) that contain information captured in the literature review and lab testing.

Methods

Literature Review

A literature review collected information on various NaCl deicing products, NaCl deicing use guidelines, phase diagram testing protocols, past research efforts in the lab and field, and the use of friction data in deicer testing methods. The review also uncovered preexisting salt phase diagrams, as well as fact sheets, images, and video-based resources, by utilizing the following databases: Transportation Research Information Database (TRID), Google Scholar, Institute of Scientific Information (ISI) Web of Science, and Montana State University (MSU) Library resources.

Laboratory Testing

Beaker Test

The beaker test was developed to further clarify the NaCl phase diagram by measuring ice crystal formation and salt precipitation in solutions of varying concentrations and temperatures. A clearer and more detailed phase diagram may aid agency personnel as they seek to understand and use the diagram in their winter maintenance work.

Testing was conducted in multiple cold rooms at Montana State Universities [Subzero Research Laboratory](#) (SRL) located on the Bozeman, Montana campus.

The first step in the testing process was to store salt brines at 35 degrees Fahrenheit (°F) (Cold room A), then cool them to their test temperatures (-6°F to 32°F) (Cold room B). A total of eight brine concentrations, 21 to 28 NaCl by percent weight (wt.%), were tested at -6, 0, 5, 10, 15, 20, 25, and 32°F, respectively. High-definition photography and stereomicroscope images were then used to identify differences in ice formation for each brine concentration and temperature (Cold room C).

A summary of the experimental procedure is described in Figure 1. Each step in the test procedure is further explained in the body of this report.

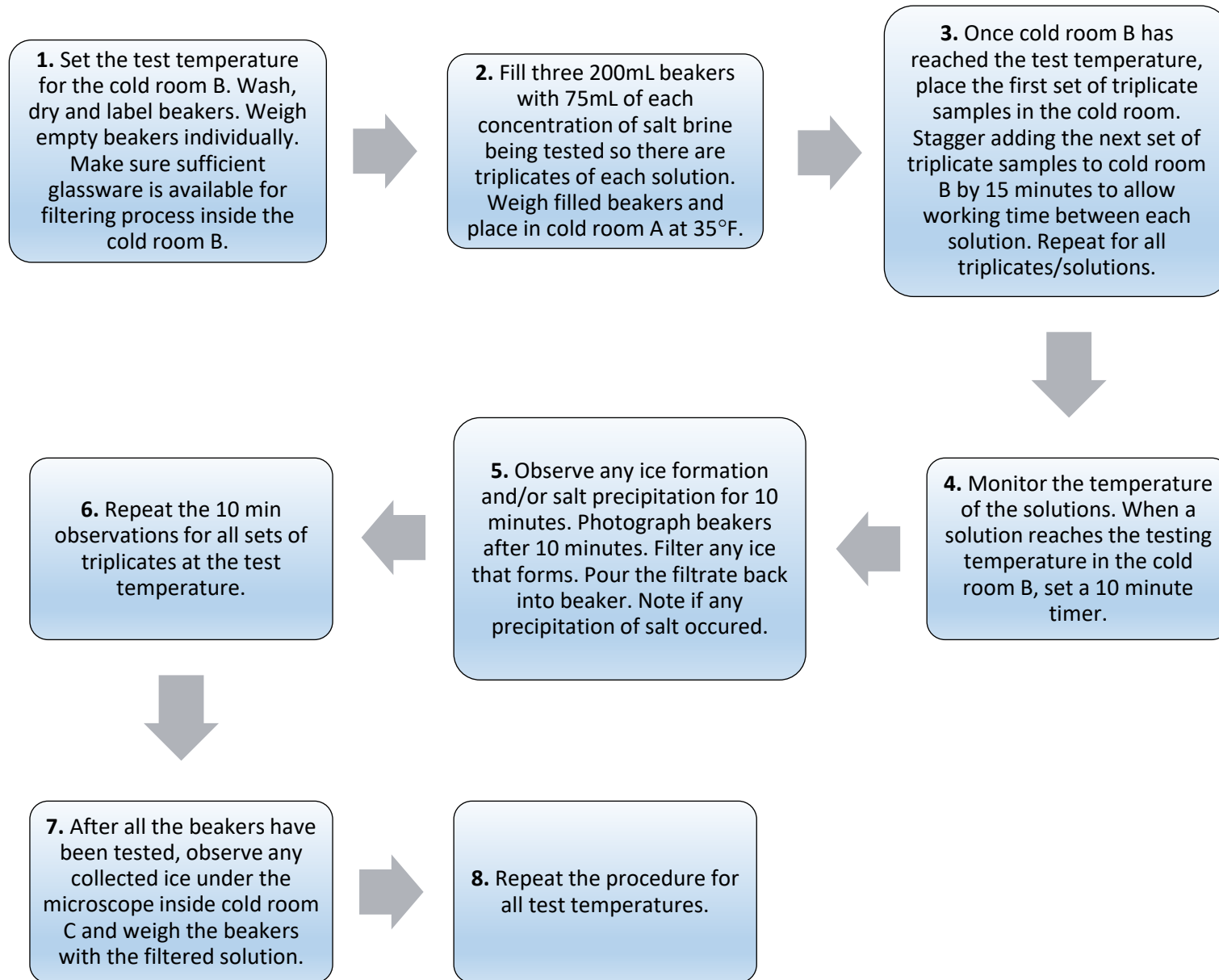


Figure 1. Flow chart describing the laboratory testing procedure.

Additional details on the lab testing procedure:

1. Cold rooms needed to be set at the desired temperatures. Targeted testing temperatures ranged from -6°F (-21°C) to 32°F (0°C). All solutions were made in bulk so each concentration was identical for each testing temperature. Each solution (NaCl 21 wt.%, 22%, 23.3%, 24%, 25%, 26%, 27%, 28% by weight) was made in a 2500 mL flask using deionized (DI) water and reagent grade crystalline NaCl. To avoid precipitation of NaCl and ice formation, solutions were stored at temperatures at 25°F and above (cold room A). After making each solution, the flasks were covered with parafilm to prevent evaporation and contamination.
2. Prior to testing, the beakers were cleaned, labeled (A-1, A-2, A-3, etc.), and weighed. Filtering flasks and filters (Figure 2) were cleaned and staged in the cold room (cold room B).
3. Twenty-four 200mL beakers were required for each test temperature to allow for triplicate samples of each of the eight NaCl brine concentrations (21%, 22%, 23.3%, 24%, 25%, 26%, 27%, 28% by weight) (Table 1). Each 200 mL beaker was filled with 75mL of solution and then weighed. To decrease the amount of cooling time required during the experiment the solutions were stored in a cold room A at 35°F.
4. Sampling for each triplicate set was staggered by 15 minutes to allow time for filtering and photography of each triplicate set of solutions (Figure 3). In addition to this, an additional 4 minutes were added in-between moving the second and third beaker of each triplicate from cold room A to the cold room with the correct test temperature (cold room B). Such that, if the beaker A-1 was added at 0 minutes, A-2 was then added at 4 minutes, and A-3 was then added at 8 minutes. Samples were filtered when ice formation was observed in the beaker. The time to ice formation varied by temperature. Photographs were taken of each beaker regardless of the presence of ice or salt precipitation. The timing of staggering samples was used for all triplicate solutions at all test temperatures.
5. A thermometer with 0.10-degree accuracy was placed in the solution during testing to monitor the temperature of each triplicate. Each set of triplicates of a solution acclimated for 10 minutes at the cold room temperature (cold room A). The thermometer was cleaned before reusing it in different brine concentrations to avoid contamination.
6. 10 minutes after the triplicate beakers reached the test temperature, each beaker was observed for ice formation and/or salt precipitation and photographed. Any visible ice was filtered out by pouring the solution onto either a perforated funnel or filter paper/funnel arrangement (Figure 2). The filtration method used varied based on ice crystal size, with the smaller ice crystals requiring filter paper. The filtrate was then poured back into the beaker and weighed. If any NaCl precipitation was present it was noted. This was repeated for all solution triplicates.
7. Metallic tweezers were used to transfer the filtered ice from the perforated funnel or filter paper and an aluminum dish that was acclimated to the test temperature. Images were taken on aluminum dishes which allowed for better quality photographs than the paper or funnel.

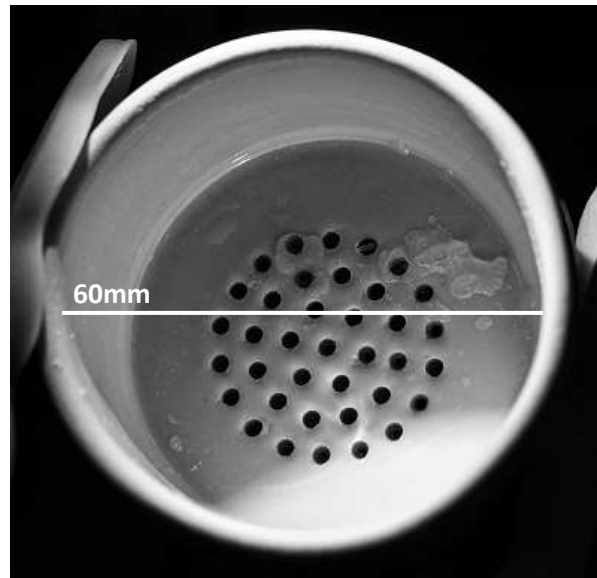


Figure 2. Ice crystals were retained using the 60 mm perforated funnel (approximate hole size 3 mm).

8. After each triplicate of solutions was photographed and filtered, the ice crystals were viewed and photographed with a high-powered microscope (WILD M5A) in cold room C. This stereomicroscope had a maximum magnification of 50 times and the eyepiece magnification was set to 1.25 times. A digital camera was attached to the microscope to take pictures.
9. Steps 1-7 were repeated for all testing temperatures (-6, 0, 5, 10, 15, 20, 25, 32°F) and NaCl solution concentrations.

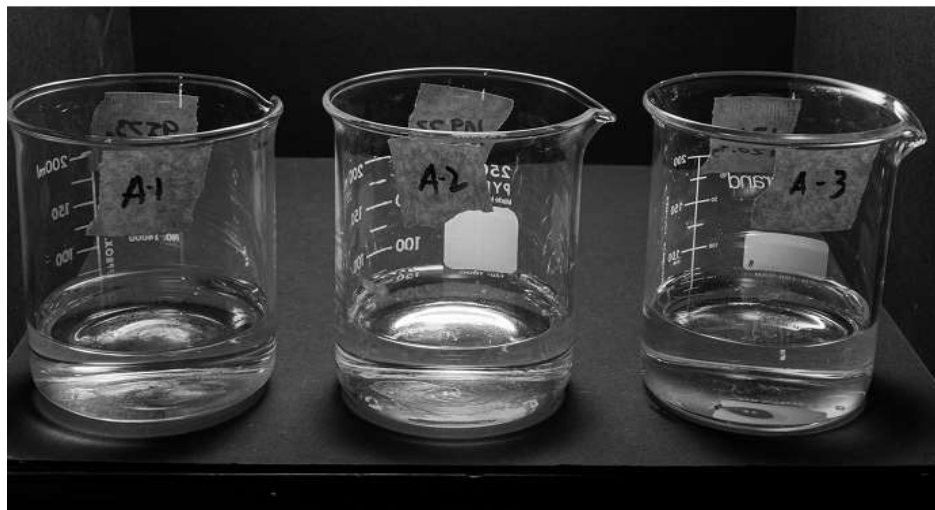


Figure 3. Triplicate samples of NaCl brine solution A (21 wt.% NaCl).

Table 1. Beaker testing design and labeling of solution concentrations.

Brine Solutions Concentrations	Designations	Triplicate Labeling
21 wt. %	A	A-1, A-2, A-3
22 wt. %	B	B-1, B-2, B-3
23.3 wt. %	C	C-1, C-2, C-3
24 wt. %	D	D-1, D-2, D-3
25 wt. %	E	E-1, E-2, E-3
26 wt. %	F	F-1, F-2, F-3
27 wt. %	G	G-1, G-2, G-3
28 wt. %	H	H-1, H-2, H-3

Friction Testing

The friction test was designed to compare pavement surface friction values when different NaCl solutions were applied as anti-icers (read: liquid deicing products applied to the pavement surface prior to precipitation). This section summarizes the anti-icer testing process using the Trafficking Machine in the MSU SRL in Bozeman, Montana. Each trafficking test takes 1.5 to 2 hours, which includes cleaning the Trafficking Machine after the test is complete. The time required to test different anti-icers and deicers varies depending on application rates and the duration and type of measurements being recorded.

First, pavement surface friction values were measured using a pull-test device (Akin et al., 2020) and a non-contact friction sensor, the Teconer RCM411. The pull-test device dragged a rubber-bottomed, weighted block across a pavement sample and the peak force, or the highest amount of force required to move the pull-device horizontally, was recorded. The peak force was then divided by the weight of the block to determine the static friction measurement. The pull-tests were repeated three times in three randomly selected locations along the trafficked area of the sample.

In addition to the friction pull-test, pavement friction measurements were collected using a Teconer RCM411 optical sensor, which used spectral analysis to measure surface condition at 1-second intervals. As the Trafficking Machine moved the pavement samples back and forth, the position of the Teconer sensor is modulated across the width of the sample area to allow for randomized data collection across the entirety of the trafficked area of the pavement. This gives an average reading over the entire sample surface. While the Teconer sensor friction values were not the focus of this study, they provided a useful comparison to the pull-test friction measurements and related the results to other published values.

Friction measurements from both the pull-test and Teconer sensor were collected on 1) bare pavement, 2) pavement with an application of NaCl brine, 3) compacted snow, 4) trafficked snow, and 5) snow-plowed pavement.

Pavement Samples

Two pavement types were used in this experiment: concrete, and asphalt. Pavement was made at MSU using Montana Department of Transportation (MDT) [design specifications](#); one cubic yard (m³) of MDT concrete consists of 689 pounds (lb) (17%) water, 1,556 lb (38%) concrete, 877 lb (22%) sand, and 940 lb (23%) stone. The concrete samples were formed and then cured in a humidity chamber for 28 days prior to use. The asphalt samples were also made to [MDT specifications](#).

Anti-icer Solutions

Eight different NaCl brine solutions were made using reagent grade fine-grain NaCl (solid) and DI water. A summary of the concentrations and their weights can be found in Table 2. A spray bottle was used to apply a fine mist of solution over the pavement. The nozzle was calibrated for each solution concentration so that a specific weight was applied with each spray for an overall application of 45 gallons per lane mile (gal/l-m). Every effort was made to evenly apply the NaCl solutions across the entire pavement surface.

Table 2. Summary of the salt brine solution made.

Wt. % NaCl	NaCl (g)	DI water (g)	45 gal/l-mi (g)
21	84	316	16.63
22	88	312	16.98
23.3	93.2	306.8	17.14
24	96	304	17.17
25	100	300	17.34
26	104	296	17.44
27	108	292	17.51
28	112	288	17.53

Snow Application

Snow was made in the SRL at MSU (Akin et al., 2020) and stored at 15°F in the cold chamber with the Trafficking Machine. The snow was then filtered through a 1 mm mesh screen to remove any snow or ice chunks and the snow density was measured before each trafficking test. Following screening, 0.5 in of snow was applied to the top of the pavement surface within five minutes of the NaCl solution application. The snow was placed on the sample to create a consistent, flat surface that simulated a 0.5 in snowfall event. The snow was then evenly compacted using a 0.25 in steel plate placed across the entire sample. The Trafficking Machine tires were then lowered onto the steel plate until 30 pounds per square inch (psi) was applied; the machine was then run for two minutes. Next, the down force of tires on the steel plate was increased to 60 psi, the equivalent of about 3,000 lbs of total downward force or 1,500 lb of downward force per tire, and the Trafficking Machine was run for an additional two minutes. Following this, the Trafficking Machine was stopped, the tires were lifted, and the steel plate was removed to reveal the compacted snow sample (Figure 4). Following compaction, the snow depth was approximately 0.25 in. The snow application and compaction process was repeated for all samples.



Figure 4. Trafficking machine in the Sub-Zero Research Lab showing (left) the tires lifted above the compacted snow sample and (right) and close up of the compacted snow sample.

Trafficking

Following snow compaction, the tires were then lowered and allowed to run over the sample, or traffic the sample, for 500 passes, or 26.6 minutes, at a trafficking rate of 56.7 ft/min. The downward force of the tires on the samples was set at 15 psi, or 750 pounds of downward force, or 375 lb per tire, during testing.

The full length of each pavement sample was trafficked by at least one tire during the testing (red) but because the tires of the Trafficking Machine are in line the middle section was consistently trafficked by two tires (green) (Figure 5). All measurements were collected from the middle section (green) of the pavement sample where it was trafficked by two tires, to ensure consistency.



Figure 5. Pavement sample with trafficked snow showing where one tire (red) versus two tires (green) traffic the sample.

Plowing

Following trafficking of the snowy pavement samples, the snow was plowed off the pavement. A plowing device was created to simulate a vehicle-mounted snowplow, using a plow angle of 69° and weight of 10.92 lb (Figure 6). A four-inch area of snow was removed from one end of the pavement sample so that the plow could be placed directly on the sample surface. The plow was then pulled across each pavement surface one time and a picture was taken. If large chunks of snow and ice remained on

the pavement surface following plowing additional weight was added to the blade and another pass of the plow was used to help remove the leftover material from the pavement surface.



Figure 6. Close up of the plow device showing the metal cutting edge of the “plow” blade.

Summary of Trafficking Procedure

Below is the step-by-step testing and measurement process for this lab experiment.

1. **Control:** Place pavement sample on the Trafficking Machine and collect friction data by recording three pull-test measurements. Run the Trafficking Machine for one minute and record data using the Teconer sensor.
2. **Anti-icer Application:** Pull pavement sample off the Trafficking Machine and apply the NaCl brine solution at 45 gal/l-m. After the anti-icer solution is applied, collect friction data by recording three pull-test measurements. Place the pavement sample back on the Trafficking Machine and record Teconer measurements for one minute.
3. **Compact Snow:** Apply snow and compact with a steel plate and the Trafficking Machine. Collect friction data by recording three pull-test measurements on top of the compacted snow. Collect friction data from the Teconer for one minute (by running the Trafficking Machine with the tires up).
4. **Trafficking:** Compress tires down onto the compacted snow at 15 psi and run the Trafficking Machine for 500 passes or 26.6 minutes. Record Teconer measurements during the entire trafficking process. After trafficking is complete, raise the tires off the sample, remove the sample from the Trafficking Machine, and collect friction data by recording three pull-test measurements.
5. **Plowing:** Pull plow across the pavement surface to remove the snow then collect friction data by recording three pull-test measurements on the plowed pavement surface. Place the sample back in the Trafficking Machine and run it with the tires up and record Teconer measurements for one minute.

Data Analysis

An Analysis of Variance (ANOVA) test was used to compare the various NaCl solutions using their pull-test and Teconer friction measurements in relation to salt concentration, snow density, and relative humidity. In addition, the individual friction measurements were compared using a Tukey Honest Significant Difference (HSD) test. This process makes simultaneous comparisons for all the pairwise combinations of NaCl solutions using a simple t-test and reports the probability of obtaining the observed results (p-value) for each comparison. The HSD also creates a 95% confidence interval for each difference in mean friction values between samples of different NaCl concentrations. The intervals are based on the studentized range distribution which estimates the population group variance from the collected measurements.

One Page Fact Sheet

A One Page Fact Sheet was developed to help winter maintenance practitioners make informed decisions on the use of NaCl-based road salts at varying temperatures and concentrations. It focuses on understanding and applying the NaCl phase diagram and contains information captured in the literature review and laboratory testing.

Educational Video

An Educational Video was developed to help winter maintenance practitioners make informed decisions on the use of NaCl-based road salts at varying temperatures and concentrations, and provides an in depth, but understandable, look at the application of the salt phase diagram. Information captured in the literature review, laboratory testing, and one-page fact sheet was used to develop this deliverable.

Literature Review Summary

Background

Sodium Chloride – Freezing Depressant for Water

Pure water freezes at 32°F (0°C) but the addition of chemicals that contain water-soluble ions can prevent freezing at that temperature. Once the ions are free, they fill the space between the water molecules, separating them, as illustrated in Figure 7, and ensuring that they are irregularly arranged. This maintains a liquid state and prevents the water molecules from forming an ordered arrangement, or the solid state known as ice. **The magnitude of freezing-point depression, or reduction in the freezing temperature of water, is directly proportional to the number of non-water ions (read: sodium and chloride) in the water solution.** For example, NaCl contains two ions (Na and Cl) that release when mixed with water while CaCl_2 (1 Ca and 2 Cl) has three. The freezing-point depression caused by a single CaCl_2 molecule (three ions) will be 1.5 times greater than that caused by a NaCl molecule (two ions) because the CaCl_2 molecule has added 1.5 times the number of ions to the water. Other fundamental characteristics of these ions, such as size, may cause further freezing-point depression.

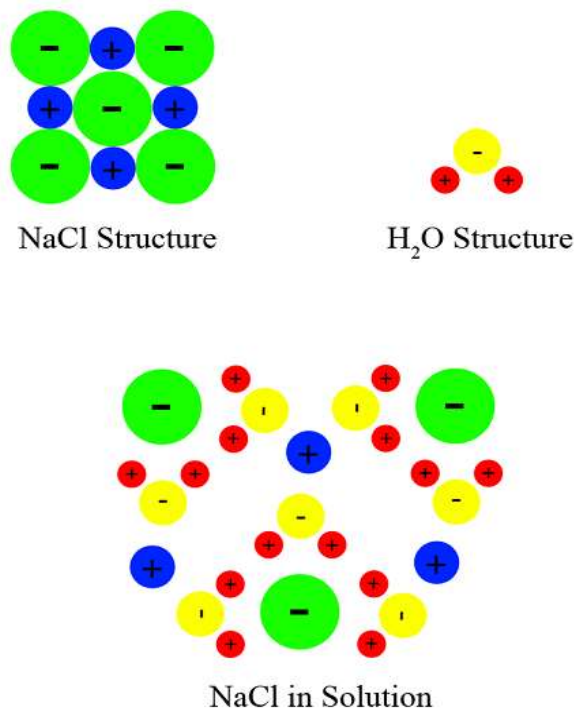


Figure 7. Sodium Chloride (NaCl) ions in a water solution [Guthrie and Thomas, 2014]

Brine, or saltwater solution, has a lower freezing temperature than pure water. This is because dissolved salt disrupts the dynamic equilibrium of ice and the water molecule surface. By adding salt to water, more liquid state water molecules are required to maintain equilibrium in the brine solution, thus causing ice to change states from solid to liquid, starting the melting process (Guthrie and Thomas, 2014).

To further convey this point, Figure 8 shows freezing point depression curves for various chloride-based deicers. As the number of dissolved deicer molecules increases the freezing point of the solution decreases. For example, as NaCl (the blue line in Figure 8) particles in solution increase from zero to approximately ten moles, the freezing point decreases from 0 to approximately -4°F (-20°C).

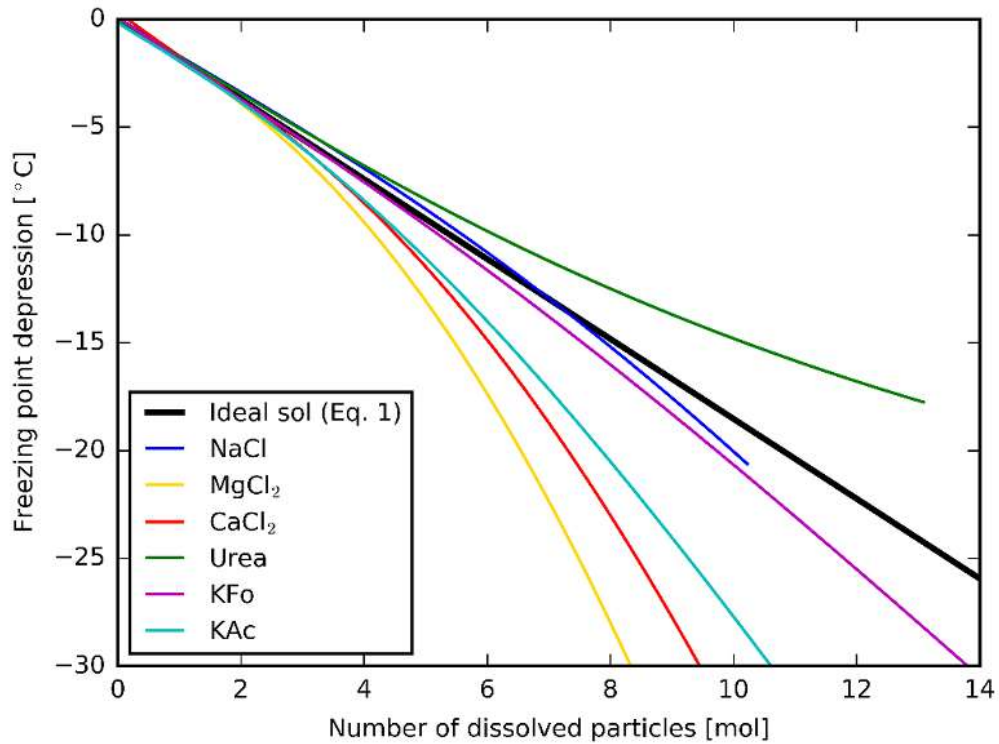


Figure 8. Freezing point depression curves for various deicers (Wåhlin et al., 2017).

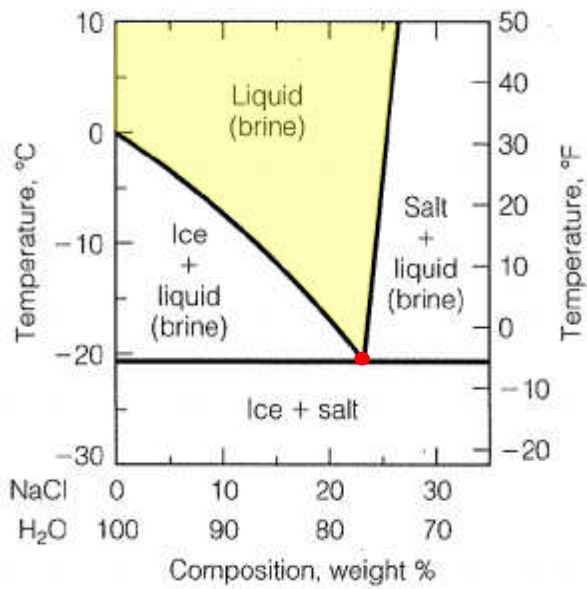
Definition of Terms

Phase Diagram

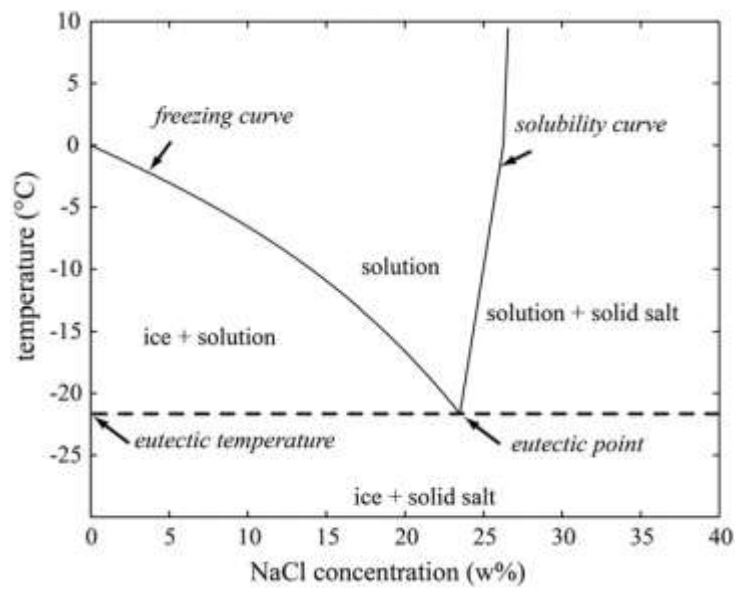
A **phase diagram** is the graphical representation of the physical states of a substance at varying temperatures and concentration. The NaCl phase diagram has temperature reported on the vertical (y-axis) and concentration reported on the horizontal (x-axis) (examples provided in Figure 9A, B, C, and D). The bold lines shown in Figure 9A denote temperature and concentration as the NaCl solution changes from:

- Liquid (brine) - liquid salt brine (water and salt in solution together),
- Ice + liquid (brine) – pure water ice crystals in a liquid salt brine solution,
- Salt + liquid (brine) – pure salt crystals in a liquid salt brine solution,
- Ice + salt - pure water ice crystals and pure salt crystals all in solid form.

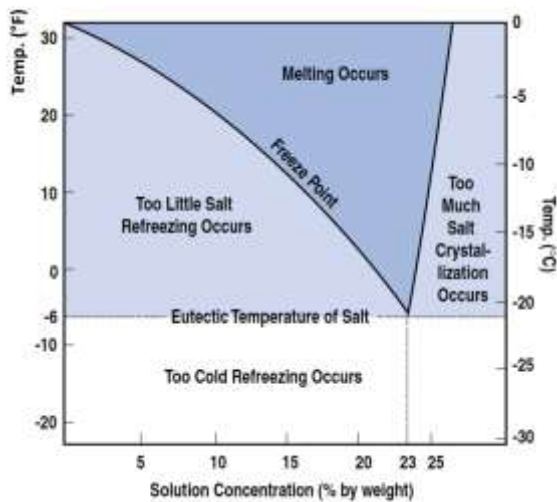
A



B



C



D

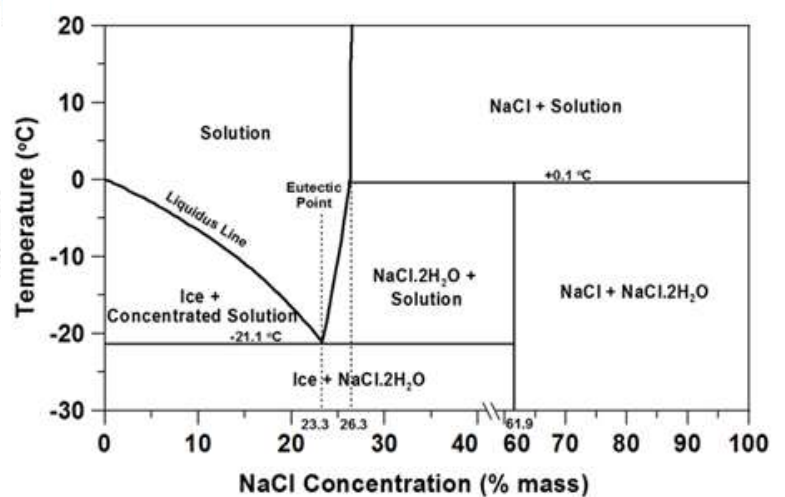


Figure 9. A) Salt phase diagram (<https://d2vlcm61l7u1fs.cloudfront.net/media%2F96e%2F96ef982e-81a2-47a8-a7c3-3c170649ee4d%2FphpIKInDF.png>), B) The NaCl-water phase diagram featuring its eutectic curve (Klein-Paste and Wählin, 2013), C) phase diagram for salt brine (republished in Du et al., 2019, originally from Salt Institute (2016), D) eutectic phase diagram for aqueous sodium chloride, indicating eutectic concentration, solubility limit and important phases or components forming upon cooling brine at various temperatures (Farnam et al., 2014)

Eutectic Temperature and Eutectic Point

The yellow area in Figure 9A represents the liquid phase for a NaCl brine within a concentration range of 0 to 30% and is the target area for use in winter maintenance operations. The coldest temperature at which the brine can remain a liquid corresponds with a concentration of 23.3% and a temperature of approximately -6°F (-21°C). This is called the **eutectic temperature**, or the lowest possible melting temperature for a eutectic mixture. This temperature also corresponds with the **eutectic point** (the red dot in Figure 9A), or the temperature and concentration at which all allowable phases (liquid and solid for a NaCl and water mixture) may occur and are in equilibrium. Any change in concentration or temperature will result in a loss of equilibrium and a phase shift.

Effective Temperature

Typically, the lower the eutectic point, the better the deicing or anti-icing performance. However, while eutectic temperature indicates the lowest temperature at which NaCl brine can remain a liquid, the effectiveness of a deicer is reduced well before temperatures reach the eutectic point. For this reason, NaCl (in solid or liquid form) is rarely used below the **effective temperature**, or the temperature at which the concentration is half the eutectic concentration, which corresponds to 11.65% and 18°F (Du et al., 2019). The effective temperature can be influenced by external factors including pavement type and condition, intensity of precipitation, traffic volume, and solar radiation as well as the salt's solubility limit of in water at room temperature. Note that the effective temperature must be determined for each deicer type and blend, including other chloride-based deicers.

Solubility Curve

By shifting right of the eutectic point and increasing salt concentration in Figure 9A, B, C, & D, it is clear that temperature must also rise to prevent salt from precipitating out of the solution. This relationship is known as the **solubility curve** (Figure 9B) and represents the solubility of NaCl, or maximum amount that will dissolve in pure water, at a given temperature. Figure 9D also indicates that a NaCl brine solution cannot exceed a concentration of 23% before hydrohalite ($\text{NaCl} \cdot 2\text{H}_2\text{O}$) becomes present and 26.4% before anhydrous NaCl precipitates. Therefore, adding extra salt to “boost” a 23% salt brine solution will not improve the brine performance but instead cause the extra salt to crystallize out of solution.

The phase diagrams are developed by plotting solution freezing points at different concentrations and the salt brine phase diagrams shown in Figure 9A, B, C, D were developed using the same approach. The standard method used is American Society for Testing and Materials (ASTM) D1177. Another source describing guidelines for deicer testing is the Handbook of Test Methods for Evaluating Chemical Deicers (SHRP-H-332), which provides a test method to find the eutectic temperature for salt (Chappelow et al., 1992).

Research

The purpose of this section is to demonstrate how winter maintenance operators can use eutectic points, phase diagrams, and freezing curves to make informed decisions about salt brine concentration functionality at changing temperatures. Information is presented from several research sources with published salt phase diagrams, many of which show three components referred to as ternary phase diagrams. For a deeper understanding of sodium chloride consult Kaufmann (1968).

Phase Diagrams

When discussing eutectic curves and phase diagrams, a key concept to understand is that as the mass percentage of NaCl in brine is increased, the temperature at which the first water crystal forms decreases until the eutectic point is reached (El Kadi and Janajreh, 2017). This is illustrated in the freezing curve (curve 1) of Figure 10, where moving to the right increases salt concentration and decreases the temperature required for ice to form. Curve 2 of Figure 10 shows the solubility curve for salt going into solution and curve 3 is the eutectic temperature curve, above which liquid brine is present with ice or salt crystals. The area below the eutectic temperature curve indicates that solids are present: solid salt (NaCl) and solid water (ice). At the eutectic point (blue dot), all liquid and solid conditions can be present.

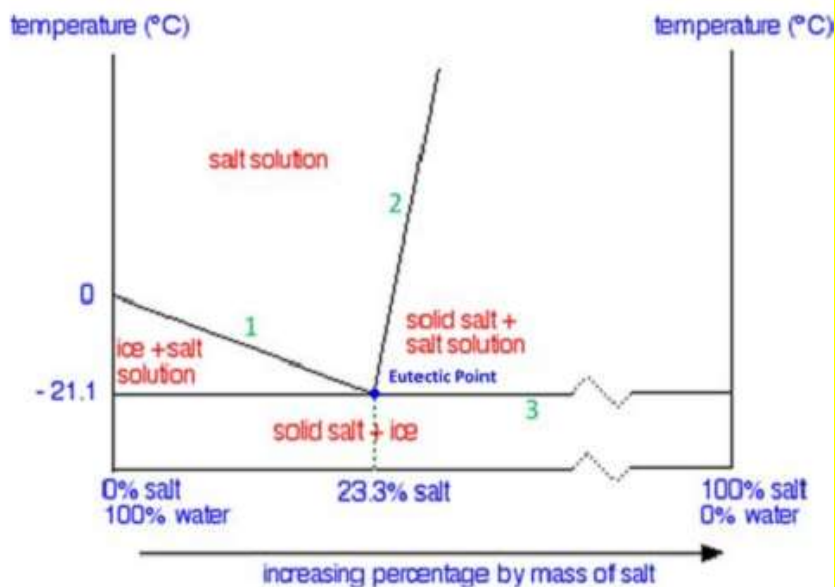


Figure 10. Variations in freezing temperature for NaCl with increasing percentage by mass (El Kadi and Janajreh, 2017).

For example, the freezing point of sea water, which is 3.5 wt. % salt, is approximately 28.5°F (-2°C). This is the temperature at which ice crystals of pure water begin to nucleate; they will continue growing as the temperature drops further (El Kadi and Janajreh, 2017).

Figure 11 shows a phase diagram for various deicers - MgCl_2 (magnesium chloride), NaCl, CaCl_2 (calcium chloride), CMA (calcium magnesium acetate), and KAc (potassium acetate). The freezing curves for MgCl_2 and CaCl_2 are much steeper (or reach colder temperatures) than NaCl, indicating that less MgCl_2 or CaCl_2 would be required to achieve the same level of ice melting performance at the same temperature. However, when all three deicers are in liquid form, they have similar refreeze characteristics (Luker et al., 2004).

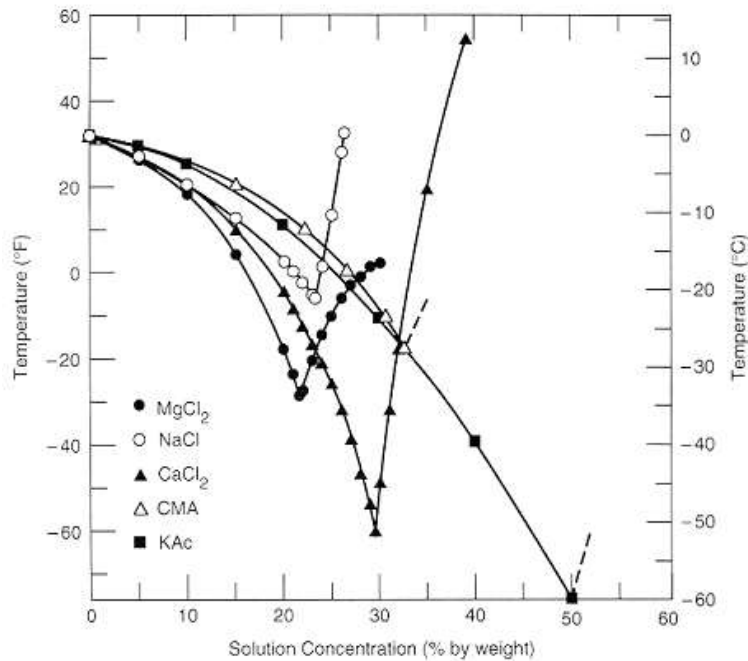


Figure 11. Phase Diagram of various deicing chemicals (Luker et al., 2004)

The phase diagrams for NaCl and CaCl₂ are provided in Figure 12 and show that the eutectic temperature for CaCl₂ solution is lower than that of NaCl brine. This information can help winter maintenance operators when choosing which deicer to use at a given temperature (Ketcham et al., 1996).

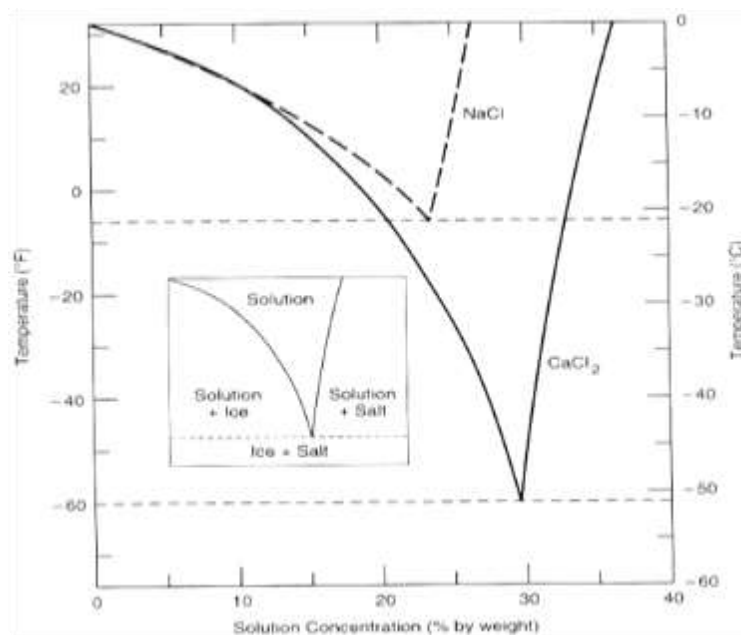


Figure 12. Salt Phase Diagram for NaCl and CaCl₂, with eutectic points (Ketchum et al., 1996).

Phase diagrams play an important role in understanding the Water, Ice and Salt (WIS) model, developed by Dan et al. (2020), that calculates “the time change of the salt solution temperatures, of the mass of water, ice, and salt on the road surface after salt application.” The experimental process used in the WIS model also developed (Figure 13), which indicates that the rate of ice melting (phase change) increases significantly, then slows down during the deicing process; the change in salt solution temperature follows a similar pattern (Dan et al., 2020). At 21 minutes ($t=21\text{min}$), the salt is completely dissolved. Prior to $t=21\text{min}$, the temperature of the solution decreases rapidly due to the heat flux created by the salt dissolution and ice melting. After $t=21\text{ min}$, the solution temperature gradually increases as the rate of ice melt slows and heat from the environment begins to transfer into the salt solution. This process is shown in the phase diagram of Figure 14 where the transition from A to B indicates a shift from ice with solid salt present to a salt brine solution, or **the deicing process**. As more ice melts, the salt brine concentration decreases until it refreezes, shown as the transition from B to C. When applying this process in the field, deicing ends when the solution concentration (salt brine concentration) reaches its freezing point (Dan et al., 2020).

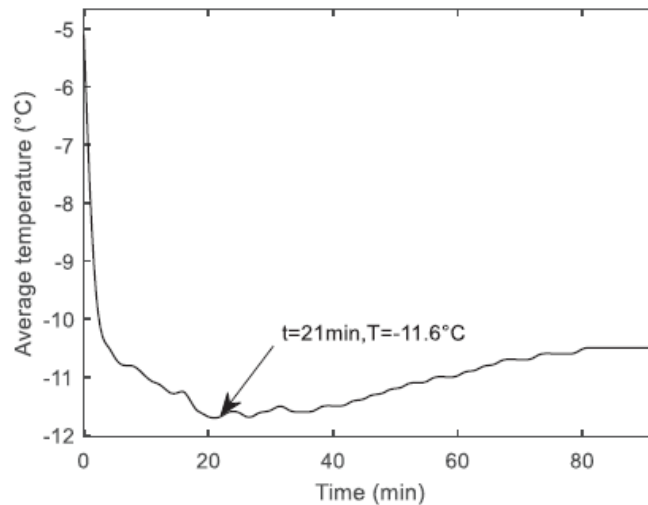


Figure 13. The variation of salt solution average temperature at a test temperature of -5°C (23°), 3 meters per second (m/s) wind speed, and 30 grams of solid salt (Dan et al., 2020).

The amount of road salt required for application, given the air temperature, wind speed, and ice thickness, can be calculated within a reasonable degree of error using the WIS model developed by Dan et al. (2020). However, the WIS model was developed using air temperature as a key variable, rather than pavement temperature, which is more often used in winter maintenance operations. Winter maintenance operators should consider this when calculating salt quantities using WIS.

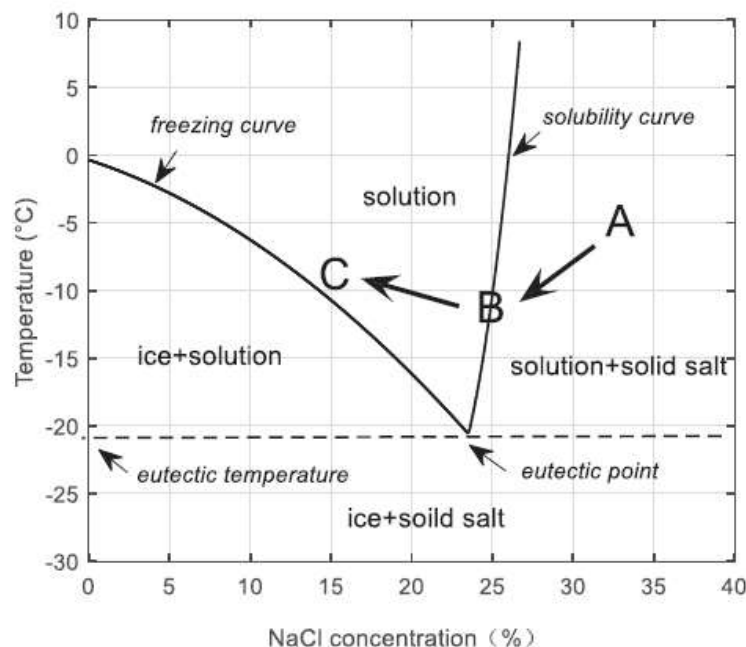


Figure 14. Phase diagram of NaCl in water (Dan et al., 2020).

Křepelová et al. (2010) developed a phase diagram using X-ray photoelectron spectroscopy (XPS) and near-edge X-ray absorption fine structure (NEXAFS) spectroscopy to study the surface chemical composition and hydrogen bonding of a frozen NaCl solution. The phase diagram shows the different phase transitions of the NaCl-H₂O system plotted using temperature, reported in Kelvin (K), and percent relative humidity (RH) (Figure 15); triangles (▲) and stars (★) define the experimental conditions, thick solid lines show the transition between test stages, the numbers represent the order of the experiments, and the thin lines show where the equilibria for solid and liquid phases occur. The dash single-dotted and dash double-dotted lines define the liquid-to-solid phase transition temperature where point E (circled in red in Figure 15) is the eutectic point and brine and NaCl·2H₂O (solid) are in equilibrium. The dashed gray lines represent the region in which brine is in the form of a metastable liquid, or where supercooling¹ can occur (Křepelová et al., 2010).

In the experiment used to develop Figure 15, 0.3 mg of NaCl was placed in a spectroscopy chamber and then water was gradually introduced. It was observed that under freezing conditions, a layer of salt brine (NaCl + water) formed on the surface of the ice with a brine composition that corresponded to that of salt solution (Křepelová et al., 2010). The surface chemistry of the ice, below the eutectic temperature, followed the NaCl·2H₂O phase shown in Figure 15.

¹ Supercooling or undercooling is the state in which a material remains a liquid at a temperature below its freezing temperature or solidification point.

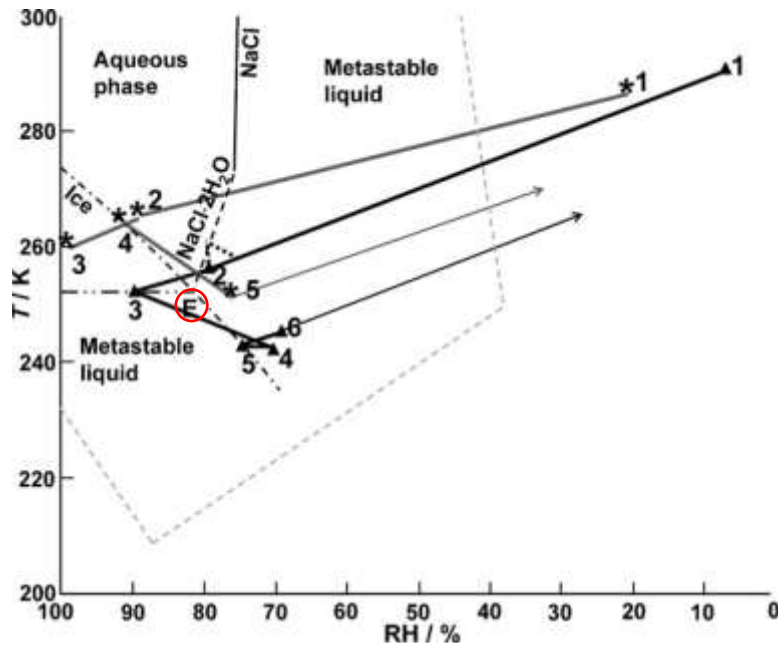


Figure 15. Phase diagram of NaCl–H₂O system. Points ▲1–6 show the first series of experiments and points ★1–5 represent the second series of experiments (Křepelová et al., 2010).

Work by Ma et al. (2019) used automatic icing pressure equipment to study the cooling process of chloride solutions (Figure 16) by examining the freezing point depression and undercooling (i.e., supercooling) degree of chloride-based deicers. During the freezing process, the formation of an ice nucleus from liquid solution requires a driving force, expressed as the Gibbs free energy change (ΔG), or the maximum amount of work that can be obtained from thermodynamic potential energy in a closed system, which is associated with the degree of undercooling (ΔT). In this case, a reaction will start when the Gibbs free energy is less than zero ($\Delta G < 0$), but when Gibbs free energy is greater than zero ($\Delta G > 0$) a reaction does not occur.

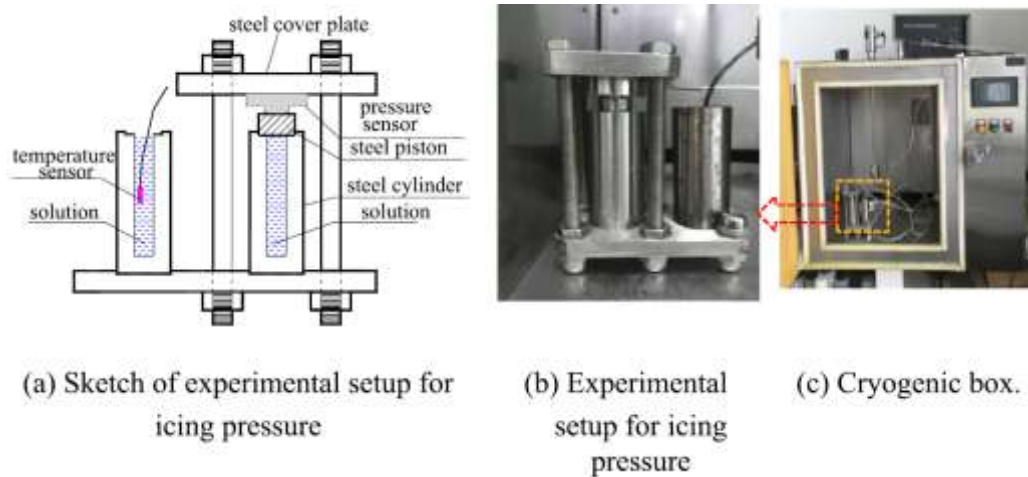


Figure 16. The device used by Ma et al. (2019) to plot the freezing curves of chloride solutions.

The following equation can be used to calculate Gibbs free energy (ΔG) (Ma et al., 2019):

$$\Delta G_V = \Delta H - T\Delta S \quad (\text{Eq. 1})$$

ΔH is the change in enthalpy (total heat content of a system), T is absolute temperature, and ΔS is the melting entropy (the degree of disorder) of ice (solid phase).

Once the solution is frozen, the following equation can be written (Ma et al., 2019):

$$\Delta G_V = G_L - G_S \quad (\text{Eq. 2})$$

Where ΔG_V is Gibbs free energy change, G_L is Gibbs free energy of salt water (liquid phase), and G_S is Gibbs free energy of ice (solid phase).

Combining Eq. 1 and Eq. 2, Eq. 3 can be achieved (Ma et al., 2019):

$$\Delta G_V = H_L - H_S - T(S_L - S_S) \quad (\text{Eq. 3})$$

By applying constant pressure to a system that is in the freezing stage, the Gibbs free energy change becomes zero ($\Delta G_V = 0$). Then, the term " $H_L - H_S$ " can be considered ΔH_P , so the following equation can be implemented (Ma et al., 2019):

$$(S_L - S_S) = \Delta H_P / T_0 \quad (\text{Eq. 4})$$

Where T is designated T_0 , or the temperature when the freezing process occurs. When $\Delta G < 0$ (Ma et al., 2019) the equation becomes:

$$\Delta G_V = \Delta H_P (T_0 - T) / T_0 < 0 \quad (\text{Eq. 5})$$

Where T is the solution temperature. If we consider $\Delta T = T_0 - T$, then Gibbs free energy will be less than zero ($\Delta G < 0$) when $\Delta T > 0$. This means that the temperature of T must be less than T_0 to perform the freezing process. ΔT is defined as the undercooling degree that is associated with the cooling rate and concentration of the solution. Therefore, it can be concluded that **when the freezing point is reached, the heat of phase conversion is completely released** (Ma et al., 2019). The cooling curves for 3.5% and 10% chloride-based solutions are shown in Figure 17. In addition, thermodynamic parameters for different chloride-based solutions and water are listed in Table 3, where it becomes clear that the order of ΔT of chloride-based solutions is $\text{CaCl}_2 > \text{NaCl} > \text{MgCl}_2$.

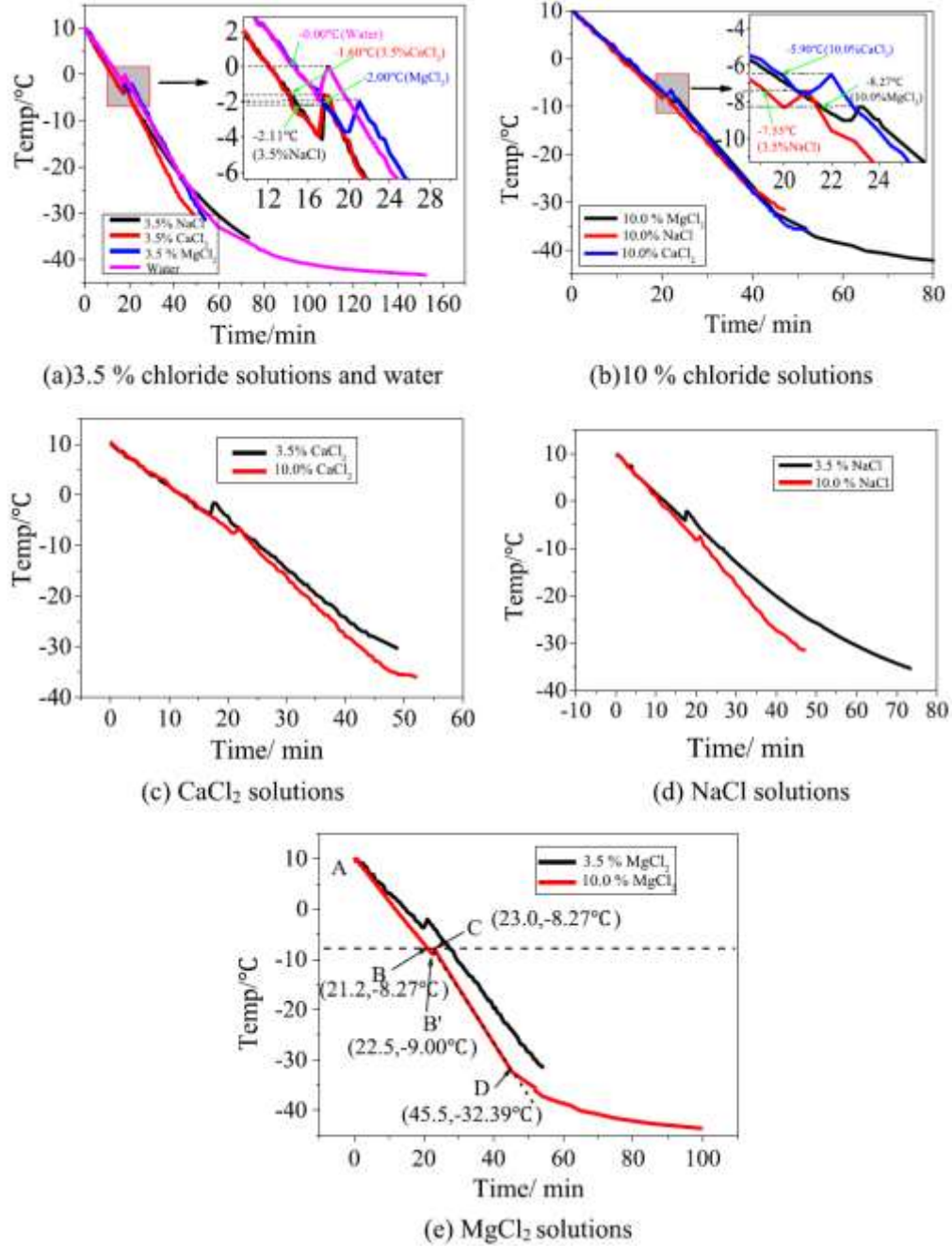


Figure 17. Cooling curves of various chloride-based solutions (Ma et al., 2019).

Table 3. Thermodynamic parameters for chloride-based solutions (Ma et al., 2019) where T_0 indicates freezing temperature and ΔT is degrees of undercooling.

Solution	NaCl		CaCl_2		MgCl_2		Water
Concentration/%	3.5	10.0	3.5	10.0	3.5	10.0	0.0
$T_0/^\circ\text{C}$	-2.11	-7.15	-1.60	-5.9	-2.00	-8.27	0.00
$\Delta T/^\circ\text{C}$	2.01	0.92	2.34	1.65	1.69	0.73	1.92

Note that phase curves for commercial sources of deicers can, and will, differ from their pure chemical equivalents because of the presence of other chemical additives. Therefore, when using blended chemical deicers, it is appropriate to generate phase curves for each product using the test procedure ASTM D1177, rather than relying on the standard phase curves (Levelton Consultants, 2007).

Ice Melting Capacity (IMC)

Numerous research studies have shown that the freezing behavior of salt brine is correlated with its ice melting capacity, and from this relationship the effective temperature for NaCl deicers can be determined. The following section provides summaries of research into the use of ice melting capacities and their potential to ascertain deicer performance.

Druschel (2012) evaluated the **ice melting capacity (IMC)** of several commercial deicers used by Minnesota Department of Transportation (MnDOT) (Table 4). The IMC is the amount of liquid brine that results from the melting of a certain amount of ice, divided by either the mass of solid deicer or volume of liquid deicer used. IMC units are reported as either mL brine/g deicer for solids or mL brine/mL deicer for liquids. The deicers used by Druschel (2012) were divided into two main groups: 1) Brine Blends, and 2) Stockpile Treatments. These groups are described below and in Table 4 and their measured ICMs are shown in Table 5:

Salt Brine Blends:

- Articlear Gold (20%)
- Calcium Chloride (10%, 20% and 30%)
- LCS (10% and 20%)
- Univar ICE BITE (10%, 20% and 30%)

Rock Salt Stockpile Treatments:

- FreezeGard Zero Chloride (6 gallons/ton)
- GEOMELT 55 (6 gallons/ton)
- IceBan 200M (6 gallons/ton)
- RGP-8 (6 gallons/ton)
- SOS (3 and 6 gallons/ton)
- Univar ICE BITE (6 gallons/ton)

Druschel's research indicated that the IMCs of Stockpile Treatments are not more than those of rock salt between 5°F and 30°F. The IMC of rock salt is as low as 1 mL/g at 8°F and as high as 8 mL/g at 30°F. In the temperature range of 5 – 30°F, the IMCs of some Stockpile Treatments are higher than the IMC of rock salt, but the difference is not large enough to be considered significant. Interestingly, the IMCs of many Stockpile Treatments are less than that of rock salt, implying less ice melting ability, but other benefits of these deicing treatments include reduced impact on motor vehicles, infrastructure, and the environment. However, residual benefits on the roadway, such as better adhesion to the pavement surface or colored products creating post-application visibility, were not captured by IMC test method (Druschel, 2012).

IMCs are relatively constant at a certain temperature in a wide range of application rates (3 – 30 gallons/ton) (Table 5). Therefore, increasing the application rate of Stockpile Treatments in that range does not improve the overall performance. Note that 6 gallons/ton is the typical application rate

recommended by the vendors and due to the low additive rate (re: stockpile treatment) of approximately 2.5%, it is reasonable to expect that any change to the IMC will not be significant (Druschel, 2012).

In contrast to Stockpile Treatments, Brine Blends have significantly higher IMCs because of secondary components at higher proportions, with IMCs of up to 4mL/mL. In the range of 0 to 30% additive (re: stockpile treatment), gains were observed in IMCs up to 2 mL/mL. This improvement likely occurred because the additive increased the total deicer quantity; if the additive components dissolved in the brine, more deicer ions were available to react with ice upon contact. As with individual compounds, the IMCs of saline mixtures are strongly correlated with application temperature (Druschel, 2012).

Druschel (2012) identified four factors that may influence deicer performance.

1. Deicer bounce and scatter: a characteristic of solid deicer failing to stay on the road surface.
2. Deicer penetration: the vertical melting ability of a deicer through ice and snow.
3. Deicer undercutting: the transverse, or lateral, melting ability of deicer on the surface of the pavement under the ice and snow after the penetration.
4. Deicer grain size: a secondary factor in which the particle size of the deicer may affect bounce, penetration, or shear reduction.

Of these four factors, **grain size made a statistically significant difference in deicer performance** (Druschel, 2012).

Table 4. Deicers used by Druschel et al. (2012), with active components as mentioned by the seller.

Deicer	Main Component	Secondary Component(s)	Company/ Manufacture
District 7 Rock Salt	NaCl	none	North American Salt
Salt Brine	NaCl (23.3%)	none	North American Salt
Blanche Rock Salt	NaCl	none	North American Salt
CaCl	CaCl	none	Tiger Calcium
Alpine Ice Melt	Potassium Acetate	Potassium Acetate	Scotwood Industries
AP Liq Deicer	MgCl ₂	not provided/none	Envirotech
Meltdown Apex	MgCl ₂	Corn based modifier	Envirotech
Apogee Non-Cl	Not Cl (possibly carbohydrate based)	not provided	Envirotech
Articlear Gold	MgCl ₂	Molasses or Sugar beet	North American Salt
CF-7	50% Potassium Acetate	Corrosion Inhibitors	Cryotech Technologies
Clearlane Enhanced	29% MgCl ₂	not provided	Cargill
Freezegard Zero	MgCl ₂	Corn based modifier	Scotwood Industries
Geomelt 55	55% sugar beet	not provided	SNI Solutions
Geomelt S	55% sugar beet	Salt Brine	SNI Solutions
Ice Ban 200M	28% MgCl ₂	Corn based modifier	Scotwood Industries
Ice Slicer Granular	Complex Cl's	Trace minerals (sulphur, iron, zinc, iodine)	Envirotech
LCS 5000	Corn salt	none	Envirotech
NAAC (pellets)	97% Sodium Acetate	none	Cryotech Technologies
RGP-8	26.5% CaCl	3.1% MgCl ₂ 2.2% other Cl	Tiger Calcium
SOS	Mg ₂ Cl	none	Envirotech
TC Econo	2% CaCl MgCl ₂	20% NaCl Brine	Tiger Calcium
Thawrox MG Plus	26% MgCl ₂	Corn based modifier	North American Salt
Thawrox MG Clear	26% MgCl ₂	Corn based modifier	North American Salt
Univar Ice Bite	Sugar beet	not provided	Univar

Table 5. Ice melt capacities in mL brine/g deicer or mL brine/mL deicer as interpreted from laboratory results (Druschel, 2012).

Temperature° F	Rock Salt	Clearlane Enhanced	SDS @ 6 gal/ton	Thawrox Gold Treated	Ice Slicer	Ice Bite @ 3 gal/ton	Salt Brine	AP Liquid Deicer	Articlear Gold	Freezeguard	Ice Ban 200M	Meltdown Apex	TC Econo	Thawrox Gold Alternative	Calcium Chloride	RGP-8	Geomelt 55	Geomelt Gen 3	LCS 5000	Ice Bite
30	10.0	11.5	11.5	10.8	7.5	9.9	3.9	6.4	3.6	7.2	4.8	5.1	4.5	5.0	6.1	5.4	3.5	4.0	2.7	12.7
25	8.0	6.5	6.9	8.7	6.6	8.2	2.8	5.2	2.9	5.1	4.0	3.6	3.3	3.5	4.6	2.6	2.2	2.1	1.3	5.8
20	5.8	4.6	5.2	6.9	5.7	7.0	2.1	4.2	2.2	3.7	3.2	3.2	2.4	2.8	3.5	2.0	2.2	2.0	1.2	4.5
15	3.9	3.6	4.2	5.4	4.5	5.0	1.6	3.1	1.9	2.8	3.0	2.7	1.6	2.3	2.7	2.1	1.6	1.2	1.0	4.2
10	2.0	3.2	2.3	3.1	2.4	2.4	1.2	2.0	1.4	2.0	2.3	2.1	1.7	1.9	1.9	2.2	1.5	1.4	0.8	4.0
5	3.4	3.0	3.2	4.3	2.2	2.0	1.5	2.8	1.0	1.4	1.4	3.9	1.8	1.3	1.2	1.3	1.5	1.5	0.3	3.8
0	0.01	2.0	2.0	0.01	0.01	0.01	0.01	2.3	1.0	1.7	1.3	2	1.5	1.3	0.01	1.7	0.01	1.6	0.01	0.01
-5	0.01	0.4	0.3	0.01	0.01	0.01	0.01	1.8	1.0	1.7	1.3	1.8	1.2	1.3	0.01	1.3	0.01	0.3	0.01	0.01
-10	0.01	0.01	0.01	0.01	0.01	0.01	0.01	1.8	1.0	1.7	1.3	1.6	0.8	1.3	0.01	1.8	0.01	0.8	0.01	0.01
-15	0.01	0.01	0.01	0.01	0.01	0.01	0.01	1.8	1.0	1.7	1.3	1.5	0.8	1.3	0.01	1.8	0.01	1.3	0.01	0.01
-20	0.01	0.01	0.01	0.01	0.01	0.01	0.01	1.8	1.0	1.7	1.3	1.5	0.8	1.3	0.01	1.8	0.01	1.3	0.01	0.01
-25	0.01	0.01	0.01	0.01	0.01	0.01	0.01	1.8	1.0	1.7	1.3	1.5	0.8	1.3	0.01	1.8	0.01	1.3	0.01	0.01
-30	0.01	0.01	0.01	0.01	0.01	0.01	0.01	1.8	1.0	1.7	1.3	1.5	0.8	1.3	0.01	1.8	0.01	1.3	0.01	0.01

NCHRP 577 *Guidelines for the Selection of Snow and Ice Control Materials to Mitigate Environmental Impacts* provides a discussion of the **melting potential (MP)** that can be applied to blended chemicals and is calculated using the following equation (Levelton Consultants, 2007):

$$MP = BC/EC - 1 \quad (\text{Eq. 6})$$

Where BC is beginning concentration (% w/w), the applied concentration for liquid chemicals and saturated concentration for solid chemicals, and EC is ending concentration (% w/w). *MP evaluates the performance of deicing chemicals independent of their application rates.* It also considers that only soluble chemicals can melt ice. However, BC values used in the Eq. 6 must be smaller than the saturation limit; otherwise, it biases the calculated MP values. The saturation limits of some common deicers are provided in Table 6.

Table 6. Saturation limit of common deicers (Levelton Consultants, 2007).

Chemical	Percent Solution at Saturation
NaCl	26.28 % at 0°C (32°F)
CaCl ₂	36.70 % at 0°C (32°F)
MgCl ₂	33.96 % at 0°C (32°F)
CMA	NA
KA (KC ₂ H ₃ O ₂)	68.40 % at 0°C (32°F)

The MPs for five NaCl-based deicers were generated using their phase curves and are provided in Table 7. Melting potentials help illustrate the effectiveness of deicers at varying temperatures. For instance, if the BC for NaCl brine is 23.3% by weight, the EC at 30°F (-1.1°C) will be only 1.9 wt. %, resulting in the highest MP (11.3 wt. %) possible for a 23.3 % NaCl brine. Then, if temperature decreases, the EC for this brine increases and MP decreases, until the eutectic point of -6°F (-21.1°C) is reached and the MP becomes zero (Levelton Consultants, 2007).

Table 7. MP examples for commonly used deicers (Levelton Consultants, 2007).

Temperature		NaCl		Ca Cl ₂		Mg Cl ₂		KAc		CMA	
		BC (%) = 23		BC (%) = 32		BC (%) = 30		BC (%) = 50		BC (%) = 25	
°F	°C	EC (%)	M P	EC (%)	M P	EC (%)	M P	EC (%)	M P	EC (%)	M P
30	-1.1	1.9	11.3	2.5	11.7	2.1	13.4	5.0	9.0	5.0	4.0
29	-1.7	2.8	7.2	3.7	7.7	3.0	8.9	6.0	7.3	6.0	3.2
28	-2.2	3.7	5.2	4.8	5.7	3.9	6.7	7.0	6.1	7.0	2.6
27	-2.8	4.6	4.0	5.7	4.6	4.7	5.4	8.0	5.3	8.0	2.1
26	-3.3	5.4	3.2	5.7	4.6	5.3	4.7	9.0	4.6	9.0	1.8
25	-3.9	6.3	2.7	6.4	4.0	6.0	4.0	10.0	4.0	10.0	1.5
24	-4.4	7.1	2.2	7.0	3.6	6.7	3.5	11.0	3.5	11.0	1.3
23	-5.0	7.9	1.9	8.0	3.0	7.3	3.1	12.0	3.2	11.9	1.1
22	-5.6	8.7	1.7	9.0	2.6	8.1	2.7	13.0	2.8	12.7	1.0
21	-6.1	9.4	1.4	9.5	2.4	8.6	2.5	13.5	2.7	13.5	0.9
20	-6.7	10.1	1.3	10.0	2.2	9.0	2.3	14.0	2.6	14.4	0.7
19	-7.2	10.8	1.1	10.5	2.0	9.5	2.2	15.0	2.3	15.0	0.7
18	-7.8	11.5	1.0	11.0	1.9	10.0	2.0	16.0	2.1	15.8	0.6
17	-8.3	12.2	0.9	11.5	1.8	10.4	1.9	16.5	2.0	16.5	0.5
16	-8.9	12.8	0.8	12.0	1.7	10.8	1.8	17.0	1.9	17.2	0.5
15	-9.4	13.4	0.7	12.5	1.6	11.1	1.7	17.5	1.9	17.7	0.4
14	-10.0	14.1	0.6	13.0	1.5	11.4	1.6	18.0	1.8	18.3	0.4
13	-10.6	14.6	0.6	13.5	1.4	11.9	1.5	19.0	1.6	18.8	0.3
12	-11.1	15.2	0.5	14.0	1.3	12.3	1.4	19.5	1.6	19.4	0.3
11	-11.7	15.8	0.5	14.5	1.2	12.7	1.4	20.0	1.5	19.9	0.3
10	-12.2	16.3	0.4	15.3	1.1	13.1	1.3	20.5	1.4	20.6	0.2
9	-12.8	16.8	0.4	15.6	1.1	13.4	1.2	21.0	1.4	21.3	0.2
8	-13.3	17.3	0.3	16.0	1.0	13.7	1.2	21.5	1.3	21.8	0.1
7	-13.9	17.9	0.3	16.3	1.0	13.9	1.2	22.0	1.3	22.3	0.1
6	-14.4	18.3	0.3	16.7	0.9	14.2	1.1	22.5	1.2	22.8	0.1
5	-15.0	18.8	0.2	17.0	0.9	14.5	1.1	23.0	1.2	23.3	0.1
4	-15.6	19.3	0.2	17.3	0.8	14.8	1.0	23.5	1.1	23.8	0.1
3	-16.1	19.7	0.2	17.8	0.8	15.2	1.0	24.0	1.1	24.3	0.0
2	-16.7	20.2	0.1	18.2	0.8	15.5	0.9	24.5	1.0	24.8	0.0
1	-17.2	20.6	0.1	18.5	0.7	15.8	0.9	25.0	1.0	NA	NA
0	-17.8	21.0	0.1	18.7	0.7	16.1	0.9	25.5	1.0	NA	NA
-1	-18.3	21.4	0.1	19.0	0.7	16.3	0.8	25.9	0.9	NA	NA
-2	-18.9	21.8	0.1	19.3	0.7	16.6	0.8	26.3	0.9	NA	NA
-3	-19.4	22.2	0.0	19.7	0.6	16.8	0.8	27.7	0.8	NA	NA
-4	-20.0	22.6	0.0	20.0	0.6	17.1	0.8	28.1	0.8	NA	NA
-5	-20.6	22.9	0.0	20.3	0.6	17.4	0.7	28.6	0.8	NA	NA
-6	-21.1	23.3	(0.0)	20.5	0.6	17.6	0.7	29.0	0.7	NA	NA
-7	-21.7	NA	NA	20.8	0.5	17.8	0.7	28.4	0.8	NA	NA
-8	-22.2	NA	NA	21.0	0.5	18.1	0.7	28.8	0.7	NA	NA
-9	-22.8	NA	NA	21.3	0.5	18.3	0.6	29.2	0.7	NA	NA
-10	-23.3	NA	NA	21.5	0.5	18.5	0.6	29.6	0.7	NA	NA
-11	-23.9	NA	NA	21.8	0.5	18.7	0.6	30.0	0.7	NA	NA
-12	-24.4	NA	NA	22.0	0.5	19.0	0.6	30.4	0.6	NA	NA
-13	-25.0	NA	NA	22.3	0.4	19.2	0.6	30.7	0.6	NA	NA
-14	-25.6	NA	NA	22.5	0.4	19.4	0.5	31.1	0.6	NA	NA
-15	-26.1	NA	NA	22.8	0.4	19.6	0.5	31.5	0.6	NA	NA
-16	-26.7	NA	NA	23.0	0.4	19.8	0.5	31.8	0.6	NA	NA
-17	-27.2	NA	NA	23.3	0.4	20.0	0.5	32.2	0.6	NA	NA
-18	-27.8	NA	NA	23.5	0.4	20.2	0.5	32.6	0.5	NA	NA
-19	-28.3	NA	NA	23.8	0.3	20.4	0.5	32.9	0.5	NA	NA
-20	-28.9	NA	NA	24.0	0.3	20.6	0.5	33.3	0.5	NA	NA

Work by Wåhlin and Klein-Paste (2016) performed a modified Strategic Highway Research Program (SHRP) test (Chappelow et al., 1992) to investigate the kinetics of freezing and melting ice. Table 8 was developed and reports the freezing point, solution concentration, and density of NaCl, MgCl₂, CaCl₂, and KFo (potassium formate) at various temperatures, including their eutectic temperature.

Table 8. Properties of solutions used for ice melting (Wåhlin and Klein-Paste, 2016).

Solution	Freezing Point (°C)	Concentration ^a (%)	Density (kg/m ³)
-10°C			
NaCl	-10.2	14.3	1,110
MgCl ₂	-10.6	12.1	1,100
CaCl ₂	-10.2	14.5	1,120
KFo	-10.1	18.1	1,110
-18°C			
NaCl	-18.6	21.6	1,160
MgCl ₂	-18.7	16.6	1,130
CaCl ₂	-18.3	20.3	1,160
KFo	-18.4	27.6	1,170
-30°C			
MgCl ₂	-29.9	20.9	1,170
CaCl ₂	-29.2	25.6	1,220
KFo	-29.3	36.3	1,230
Eutectic			
NaCl	-21.2 ^b	23.3	1,170
MgCl ₂	-33.5 ^b	21.9	1,180
CaCl ₂	-49.5 ^b	32.1	1,280
KFo	-51 ^c	48.2	1,320

NOTE: KFo = potassium formate.

^aEstimated by using freezing point depression data for NaCl and CaCl₂ from Haynes et al. (28) and for MgCl₂ and KFo from Melinder (29).

^bFrom Yatsenko and Chudotvortsev (17).

^cFrom Melinder (29).

Wåhlin and Klein-Paste (2016) found that the initial ice melting is rapid, with 35-40% occurring in the first 30 minutes, for all deicer types and that the solution freezing point has an impact on how much ice a solution can melt (Figure 18). Figure 18 also shows that the closer the solution freezing point comes to the experimental temperature, the slower the ice melts. Two groups of deicers emerge, high ice-melting rate (KFo and NaCl) and lower ice-melting rate (MgCl₂ and CaCl₂), based on the products freezing point and diffusion coefficient (Wåhlin and Klein-Paste, 2016). To apply this work to maintenance operations: **if a rapid melting rate is a key deicer parameter, then a chemical with a low eutectic point should be**

selected. In addition, the freezing point can be used to assess liquid deicer melting abilities and when deicing chemicals are used at cold temperatures near their freezing point, ice melting may be very slow.

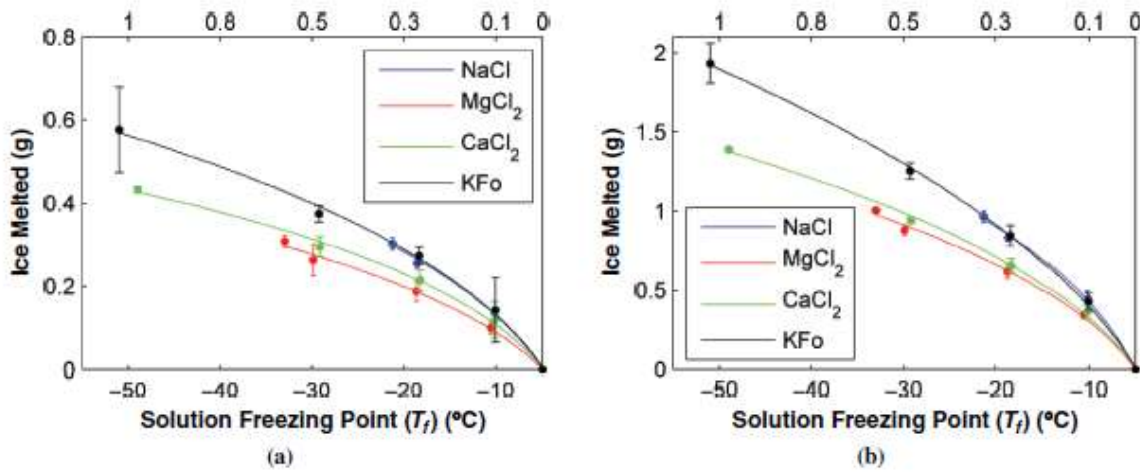


Figure 18. The amount of ice melted as a function of the solution freezing point for all chemicals after a) 10 minutes and b) 60 minutes. Error bars shows 95% confidence intervals. Note the different scale used for the y-axis in the two subfigures. Upper x-axes show the chemical potential difference (joules per mole) between ice and solutions ($\Delta\mu$), as calculated from eq. 2 and 3 from Wählin and Klein-Paste (2016).

Nilssen et al. (2016) used freezing curves to calculate the IMC (Figure 19) for NaCl brine. Using the derived equation (Eq 7):

$$I_{mc \text{ brine}} = [0.23 / (-3.6233 \cdot 10^{-4} \cdot T^3 - 3.8985 \cdot 10^{-2} \cdot T^2 - 1.7587 \cdot T)] - 0.23 - (1 - 0.23) \quad (\text{Eq. 7})$$

Where $I_{mc \text{ brine}}$ is the ice melting capacity of NaCl brine and T is temperature. The results of Eq. 7 are shown in Figure 20 where the ice melting capacity for 1 gram of solid salt (NaCl) and 1 gram of liquid salt (NaCl) brine are graphed.

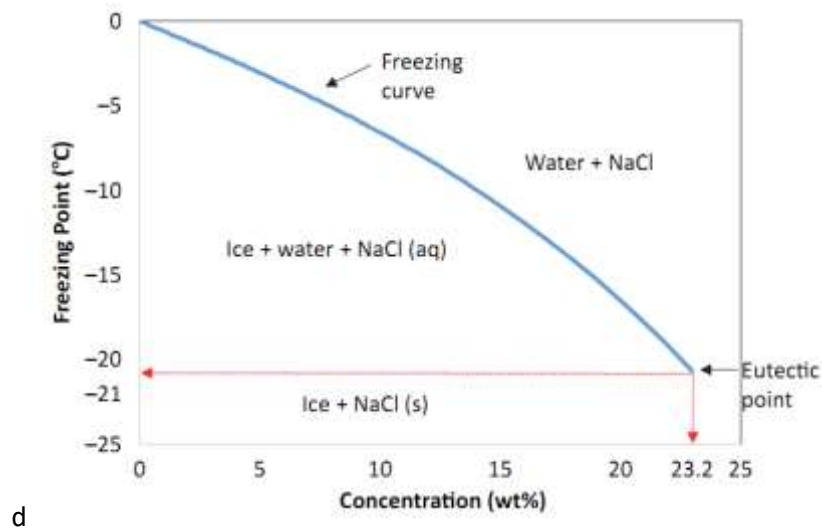


Figure 19. Freezing point curve for NaCl Brine, used to find IMCs for salt deicer (Nilssen et al., 2016).

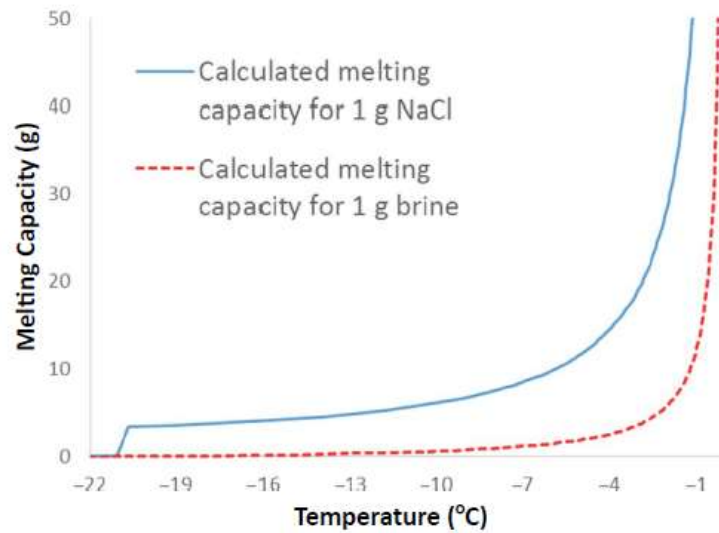


Figure 20. Ice melting capacity calculated for 1 gram of solid NaCl and 1 gram of liquid 23% NaCl brine (Nilssen et al., 2016).

Several other test methods can be used to assess IMC, such as the “shaker test” or “mechanical rocker test.” Some of these test methods are in accordance with SHRP protocols and others were modified versions of SHRP lab testing procedures (Nilssen et al., 2016). **Many of the published IMC results using similar or the same test methods produce varying results between labs and research groups.** This is a function of equipment, atmospheric conditions, and method procedures, and **these varying results make it challenging to use IMC to assess a deicers potential performance.**

Influence of Deicers on Ice Structure

A laboratory investigation by Klein-Paste and Wåhlin (2013) demonstrated that anti-icers “weaken the ice that forms when a wet pavement freezes which allows traffic to destroy the ice,” shown in the microscopic observations in Figure 21. This was validated in work by Malley et al (2018) which used Raman microscopy, a tool that can be used to determine the surface and internal structure and composition of solids; in this case water, ice, and NaCl brine. Surface and 3D mapping showed that liquid water and salt brine form pockets and channels in ice (Figure 22). Work by Cho et al. (2002) found that the addition of NaCl to water can allow for a ‘quasi brine layer’ to be present at temperatures well below eutectic.

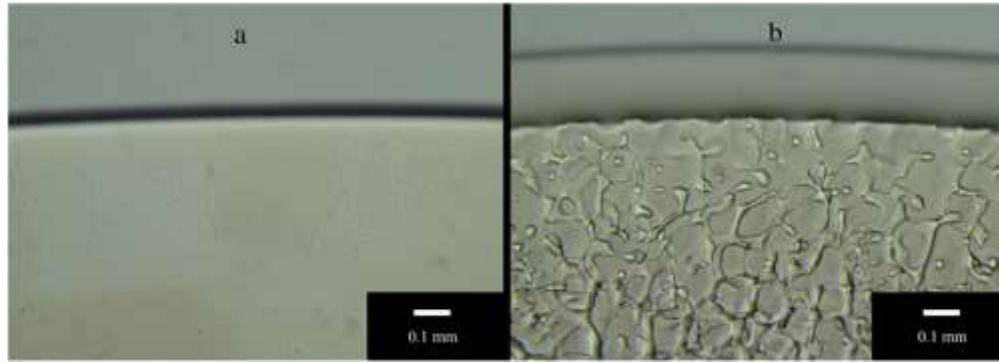


Figure 21. (a) The ice from distilled water contains grain and subgrain boundaries. (b) The saline ice includes numerous interconnected brine channels within the ice (Klein-Paste and Wählin, 2013).

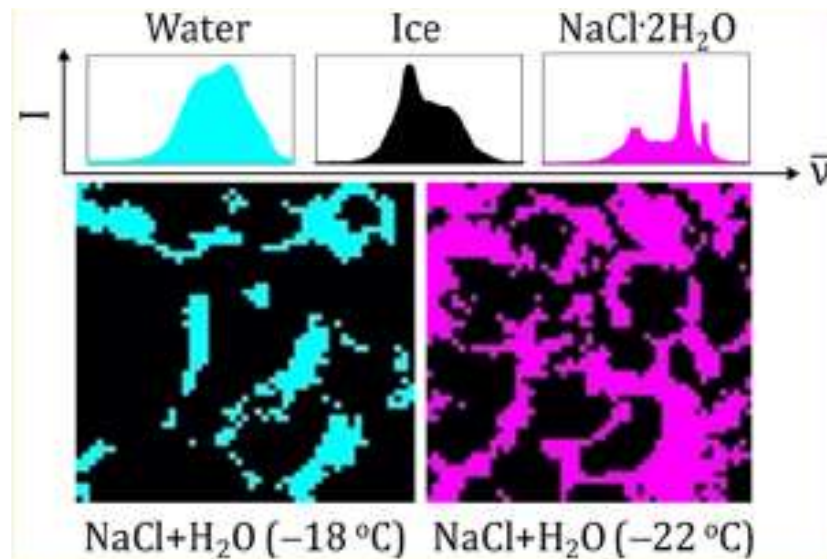


Figure 22. Raman microscopy maps showing water, ice, and salt brine (06M or 3%NaCl brine solution) makeup at on the surface at -0.4°F (-18°C) and -7.6°F (-22°C). (Malley et al., 2018).

Additional information on NaCl Based Deicers Used for Melting Snow and Application Guidelines for Deicers can be found in Appendix A – Literature Review Appendix A – Literature Review .

Future Work using Advanced Imaging

Work by NASA and a significant amount of other research in materials engineering, the geosciences, surface water and snow chemistry, has applied advance imaging techniques like Raman microscopy, scanning electron microscopy (SEM), x-ray fluorescence (XFR), nuclear magnetic resonance (NMR) spectroscopy, and reflection infrared spectroscopy, to better ascertain the chemistry and physics, specifically the kinetics, of water, ice, salt, and salt brine interactions. These newer imaging techniques are providing significant advances in knowledge and understanding in this field and, while broader than the scope of this effort, the following resources could be used in future work.

- Blackford, J. R.; Jeffree, C. E.; Noake, D. F. J.; Marmo, B. A. Microstructural Evolution in Sintered Ice Particles Containing NaCl Observed by Low-Temperature Scanning Electron Microscope. *Proc. Inst. Mech. Eng., Part L* 2007, 221, 151–156.
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- Kahan, T. F.; Wren, S. N.; Donaldson, D. J. A Pinch of Salt Is All It Takes: Chemistry at the Frozen Water Surface. *Acc. Chem. Res.* 2014, 47, 1587–1594.
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Fact Sheets, Images, and Messaging

The objective of this project was to develop materials to help winter maintenance practitioners make informed decisions on the use of road salts, including a One Page Fact Sheet and Educational Video explaining how to read and apply the information in a NaCl phase diagram. Available phase diagrams, fact sheets, images, and messaging tools were identified and are provided below.

Phase Diagrams

As can be observed in Figure 9 A, B, C, D, Figure 10, Figure 11, Figure 12, Figure 14, Figure 15, and Figure 19, the phase diagrams for NaCl salt show important information applicable to winter maintenance operations. The challenge in reading them is that each diagram shows this critical information differently or includes some but not all information.

Fact Sheets, Images, and Messaging about Salt Use

The following fact sheets, images, and messaging on the use of salt-based deicer functionality in relationship to temperature were found on the websites of various winter maintenance organizations and companies.



Figure 23. A pamphlet published by the Iowa DOT titled Roadway Deicing; Cold Temperatures Reduce Salt's Effectiveness for Roadway Deicing (<https://iowadot.gov/maintenance/Winter-Operations/Roadway-deicing>)



Figure 24. An educational graphic titled *More Salt is Not Always the Cure for Slippery Roads!* MnDOT, <https://www.dot.state.mn.us/mediaroom/graphics.html>



Figure 25. A graphic published by the Ontario Ministry of Transportation indicating the appropriate temperatures for Salt and Sand use. (Formerly available on the website: <https://www.ontario.ca/page/how-we-clear-ontarios-highways-winter>)

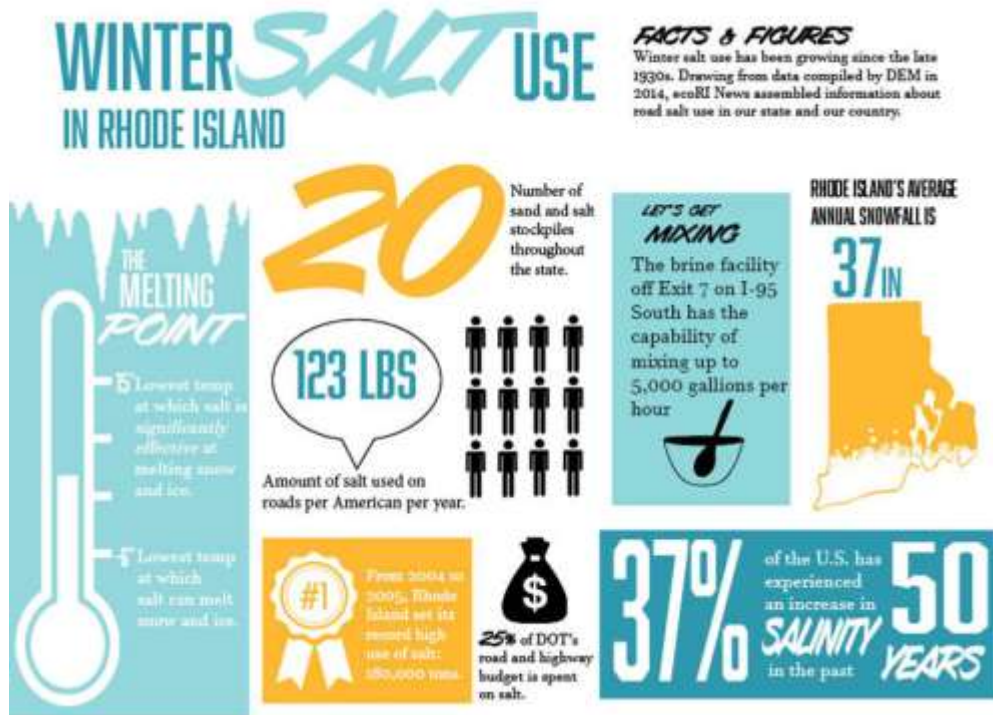


Figure 26. Winter Salt use in Rhode Island, G. Kelly, ecoRI news, <https://www.ecori.org/pollution-contamination/2019/12/23/road-salt-can-harm-aquatic-creatures>.

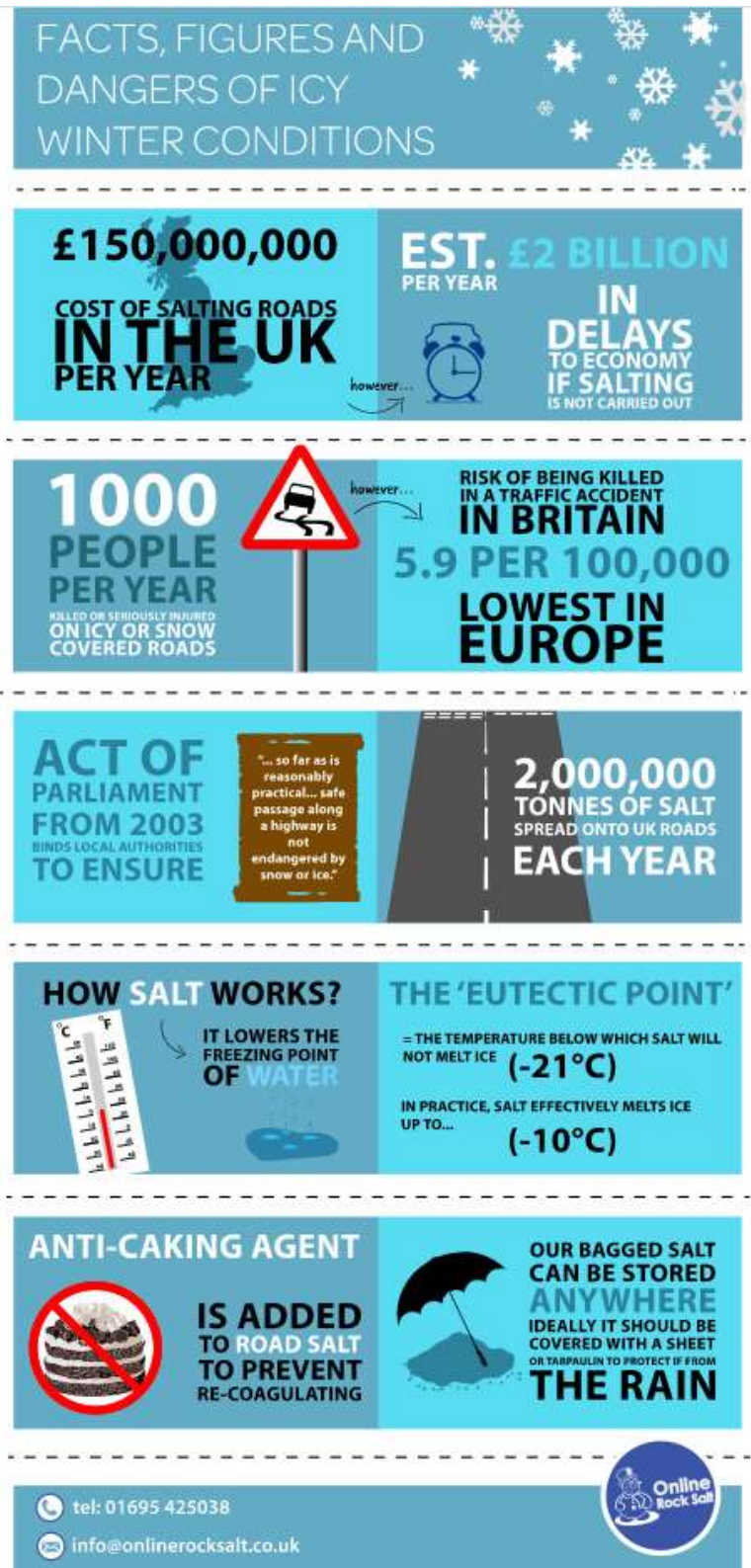


Figure 27. An educational graphic demonstrating the value and cost of salting roads in the United Kingdom titled Facts, Figures and Dangers of Icy Winter Conditions, Online Rock Salt, UK, <https://www.onlinerocksalt.co.uk/knowledge-base/salt-basics/facts-and-figure>

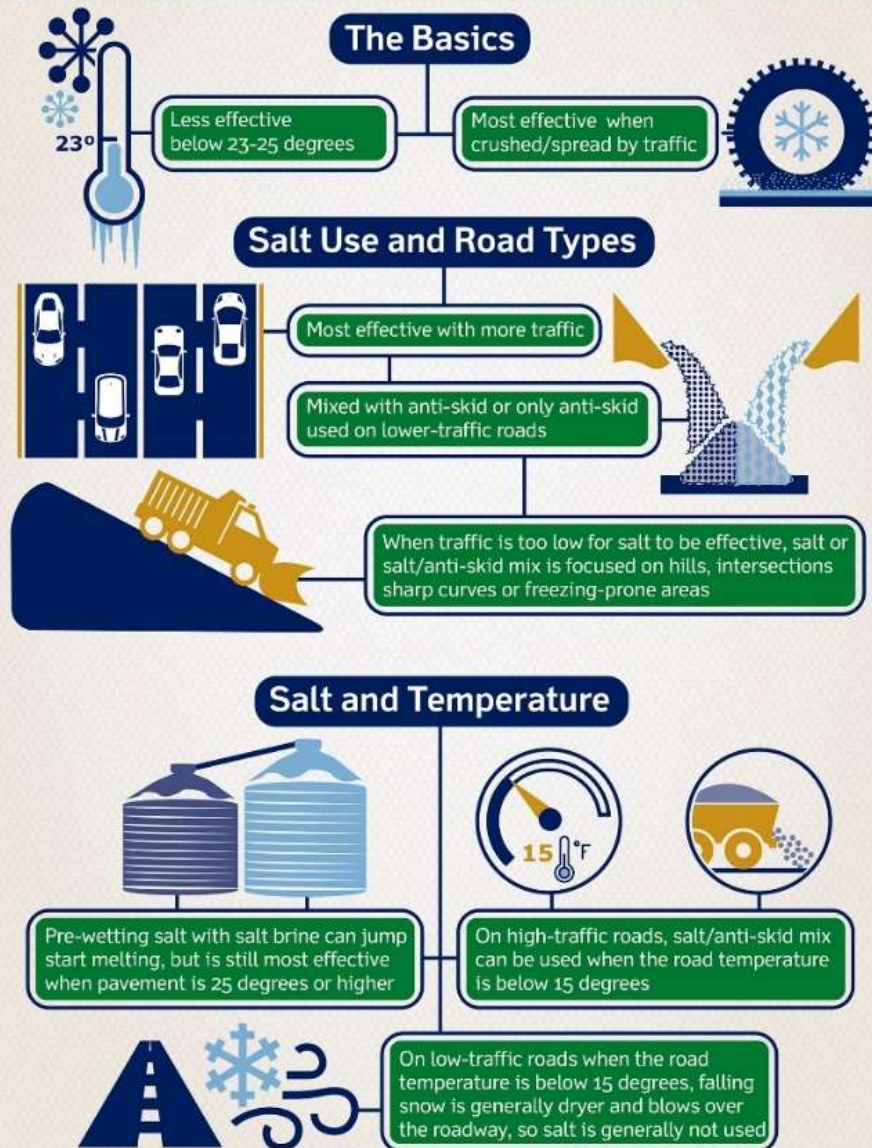


The Science of Winter Road Treatments



pennsylvania
DEPARTMENT OF TRANSPORTATION

Winter road treatment tactics depend on **temperature**, **precipitation type** and **traffic volume**.
Salt isn't a silver bullet and may not be effective on every roadway.



More on winter operations and safety at [PennDOT.gov/winter](https://www.pennDOT.gov/winter)

#PAWinter

Figure 28. The Science of Winter Road Treatments, PennDOT, <https://www.pennDOT.gov/about-us/media/PublishingImages/Winter%20Safety/Winter-Infographic-Long.jpg>

ICE & SNOW TAKE IT SLOW



LIQUID DE-ICER FACT-SHEET

GENERAL DESCRIPTION

Liquid anti-icers and de-icers are salt compounds extracted from the Great Salt Lake or Salt Flats with added corrosion inhibitors used to prevent or remove the build up of ice and snow on roads and minimize the impact on vehicles.

HOW IT WORKS

The products are called freezing point depressants, and work to lower the freezing point of moisture. What's more, they can help prevent the build-up and bonding of ice and snow in addition to their melting characteristics.

ENVIRONMENTAL IMPACTS

Liquid anti-icers and de-icers are better for the environment than other alternatives including sand and salt. While some sand and salt use is still necessary for CDOT's overall winter maintenance program, increased use of liquids has drastically reduced air pollution and the damage to roadside plant and aquatic life, all associated with sand use.

SAFETY

Over the years, CDOT has found that liquid de-icers improve safety. In fact, on I-25, over an 18-year period, snow and ice-related traffic crashes decreased by an average of 12% while traffic volumes increased over 26%.

IMPACT TO VEHICLES

Salt products naturally lower the freezing temperature of water, but do have some corrosive properties. Motorists should always wash their vehicles after any snowstorm to remove liquid de-icer residue that may come into contact with your vehicle, just as you always should with salt and sand/salt mixtures. Unlike sand and sand/salt mixtures, however, liquid de-icers will not scratch your car's paint or pit the windshield. Liquid de-icers are generally less corrosive than sodium chlorides, traditionally used during snow removal.

ECONOMICS

At approximately \$62 a gallon, CDOT's most widely used liquid anti-icers and de-icers are the least expensive alternatives to sand and salt on the market. In addition to reducing the need for the less environmentally friendly sand/salt mixture, the application of liquids helps to reduce maintenance costs by lessening the need for plowing and after-storm sweeping.

www.dot.state.co.us | 800-999-4997

WHAT PRODUCTS DOES CDOT USE DURING WINTER STORMS?

- Sand or sand/salt mixture
 - Ice Slicer
 - Solid de-icer made of granular salt and magnesium chloride mined in Redmond, Utah
 - Liquid de-icers (27-29% de-icer)*
 - Magnesium chloride (used above 16 degrees pavement temperature)
 - Cold temperature magnesium chloride (used below 16 degrees pavement temperature)
 - Includes a corn bi-product to lower the freezing point
 - APEX
 - Magnesium chloride-based product (used above -4 degrees pavement temperature)
 - Due to a lower freezing point, can substitute for regular and cold temperature magnesium chloride
- * Used for anti-icing and de-icing on roadways during winter weather conditions

ENVIRONMENT IMPACT STUDIES

CDOT has invested in numerous environmental impact studies which have shown that the use of de-icers like magnesium chloride have little or no environmental impact. Some studies have led to changes in specifications, making the de-icers more environmentally friendly and less corrosive.

- Effect of Magnesium Chloride on Asphalt pavements (Werner Hutter, CDOT) February 1999
- Studies of Environmental Effects of Magnesium Chloride De-icer in Colorado (Professor William M. Lewis) November 1999
- Preliminary Environmental Evaluation of Caliber M1000 De-icer for Use in Colorado (Professor William M. Lewis) December 2000
- Evaluation and Comparison of Three Chemical De-icers for Use in Colorado (Professor William M. Lewis) August 2001
- Evaluation of Selected De-icers Based on a Review of the Literature (The SeaCrest Group) October 2001
- Corrosion Effects of Magnesium Chloride and Sodium Chloride on Automobile Components (Professors Yunping Xi and Zhaihui Xie) May 2002
- Cost of Sanding (Professor Nien-Yin Chang) June 2002
- Roadside Vegetation Health (University of Northern Colorado) April 2007

Each year, CDOT spends more than \$200,000 on quality assurance testing of its de-icer products. CDOT's de-icer specifications are set by Dr. William Lewis, University of Colorado professor and water quality expert.

FOR MORE INFORMATION ON CDOT'S WINTER DRIVING MEASURES:

VISIT www.coloradodot.info

Call: 800.999.4997

Send feedback or questions to info@dot.state.co.us



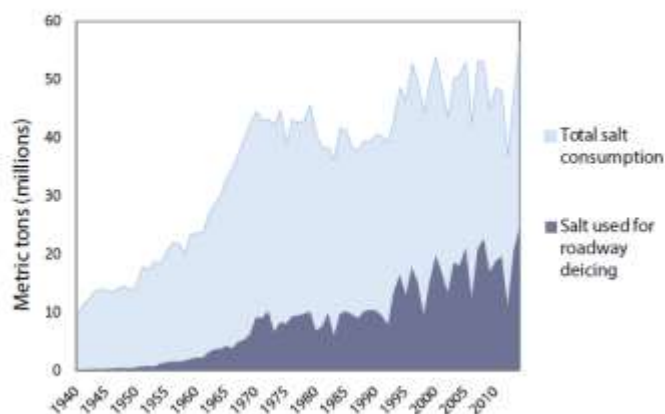
Figure 29. An infographic published by CDOT titled *Ice & Snow; Take it Slow*, https://www.codot.gov/library/Brochures/DeicerFactSheet.pdf/@download/file/ICE&SNOW_FactSheet_Revised.pdf

Roadway deicing in the United States

How a few industrial minerals supply a vital transportation service

Background

In areas prone to winter precipitation, transportation infrastructure must be able to quickly respond to snow and ice on roadways. Ice removal is a vital service in these communities. Deicing chemicals melt ice by lowering the temperature at which it melts. They can also prevent new ice from forming and improve traction. Salt (sodium chloride) is a popular deicing chemical because it is cheap and abundant. Geoscientists help to find and mine salt and other industrial minerals that help keep our roads safe.



Salt consumption in the United States, 1940-2014. Domestic salt production quadrupled from 1940 to 1970, owing in large part to the adoption of road salt deicing practices on the new Interstate Highway System.¹ By the 1970s, road salt deicing had replaced or augmented other techniques in nearly all deicing applications.² In 2014, roadway deicing accounted for 45% of total salt consumed.³ Data source: U.S. Geological Survey

Salt

The most common deicing method is the use of sodium chloride in the form of crushed rock salt, which is inexpensive, abundant, and easy to mine, store, distribute, and apply. Salt brines are increasingly used in some areas, but the vast majority is still rock salt. Present-day deposits of rock salt were formed by widespread evaporation of ancient inland seas.⁴ Rock salt deposits are geographically diverse, but consumption of rock salt is concentrated in the Great Lakes region (see map on reverse). Rock salt used for deicing may contain other chloride minerals in addition to sodium chloride (see next page).

Just the numbers (2014)

Salt in the U.S. (million metric tons)¹

- Consumption: 56.5
- Production: 45.3
- Imports: 20.1
- Exports: 0.94

Rock salt (million metric tons)²

- Consumption: 27.9
- Consumption for roadway deicing: 24.5
- Domestic production capacity: 22.9
- Top producing states*:
 - Louisiana: 7.3
 - New York: 6.3
 - Ohio: 5.4
- Top consuming states:
 - New York: 3.6
 - Ohio: 3.5
 - Illinois: 3.0
- National average price per ton: \$48.11
- 42% of total salt consumption

Total cost of rock salt used for roadway deicing, \$1.18 billion³

* Based on reported production capacities of industrial salt producers
³ 24.5 million tons at \$48.11 per ton

Different forms of salt

Rock salt: solid masses of salt crystals that form rocks made almost entirely of salt. Mostly used in roadway deicing.

Brine: Salt-rich liquid, either extracted directly from salt lakes/salty groundwater, or by dissolving salt in water. Mostly used in the chemical industry.

Drawbacks & Limitations of Salt

- **Chemical limitations.** Sodium chloride cannot effectively melt ice below 10°F (-12.2°C).³
- **Saltwater runoff** can contaminate surface and groundwater, and damage soils, plants, and crops.⁵ Too much sodium in drinking water can be a concern for people who require low-sodium diets.⁵
- **Corrosion.** Salt eats away at metals used in bridges, buildings, and automobiles.



Top rock salt producing (yellow) and consuming (blue) states in 2014. Top 3 producing states: LA (32%), NY (27%), OH (24%). Top 3 consuming states: NY (13%), OH (12%), IL (11%).
Data source: U.S. Geological Survey²

Other deicing materials & their sources

- **Calcium chloride** – commonly used; works above -20°F.⁵ Made by reacting sodium chloride with calcium carbonate, largely from the central and eastern U.S.⁶
- **Magnesium chloride** – works above 5°F.⁵ Domestic production capacity was 300,000 metric tons in 2015; 99% of domestic production is extracted as brine from Utah's Great Salt Lake.⁷
- **Potassium chloride** – works above 20°F.⁵ About 460,000 tons were produced domestically in 2015, largely refined from potassium ores mined in New Mexico and Utah.⁸
- **Acetates** – Potassium acetate works above -15°F, calcium magnesium acetate above 20°F.⁵ Acetates do not corrode metal but do damage concrete.⁹ They are biodegradable but can affect oxygen levels in lakes.⁵
- **Sand** – does not melt ice, but provides traction and helps to mechanically break up ice. Not all states use sand, but roughly nine million tons of sand were used for snow and ice control on U.S. roadways in 2015.¹⁰

More Resources

Mineral Commodity Summaries and Minerals Yearbooks, published annually by the U.S. Geological Survey, provide global statistics and information for over 90 minerals and materials. These resources are freely available online at: <https://minerals.usgs.gov/>

New Hampshire Department of Environmental Services - Environmental, Health, and Economic Impacts of Road Salt:
<http://des.nh.gov/organization/divisions/water/wmb/was/salt-reduction-initiative/impacts.htm>

AGI Critical Issues Program - Industrial Minerals:
<https://www.americangeosciences.org/critical-issues/industrial-minerals>

References

- ¹ Mineral Commodity Summaries 2016, Salt - U.S. Geological Survey: <https://minerals.usgs.gov/minerals/pubs/commodity/salt/mcs-2016-salt.pdf>
- ² Minerals Yearbook 2014, Salt - U.S. Geological Survey: <https://minerals.usgs.gov/minerals/pubs/commodity/salt/myb1-2014-salt.pdf>
- ³ Special Report 235: Highway Deicing - National Research Council: <http://onlinepubs.trb.org/onlinepubs/sr/sr235.html>
- ⁴ The Material Flow of Salt - U.S. Department of the Interior: <https://pubs.usgs.gov/usbm/cic-9343/ic9343.pdf>
- ⁵ Road Salt and Water Quality Fact Sheet - New Hampshire Department of Environmental Services: <http://des.nh.gov/organization/commissioner/pip/factsheets/wmb/documents/wmb-4.pdf>
- ⁶ Mineral Commodity Summaries 2016, Stone (Crushed) - U.S. Geological Survey: https://minerals.usgs.gov/minerals/pubs/commodity/stone_crushed/mcs-2016-stonc.pdf
- ⁷ Minerals Yearbook, 2015, Magnesium Compounds - U.S. Geological Survey: <https://minerals.usgs.gov/minerals/pubs/commodity/magnesium/myb1-2015-mgcom.pdf>
- ⁸ Mineral Commodity Summaries 2016, Potash - U.S. Geological Survey: <https://minerals.usgs.gov/minerals/pubs/commodity/potash/mcs-2016-potas.pdf>
- ⁹ Physical and Chemical Effects of Deicers on Concrete Pavement - Utah Department of Transportation: <https://www.udot.utah.gov/main/uconowner.gft?n=8081525197623431>
- ¹⁰ Mineral Commodity Summaries 2016, Sand and Gravel (Construction) - U.S. Geological Survey: https://minerals.usgs.gov/minerals/pubs/commodity/sand_gravel_construction/mcs-2016-sandc.pdf

Figure 30. An American Geosciences Institute factsheet for deicer use in the United States titled Roadway deicing in the United States; How a few industrial minerals supply a vital transportation service, https://www.americangeosciences.org/sites/default/files/CI_Factsheet_2017_3_Deicing_170712.pdf

Laboratory Testing Results

Beaker Test

Observations

A set of 3 beakers, containing 75mL of brine each, was prepared for each of the eight NaCl solution concentrations (Table 1). These triplicates were observed for any visible changes during the beaker test (Figure 3) and two main observations were made: 1) ice crystal formation in the solution, and 2) salt (NaCl) precipitating out of solution. The following section provides a description of the observations made during the beaker test.

Table 9 provides a summary of the observed ice crystal formation and NaCl precipitating out of solution for all solution concentrations and temperatures. From the observations, it can be stated that compositions A, B, and C (21 wt. %, 22 wt.%, and 23.3 wt. %, respectively) did not have ice crystals form or NaCl precipitate out of solution at any of the temperatures tested in this experiment. Note that solution F (NaCl 26 wt.%) is around the solubility limit for NaCl (shown in Figure 9D).

Table 9. Observations of ice formation and/or NaCl precipitation for all solutions at all temperatures, with a “check mark” indicating that ice formation or salt precipitation was observed and an X indicating that no ice or salt precipitate was observed.

Cold Room Temperature: 25 °F (-3.8 °C)																								
Concentrations	21 wt. %			22 wt. %			23 wt. %			24 wt. %			25 wt. %			26 wt. %			27 wt. %			28 wt. %		
Designations	A			B			C			D			E			F			G			H		
Triplicates	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3
Ice Formation	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	✓	✓	✓	✓	✓	✓
Precipitating	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	✓	✓	✓	✓	✓	✓	✓	✓	✓
Cold Room Temperature: 20 °F (-6.7 °C)																								
Concentrations	21 wt. %			22 wt. %			23 wt. %			24 wt. %			25 wt. %			26 wt. %			27 wt. %			28 wt. %		
Designations	A			B			C			D			E			F			G			H		
Triplicates	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3
Ice Formation	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	✓	✓	✓	✓	✓	✓
Precipitating	x	x	x	x	x	x	x	x	x	x	x	x	✓	x	x	✓	✓	✓	✓	✓	✓	✓	✓	✓
Cold Room Temperature: 15 °F (-9.4 °C)																								
Concentrations	21 wt. %			22 wt. %			23 wt. %			24 wt. %			25 wt. %			26 wt. %			27 wt. %			28 wt. %		
Designations	A			B			C			D			E			F			G			H		
Triplicates	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3
Ice Formation	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	✓	✓	✓	✓	✓	✓	✓	✓	✓
Precipitating	x	x	x	x	x	x	x	x	x	x	✓	x	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Cold Room Temperature: 10 °F (-12.2 °C)																								
Concentrations	21 wt. %			22 wt. %			23 wt. %			24 wt. %			25 wt. %			26 wt. %			27 wt. %			28 wt. %		
Designations	A			B			C			D			E			F			G			H		
Triplicates	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3
Ice Formation	x	x	x	x	x	x	x	x	x	x	x	x	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Precipitating	x	x	x	x	x	x	x	x	x	x	x	x	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Cold Room Temperature: 5 °F (-15 °C)																								
Concentrations	21 wt. %			22 wt. %			23 wt. %			24 wt. %			25 wt. %			26 wt. %			27 wt. %			28 wt. %		
Designations	A			B			C			D			E			F			G			H		
Triplicates	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3
Ice Formation	x	x	x	x	x	x	x	x	x	x	x	x	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Precipitating	x	x	x	x	x	x	x	x	x	✓	x	x	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Cold Room Temperature: 0 °F (-17.8 °C)																								
Concentrations	21 wt. %			22 wt. %			23 wt. %			24 wt. %			25 wt. %			26 wt. %			27 wt. %			28 wt. %		
Designations	A			B			C			D			E			F			G			H		
Triplicates	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3
Ice Formation	x	x	x	x	x	x	x	x	x	x	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Precipitating	x	x	x	x	x	x	x	x	x	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Cold Room Temperature: -6 °F (-21.1 °C)																								
Concentrations	21 wt. %			22 wt. %			23 wt. %			24 wt. %			25 wt. %			26 wt. %			27 wt. %			28 wt. %		
Designations	A			B			C			D			E			F			G			H		
Triplicates	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3
Ice Formation	x	x	x	x	x	x	x	x	x	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Precipitating	x	x	x	x	x	x	x	x	x	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓

Results and Images

The mass of the filtered ice crystals is provided along with photographs of the ice and/or precipitated NaCl. Microscopic images were taken to document ice crystal structure.

Microscopy images were not collected at 32°F and 25°F because ice crystals were either absent, or in the case of some solutions at 25°F, were too small to be filtered and collected for imaging. See Table 9 for a review of solution concentrations and temperatures that resulted in ice crystals and/or salt precipitate. There was no significant ice crystal formation or precipitation from solution concentrations at or below 26 wt.%, or additional precipitation from solution concentrations of 27 wt.% and 28 wt. % NaCl at 32°F; thus, for each group of triplicates for each solution concentration, only one photograph was selected to best represent the changes that occurred (if any).

According to the salt phase diagram (Figure 9D), concentrations above the solubility limit of NaCl at room temperature, in this instance 27 wt. % and 28 wt. %, could precipitate NaCl.2H₂O, sodium chloride dihydrate (Kaufmann, 1960), below 32°F. NaCl.2H₂O was discovered by Johann Tobias in 1973, when he exposed fully saturated salt brine, 26.3 wt. % NaCl solution, to cold Russian winter temperatures and noted crystallization at 10.4°F (-12°C) (Kaufmann, 1960). It is possible that the crystals present at the bottom of the beakers in this laboratory experiment, with concentrations above 23 wt. % (for certain temperatures) and with concentrations above 26 wt. % (for all the testing temperatures), could be NaCl dihydrate, but this was not validated with additional testing.

Test Temperature: 32°F (0°C)

Photographs of the 32°F triplicate samples A through G are provided in Figure 31. Microscopy images were not collected at 32°F due to lack of ice crystal formation. Solution F started to show signs of salt precipitation after 10 minutes, which can be seen in Figure 31– Triplicates for F. Solutions G (27 wt.%) and H (28 wt.%) exceeded the solubility limit of NaCl, therefore some salt was present at the bottom of the beakers (Figure 31– Triplicates for G and H). Solution G triplicates did have some ice crystal formation at the top of the beakers (Figure 32).

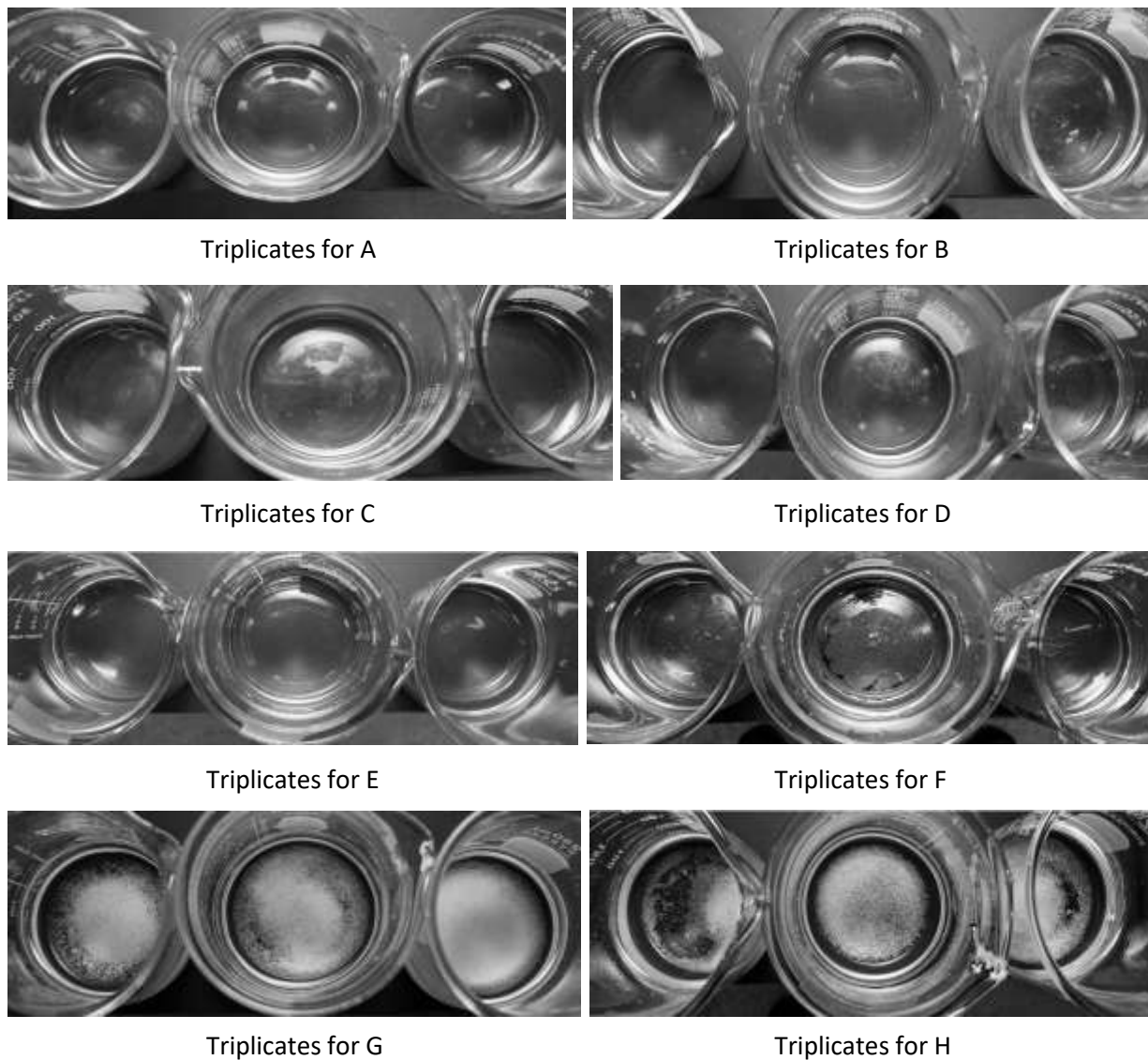


Figure 31. Photographs of triplicates solutions A, B, C, D, E, F, G, and H at 32°F.



Figure 32. Ice crystal formation in beakers G2 (left) and G3 (right) at 32°F.

Test Temperature: 25°F (-3.8°C)

Photographs of the triplicate samples A through H at 25°F are provided in Figure 33. Microscopy images were not collected at 25°F due to lack of ice crystal formation. Solution F (26 wt.%) showed minute quantities of precipitated salt (Figure 33– Triplicates for F). Solutions G (27 wt.%) and H (28 wt.%) showed both ice crystal formation and precipitated salt (NaCl and NaCl.2H₂O) in the beakers (Figure 34).

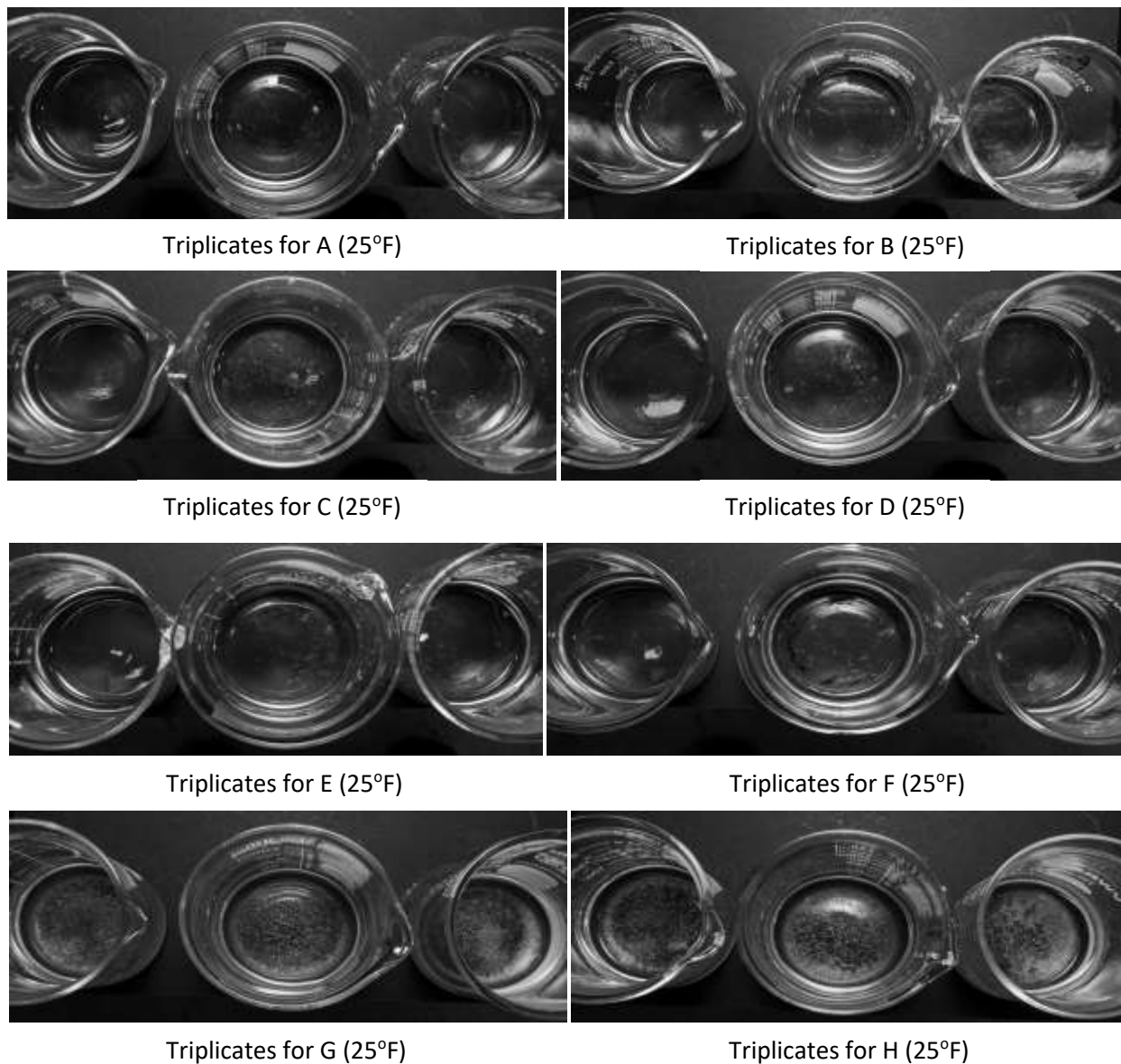


Figure 33. Photographs of triplicates of solutions A, B, C, D, E, F, G, and H at 25°F.

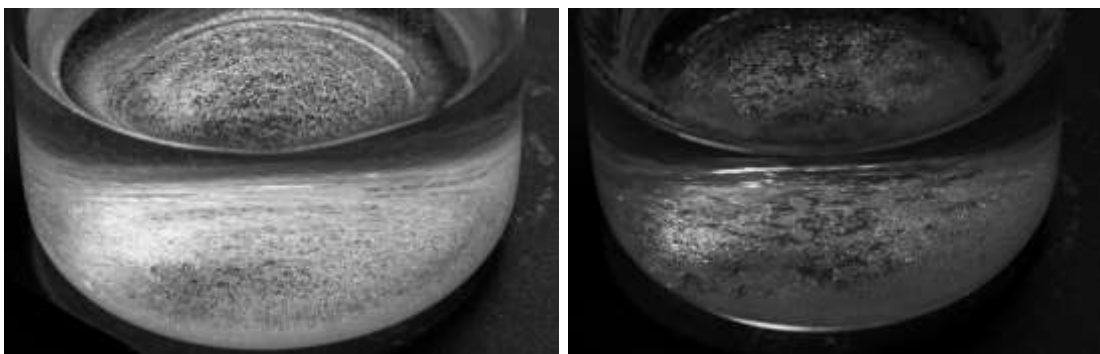


Figure 34. Solution G2 (left) and H3 (right) experienced ice crystal formation and salt precipitation in the beakers at 25°F.

Test Temperature: 20°F (-6.7°C)

Microscopy was used to capture images of ice crystals collected from the various brine solutions. Ice crystal structures from solution G1 and H1 are shown in Figure 35 and the mass of the filtered ice crystals are provided in Table 10

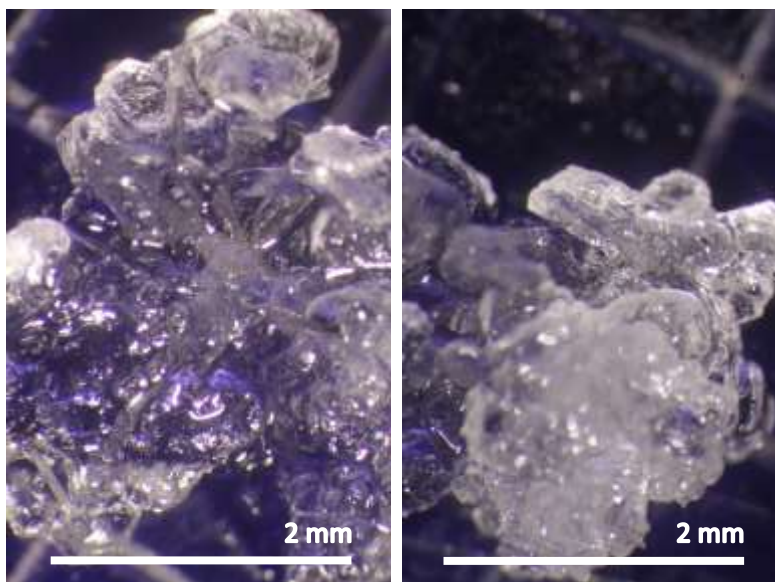


Figure 35. Ice crystal structures filtered from G1 (27 wt.%) at 20°F shown, 31.25x magnification.

Table 10. Mass of ice crystals filtered from solutions G1 and H1 at 20°F.

Brine Solutions (20°F)	Mass of empty beaker (g)	Mass of beaker + brine (g)	Mass of 75mL brine solution (g)	Mass of empty beaker (g)	Mass of the filtrate + beaker (g)	Mass of the filtrate (g)	Approx. mass of ice crystals (g)
H1	108.93	202.89	93.96	108.93	194.52	85.59	8.37
G1	113.33	203.18	89.85	113.33	191.73	78.4	11.45

Photographs of the triplicate samples of solution A through G at 20°F are provided . Salt began to precipitate out of solution F (26 wt.%) at 20°F, as shown in Figure 37.



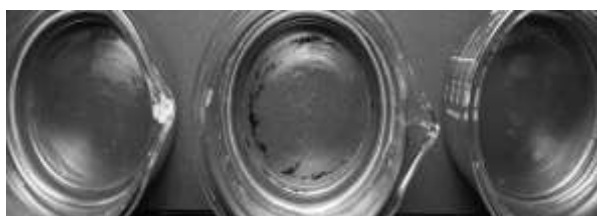
Triplicates of A (top) and B (bottom)



Triplicates of C (top) and D (bottom)



Triplicates for E (20°F)



Triplicates for F (20°F)



Triplicates for G (20°F)



Triplicates for H (20°F)

Figure 36. Photographs of triplicates of solutions A, B, C, D, E, F, G, and H at 20°F.

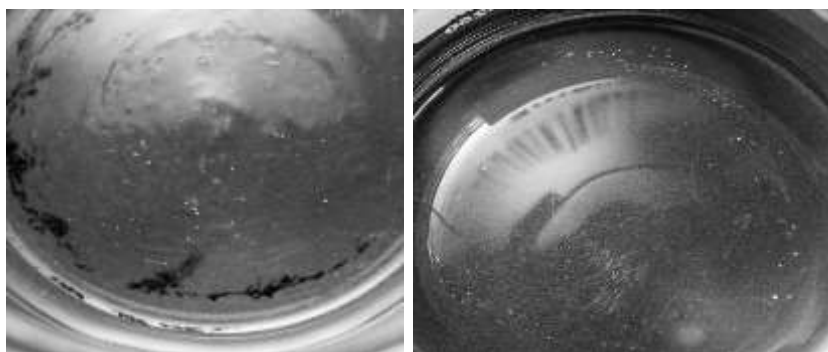


Figure 37. Salt precipitation out of solution F2 (left) and F3 (right) (26 wt.%) at 20°F.

At 20°F, ice crystals formed at the top and salt precipitated to the bottom of the beaker for solutions G (27 wt.%) and H (28 wt.%) and shown in Figure 38.

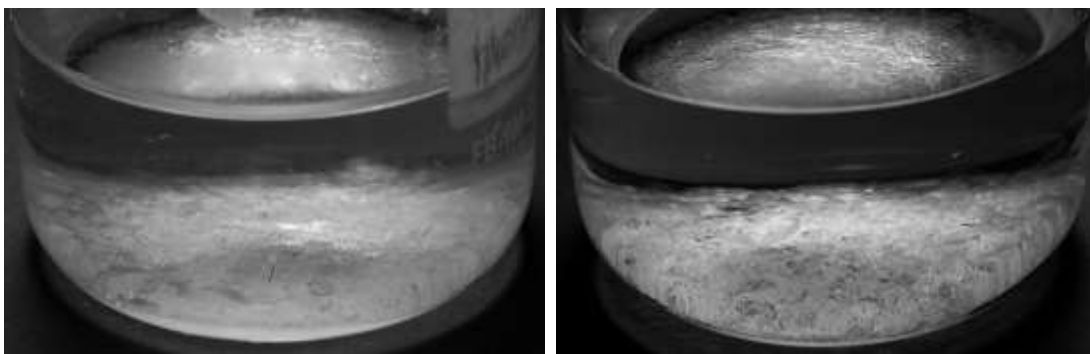


Figure 38. Ice crystal formation and salt precipitation in solutions G1 (left) and H3 (right) at 20°F.

Test Temperature: 15°F (-9.4°C)

Microscopy was used to capture images of ice crystals collected from solutions F2 (26 wt.%) (Figure 39), G1 (27 wt.%) (Figure 40), and H1 (28 wt.%) (Figure 41). The mass of the filtered ice crystals are provided in Table 11.

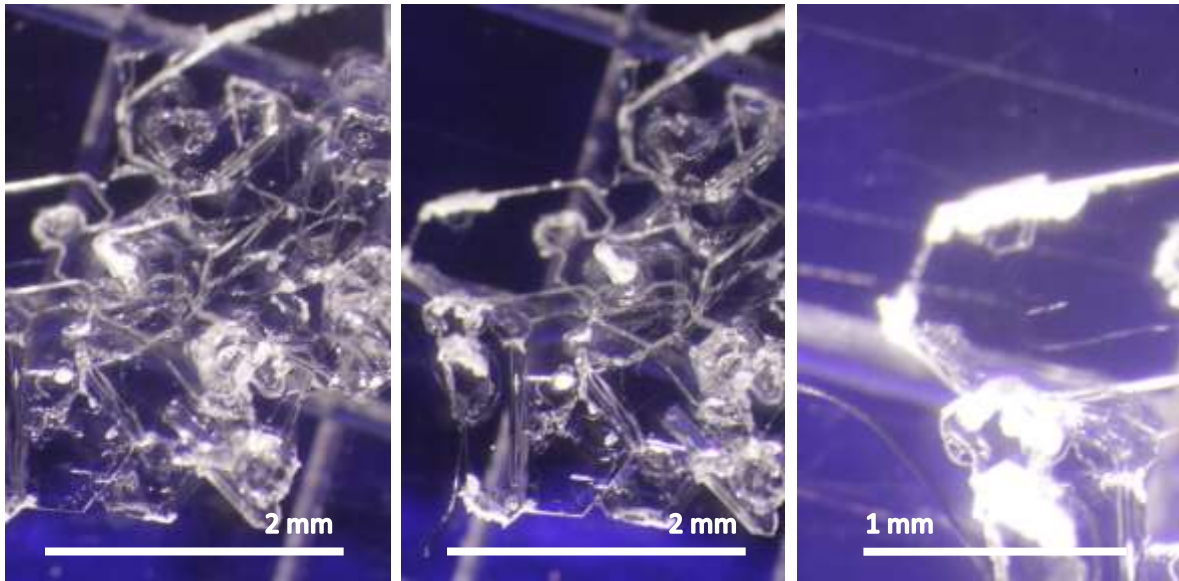


Figure 39. Ice crystal structure images for F2 (26 wt.%) at 15°F. Left and middle images at 31.25x magnification and the right image at 62.5x magnification.

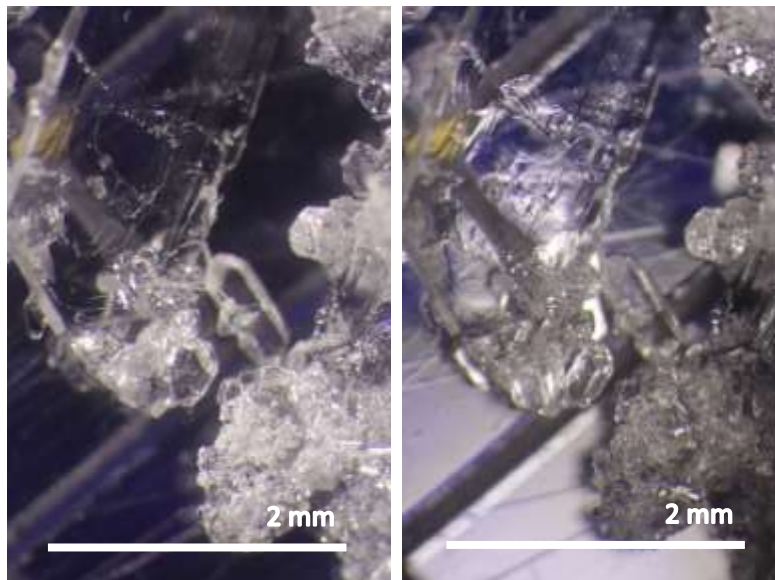


Figure 40. Ice crystal structure images for G1 (27 wt.%) at 15°F. Both images at 31.25x magnification.

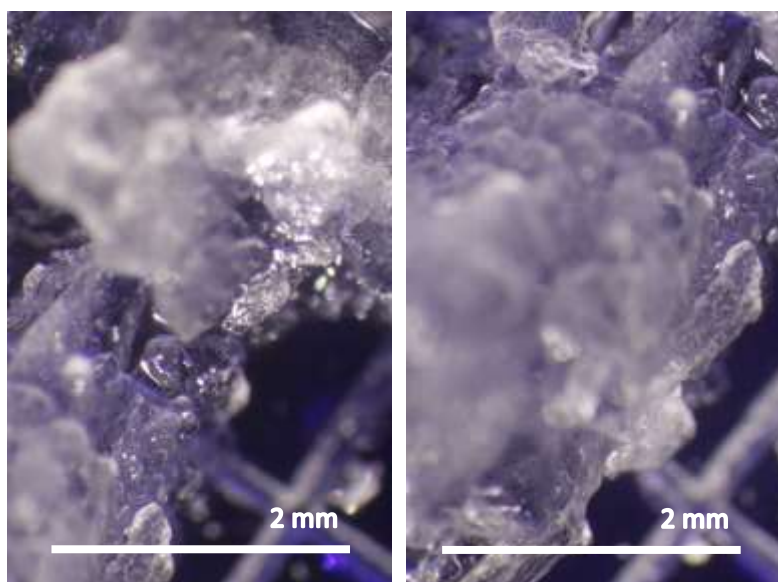


Figure 41. Ice crystal structure images for H1 (27 wt.%) at 15°F. Both images at 31.25x magnification.

Table 11. Mass of ice crystals filtered from solutions F2, G1, and H1 at 15°F.

Brine Solutions (15°F)	Mass of empty beaker (g)	Mass of beaker + brine (g)	Mass of 75mL brine solution (g)	Mass of empty beaker (g)	Mass of the filtrate + beaker (g)	Mass of the filtrate (g)	Approx. mass of ice crystals (g)
F2	120.49	202.31	81.82	120.49	197.78	77.29	4.53
G1	114.38	202.95	88.57	114.38	199.3	84.92	3.65
H1	102.7	195.08	92.38	102.7	188.99	86.29	6.09

Photographs of the triplicate samples of solution A through D at 15°F are provided in Figure 42. A minute amount of salt precipitated out of solution D2, shown in Figure 43 and E solutions shown in Figure 44, at 15°F. Both ice crystal formation and salt precipitation were observed in all F, G, and H triplicates at 15°F, as shown in Figure 44.

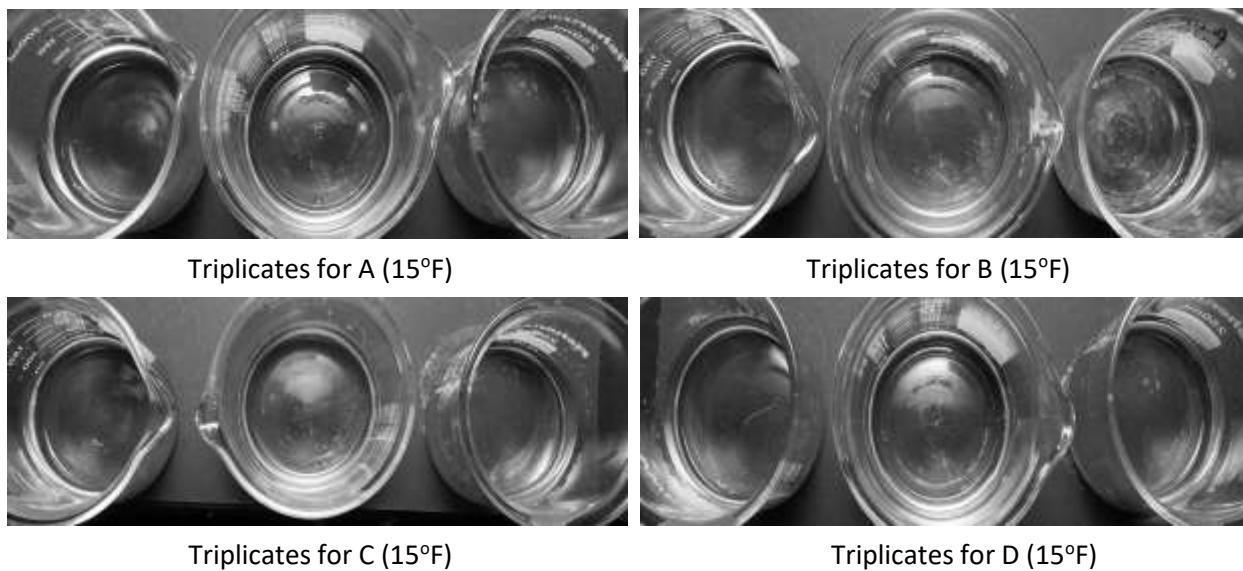


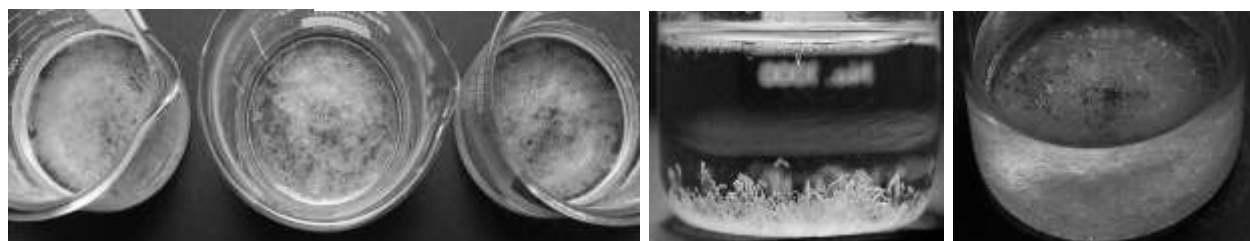
Figure 42. Photographs of triplicates of solutions A, B, C, and D at 15°F.



Figure 43. Salt precipitation out of solution E (left to right: E1, E2, E3) at 15°F.



Triplicates for F at 15°F (left), F1 (middle and right)



Triplicates for G at 15°F (left), G1 (middle), and G2



Triplicates for H at 15°F (left), H1 (middle), and H3

Figure 44. Ice crystal formation and salt precipitation shown in solutions F, G, H at 15°F.

Test Temperature: 10°F (-12.2°C)

Microscopy was used to capture images of ice crystals collected from solutions F1 (Figure 45), G2 (Figure 46), and H1 (Figure 47). The mass of the filtered ice crystals are provided in Table 12.

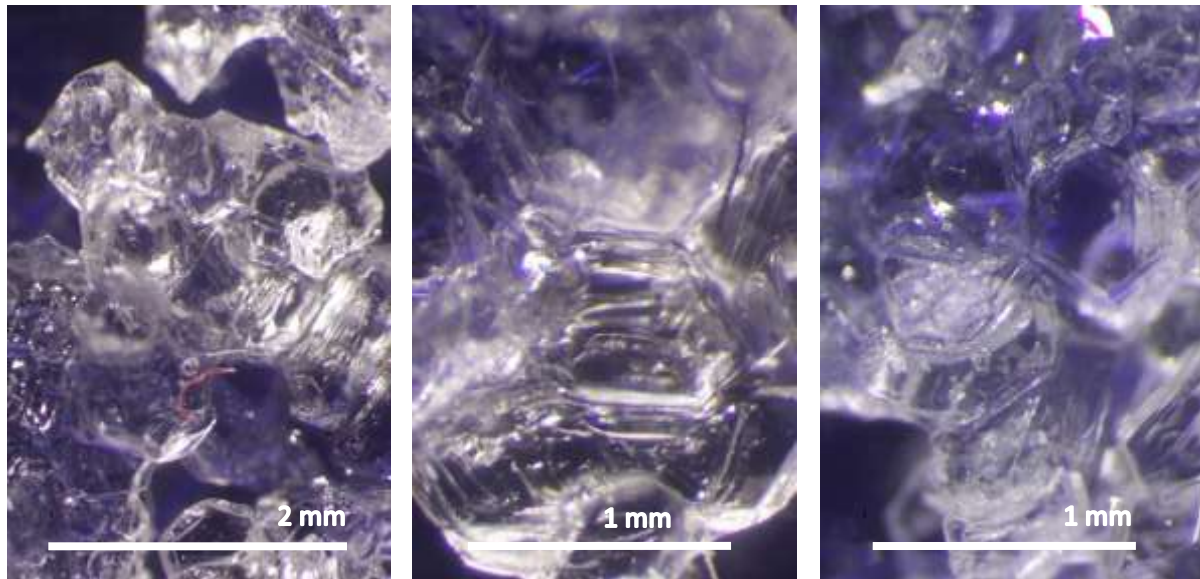


Figure 45. Ice crystal structure images for F1 (26 wt.%) at 10°F. Left image at 31.25x magnification and the middle and right images at 62.5x magnification.

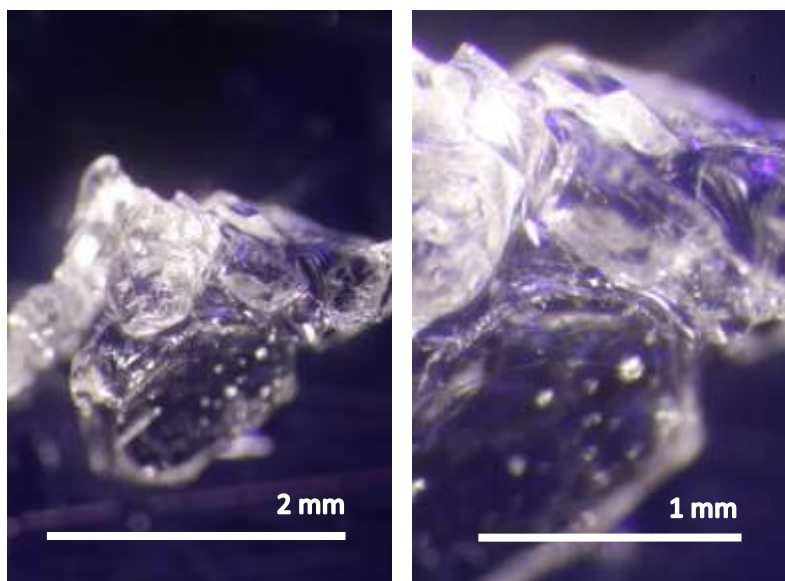


Figure 46. Ice crystal structure images for G2 (27 wt.%) at 10°F. Left image at 31.25x magnification and the right image at 62.5x magnification.

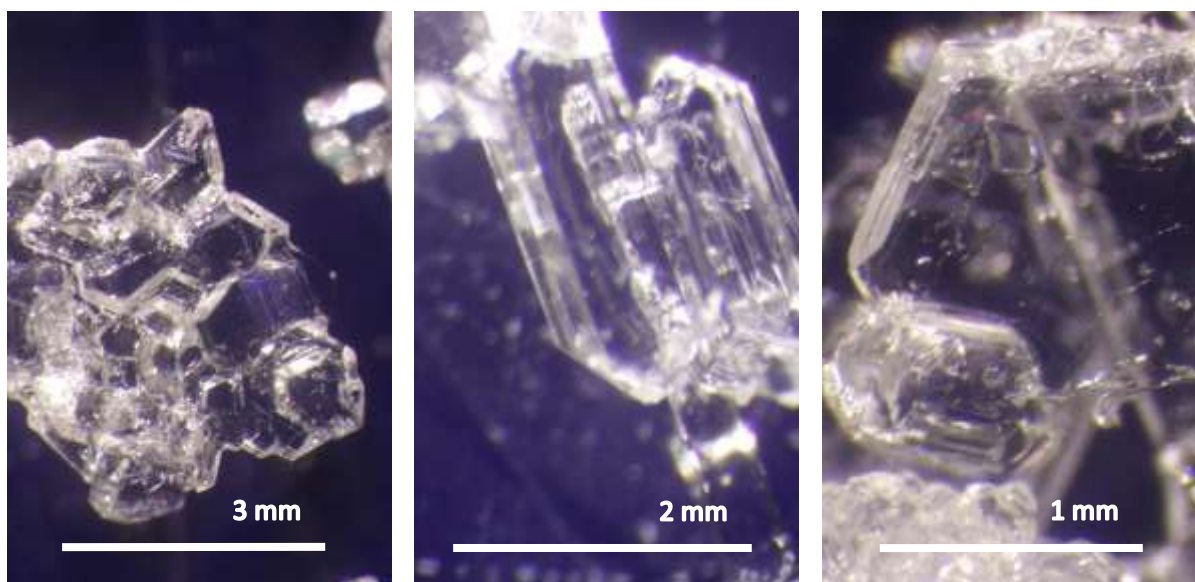


Figure 47. Ice crystal structure images for H1 (28 wt.%) at 10°F. Left image at 15x magnification, middle image at 31.25x magnification, and the right image at 62.5x magnification.

Table 12. Mass of ice crystals filtered from solutions F1, G2, and H1 at 10°F.

Brine Solutions (10°F)	Mass of empty beaker (g)	Mass of beaker + brine (g)	Mass of 75mL brine solution (g)	Mass of empty beaker (g)	Mass of the filtrate + beaker (g)	Mass of the filtrate (g)	Approx. mass of ice crystals and salt (g)
F1	116.45	198.21	81.76	294.97	363.2	68.23	13.53
G2	125.57	222.27	96.7	NA	NA	53.11	43.59
H1	108.95	191.75	82.8	NA	NA	56.3	26.5

Photographs of the triplicate samples of solution A through D at 10°F are provided in Figure 48. Both ice crystal formation and salt precipitation were observed in all E, F, G, and H triplicates at 10°F, as shown in Figure 49.



Triplicates for A at 10°F



Triplicates for B at 10°F

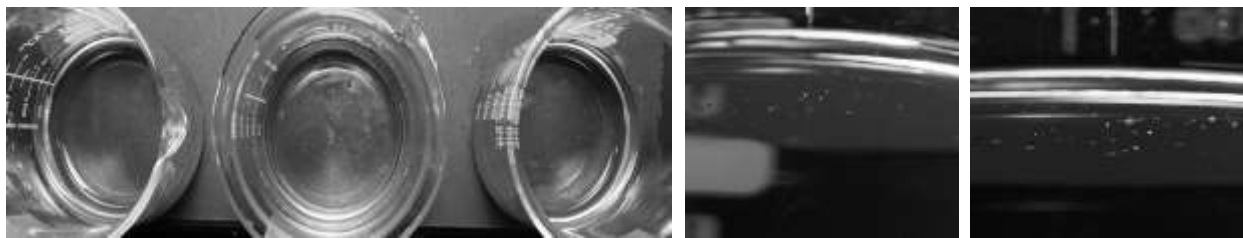


Triplicates for C at 10°F



Triplicates for D at 10°F

Figure 48. Photographs of triplicates of solutions A, B, C, and D at 10°F.



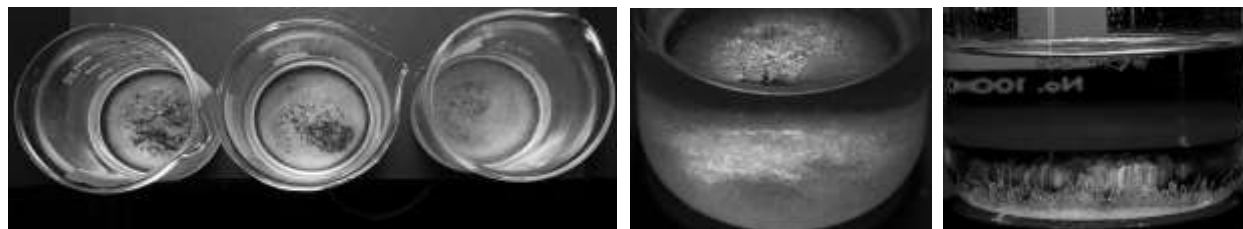
Triplicates for E (left), E1 (middle), and E3 (right) at 10°F



Triplicates for F (left), F3 (middle and right) at 10°F



Triplicates for G (left), G3 (middle and right) at 10°F



Triplicates for H (left), H1 (middle and right) at 10°F

Figure 49. Ice crystal formation and salt precipitation observed in solutions E, F, G, H at 10°F.

Test Temperature: 5°F (-15°C)

Photographs of the triplicate samples of solution A through D at 5°F are provided in Figure 50. However, microscopy images of ice crystal structures were not captured due to a shortage of time. Large ice crystals formed and salt precipitated out of solutions E, F, G, and H (Figure 51) at 5°F; in contrast, only small ice crystals formed and salt precipitated out in solution D1.



Triplicates for A at 5°F



Triplicates for B at 5°F



Triplicates for C at 5°F



Triplicates for D at 5°F

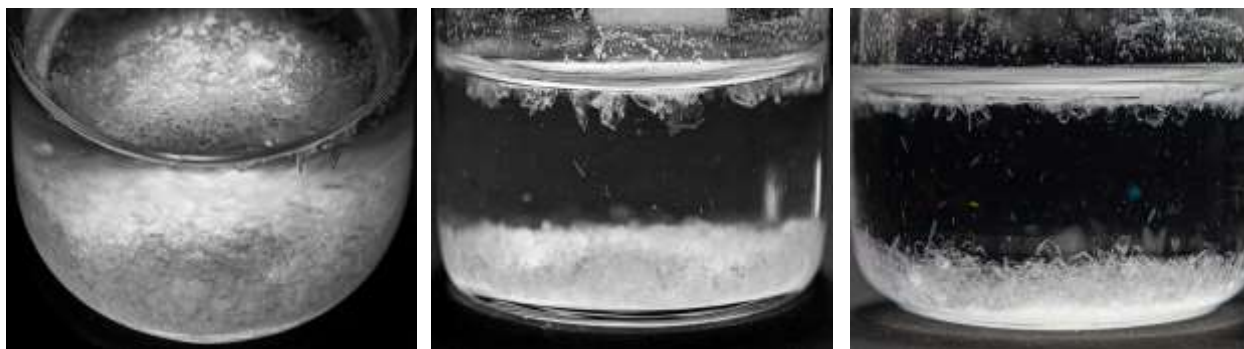
Figure 50. Photographs of triplicates of solutions A, B, C, and D at 5°F.



Ice crystal formation and salt precipitation at 5°F for E triplicates (E1 to E3: left to right)



Ice crystal formation and salt precipitation at 5°F for F triplicates (F1 to F3: left to right)



Ice crystal formation and salt precipitation at 5°F for G triplicates (G1 to G3: left to right)



Ice crystal formation and salt precipitation at 5°F for H triplicates (H1 to H3: left to right)

Figure 51. Ice crystal formation and salt precipitation shown observed in solutions E, F, G, and H at 5°F.

Test Temperature: 0°F (-17.7°C)

Microscopy was used to capture images of ice crystals collected from solutions E1 (Figure 52), F1 (Figure 53), G1 (Figure 54), and H1 (Figure 55) at 0°F. At this temperature, it was difficult to separate the ice crystals from the precipitated salt during the filtering process; as such, the ice crystals and precipitated salt may both be present. The mass of the filtered ice crystals for solutions E1, E2, F, F3, G2, H1, H2, and H3 are provided in Table 13.

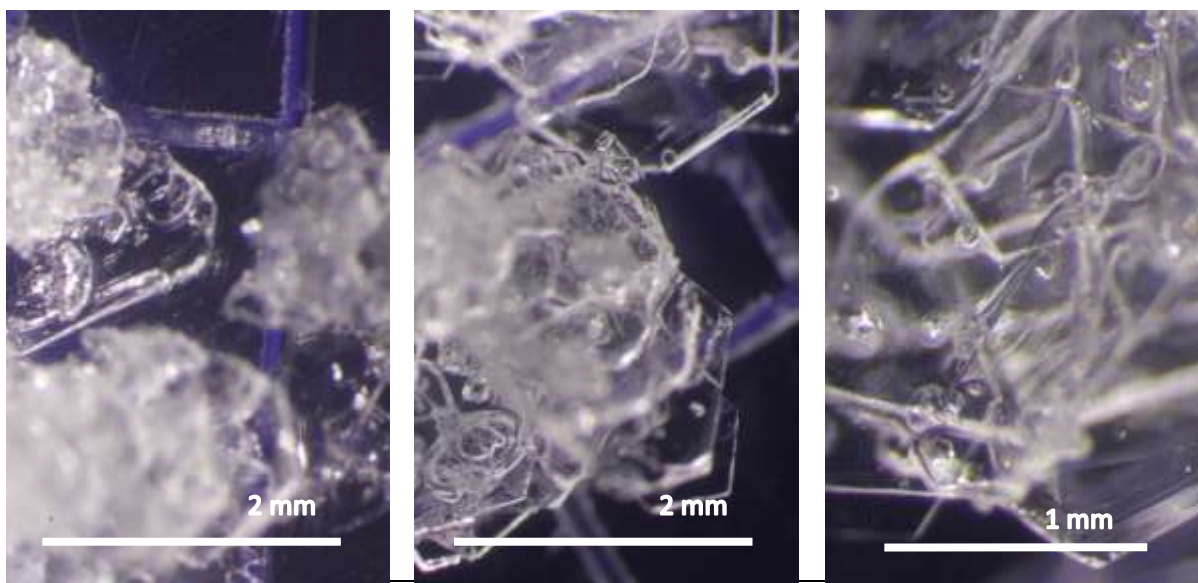


Figure 52. Ice crystal structure images for E1 at 31.25x magnification (left and middle) and 62.5x magnification (right) at 0°F.

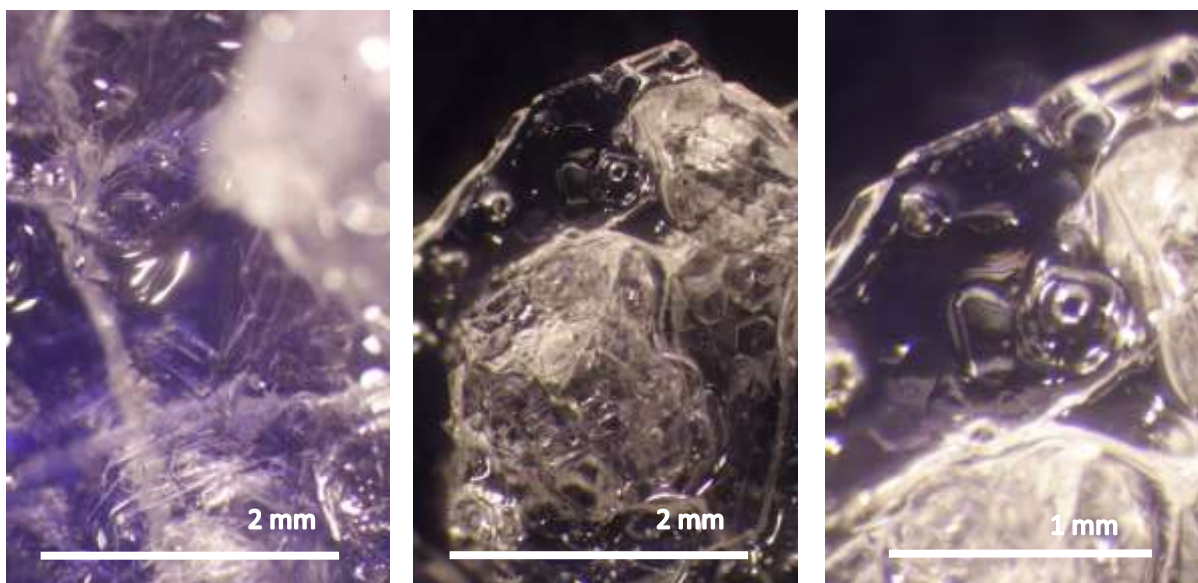


Figure 53. Ice crystal structure images for F1 at 31.25x magnification (left and middle) and 62.5x magnification (right) at 0°F.

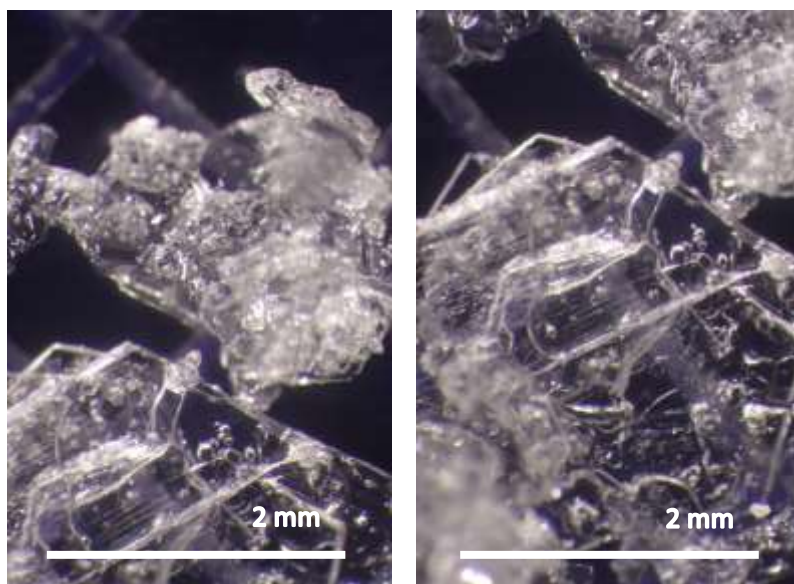


Figure 54. Ice crystal structure images for G1 at 31.25x magnification at 0°F.

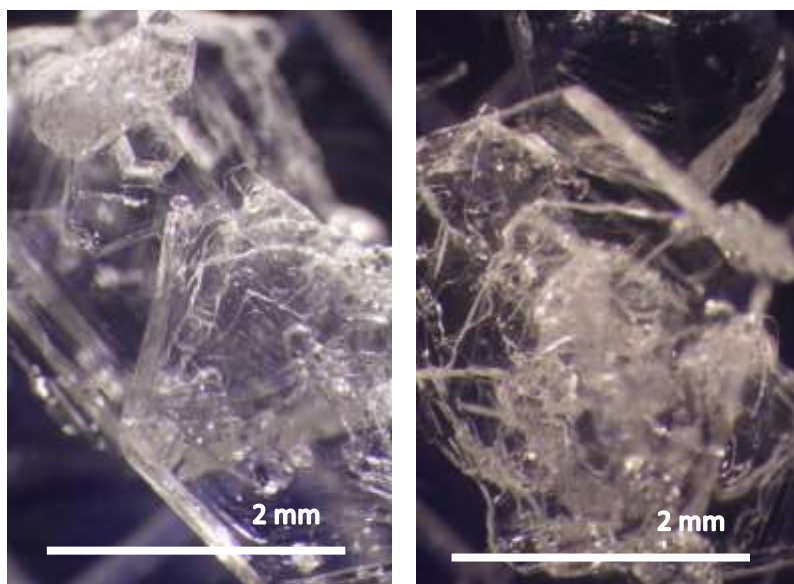


Figure 55. Ice crystal structure images for H1 at 31.25x magnification at 0°F.

Table 13. Mass of ice crystals and precipitated salt filtered from solutions E1, E2, F1, F3, G2, H1, H2, and H3 at 0°F.

Brine Solutions (0°F)	Mass of empty beaker (g)	Mass of beaker + brine (g)	Mass of 75mL brine solution (g)	Mass of empty beaker (g)	Mass of the filtrate + beaker (g)	Mass of the filtrate (g)	Approx. mass of ice crystals + salt (g)
E1	90.03	184.42	94.39	156.6	226.69	70.09	24.3
E2	121.34	196.47	75.13	162.56	222.47	59.91	15.22
F1	116.45	197.59	81.14	195.61	270.33	74.72	6.42
F3	111.52	184.5	72.98	176.48	235.59	59.11	13.87
G2	125.57	201.72	76.15	176.48	239.31	62.83	13.32
H1	109.52	189.03	79.51	168.17	226.92	58.75	20.76
H2	86.72	164.71	77.99	NA	NA	65.86	12.13
H3	106.62	185.71	79.09	NA	NA	63.26	15.83

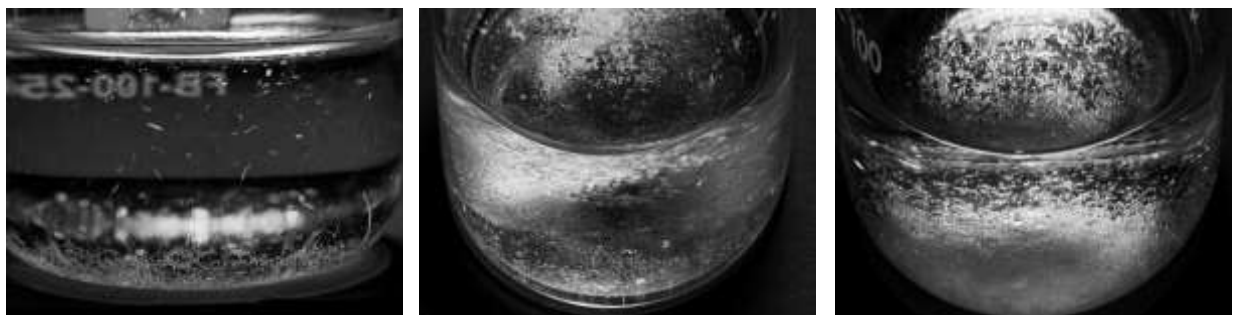
Photographs of the triplicate samples of solution A, B, and C at 0°F are provided in Figure 56. Minute amounts of salt precipitated out of solutions D1-3, but no ice crystal formation was visible (Figure 57). Ice crystals formed and salt precipitated out of solutions E, F, G, and H at 0°F (Figure 58).



Figure 56. Images of triplicate samples for solutions A (top), B (middle), and C (bottom) at 0°F.



Figure 57. Minor salt precipitation from solution D1-3 (left to right) at 0°F. No visible ice crystal formation.



Significant ice crystal formation and minor salt precipitation at 0°F for E triplicates (1 to 3: L to R)



Significant ice crystal formation and minor salt precipitation at 0°F for F triplicates (1 to 3: L to R)



Significant ice crystal formation and minor salt precipitation at 0°F for G triplicates (1 to 3: L to R)



Significant ice crystal formation and minor salt precipitation at 0°F for H triplicates (1 to 3: L to R)

Figure 58. Ice crystal formation and salt precipitation shown in solutions E, F, G, and H at 0°F.

Test Temperature: -6°F (-21.1°C)

Microscopy was used to capture images of the solution A triplicates but no ice crystals were present (Figure 59). Microscopy images and filtered ice crystals were not captured for the remaining solutions due to time constraints. Photographs taken of the triplicate samples A, B, and C at -6°F are provided in Figure 59. At -6°F, solution D showed ice crystal formation and salt precipitation in all triplicates (Figure 60) while E, F, G, and H showed significant ice crystal formation and salt precipitation (Figure 61).

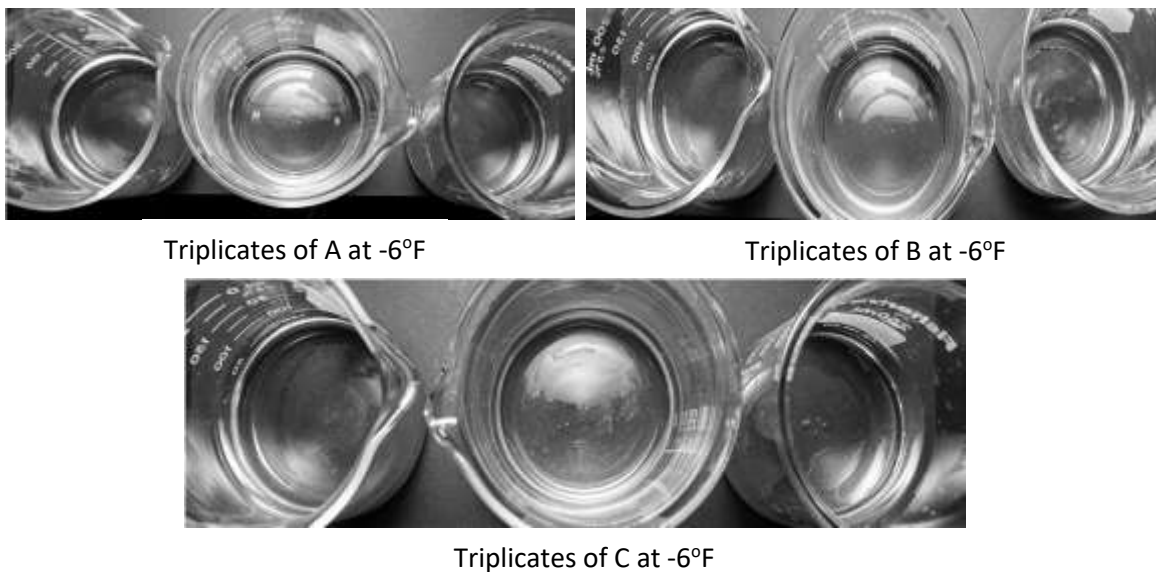


Figure 59. Images of triplicate samples for solutions A (top), B (middle), and C (bottom) at -6°F.



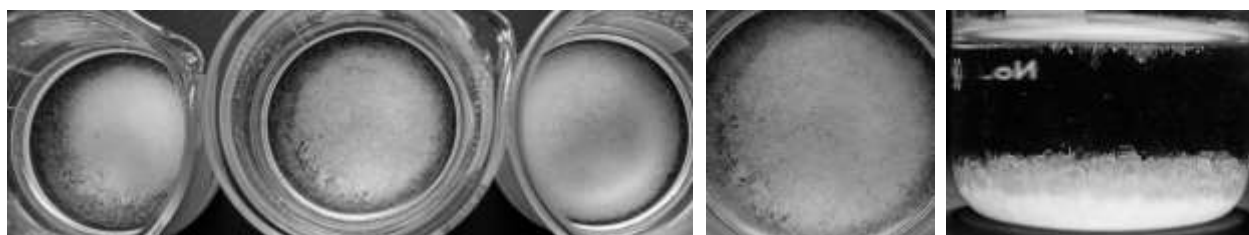
Figure 60. Ice crystal formation and salt precipitation in solution D2 (left) and D3 (right) at -6°F.



Significant ice crystal formation and salt precipitation for solution E triplicates (left), E1 (middle), E3 (right) at -6°F



Significant ice crystal formation and salt precipitation for solution F2 and F3 (left), close-up images of F2 (middle) and F3 (right) at -6°F



Significant ice crystal formation and salt precipitation for solution G triplicates (left), G2 (middle), and G3 (right) at -6°F



Significant ice crystal formation and salt precipitation for solution H triplicates (left), H2 (middle), and H3 (right) at -6°F

Figure 61. Ice crystal formation and salt precipitation shown in solutions E, F, G, and H at -6°F .

Discussion

Analysis of Ice Crystals (solids) Filtered out of Solution

No visible ice crystal formation or salt precipitation occurred at any tested temperatures for brine solutions A, B, or C (21 wt.%, 22 wt.%, and 23.3 wt.%, respectively) but ice crystals did form in brine concentrations D, E, F, G, and H (24 wt.%, 25 wt.%, 26 wt.%, 27 wt.%, and 28 wt.%, respectively) at various temperatures (Table 9).

When looking at the mass of the filtered ice crystals, an average of 15.0 ± 10.1 g of solids was filtered out of the brine solution; on average, approximately 82% of the solution remained liquid brine and 18% formed into ice crystals (and potentially some salt precipitate). All data can be found in Table 14. For temperatures 10°F, 15°F and 20°F, where every effort was made to remove only ice crystals, the average mass was 16.4 ± 14.6 g. In contrast, the solids filtered out at test temperature 0°F had an average mass of 19.0 ± 5.8 g. Note that a larger quantity of solids was filtered out of the brine solution at test temperature 0°F.

Table 14. Summary of ice crystal (or solids) mass filtered from samples.

Test Temp (°F)	Solution & Sample Number	NaCl brine concentration (wt.%)	Weight of the filtrate (g)	Weight of ice crystals (solids) (g)
20	H1	28	85.59	8.37
20	G1	27	78.4	11.45
15	F2	26	77.29	4.53
15	G1	27	84.92	3.65
15	H1	28	86.29	6.09
10	F1	26	68.23	13.53
10	G2	27	53.11	43.59
10	H1	28	56.3	26.5
0	E1	25	70.09	24.3
0	E2	25	59.91	15.22
0	F1	26	74.72	6.42
0	F3	26	59.11	13.87
0	G2	27	62.83	13.32
0	H1	28	58.75	20.76
0	H2	28	65.86	12.13
0	H3	28	63.26	15.83

Due to limited filtered ice crystal (or solids) data captured - no ice crystals present in solutions A, B, and C; no filtered ice crystal (or solids) data captured at 5°F and -6°F; and the difference in filtering methods used (i.e., only attempting to capture ice crystals versus filtering the entire brine solution (at 0°F only)), provided limited and inconsistent data, which was insufficient for further analysis. Figure 62 graphically

represents the mass in grams of filtered solids in relation to test temperature. No clear trends can be observed.

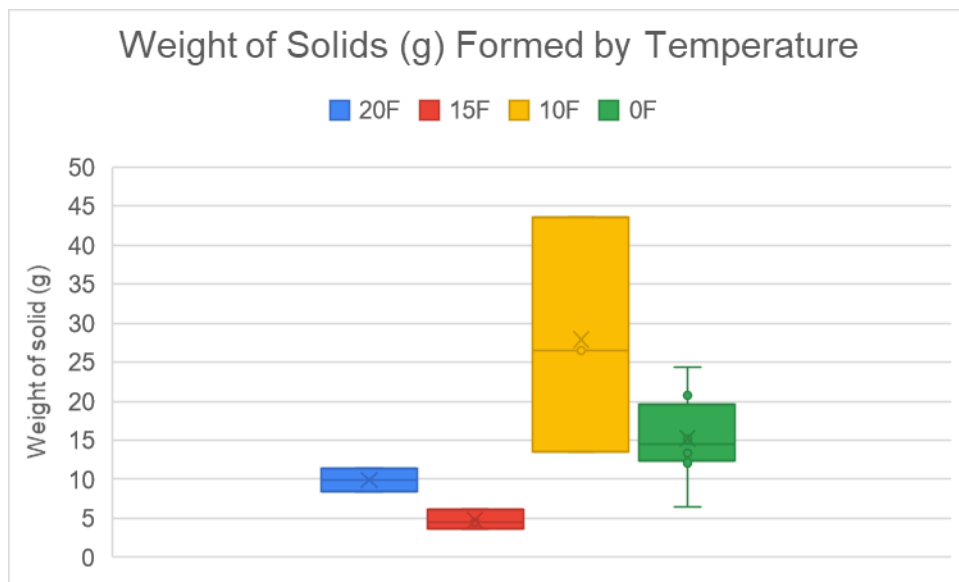


Figure 62. Mass of solids (ice crystals and potentially precipitated salt) filtered out of the brine solution shown by test temperature.

Figure 63 graphically represents the mass in grams of filtered solids in relation to NaCl solution concentration. It can be observed that a wide range of results were found for the various E, F, G, and H NaCl solutions (25 wt.%, 26 wt.%, 27 wt.%, and 28 wt.%, respectively).

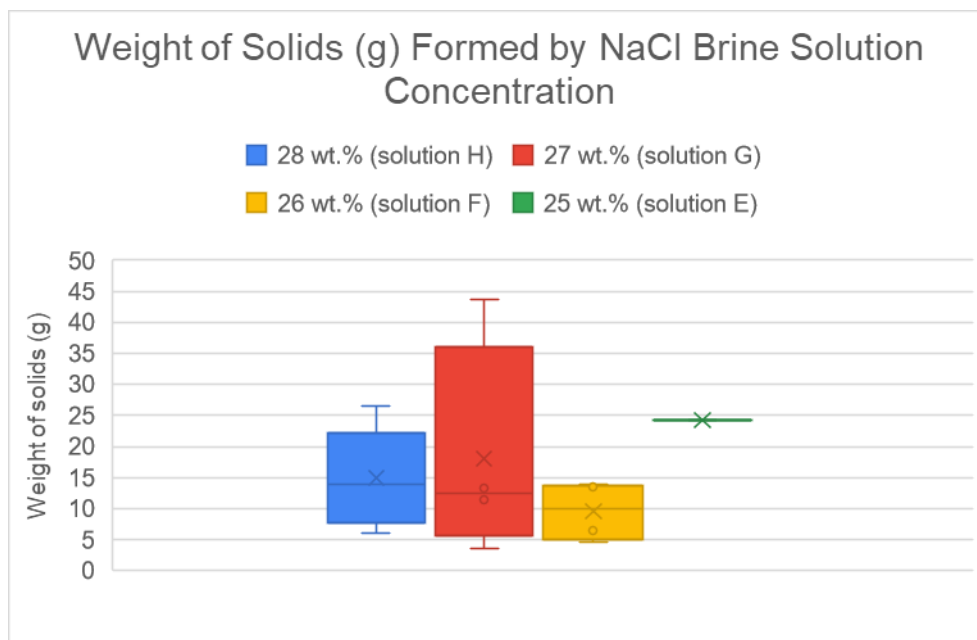


Figure 63. Mass of solids (ice crystals and potentially precipitated solids) filtered out of the brine solution in relation to NaCl brine solution concentration.

The limited data capture and high variability between replicates may indicate the following:

- The time allowed for ice crystal formation may need to be increased from 10 to 30 minutes.
 - The filtering method needs to be consistent, and likely refined, to produce consistent results.
 - Filtering methods may be compromised by the difficulty in distinguishing ice crystals from precipitated salt. Advanced imaging techniques may be required to address this issue.
- More refined methods are required before a detailed, accurate isothermal cooling diagram can be created.

Ice and Salt Crystals Under the Microscope

Ice crystals can grow in over 20 different shapes, but the conditions present during these tests resulted in generally a hexagonal or cubic shapes (Kaufmann, 1968). Examples of ice crystal structures found in this experiment can be seen in Figure 35, Figure 39, Figure 40, Figure 41, Figure 45, Figure 46, and Figure 47.

$\text{NaCl} \cdot 2\text{H}_2\text{O}$ crystals, or salts hydrate (also known as hydro-halite), go mostly unrecognized because of their superficial resemblance to ice (Kaufmann, 1968; Swenne, 1983); they are monoclinic (or cubic) with beveled edges (Figure 64) (Kaufmann, 1968). Both NaCl and $\text{NaCl} \cdot 2\text{H}_2\text{O}$ solids can precipitate out of brine solutions. At the temperatures and NaCl concentrations present in this experiment, $\text{NaCl} \cdot 2\text{H}_2\text{O}$ was expected to be present at temperatures below 32°F (0°C) and NaCl concentrations of 23.3% or higher (based on solution temperature), or for any NaCl solution below the eutectic temperature (-6°F or -21.1°C) (Figure 9D).

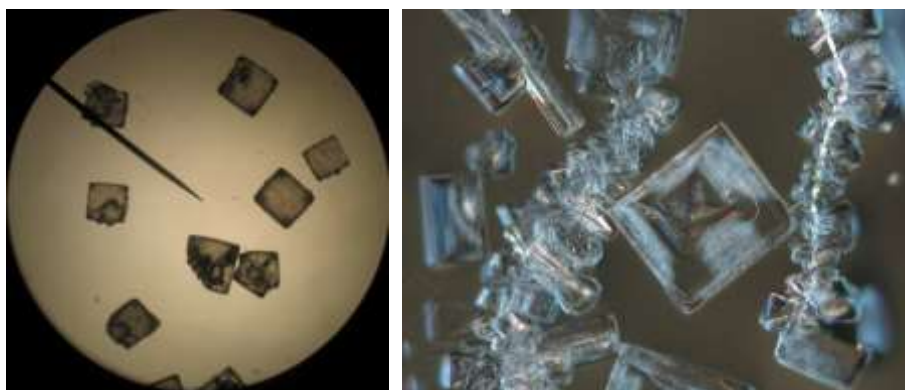


Figure 64. Microscopy images of NaCl crystals at [40x magnification](#) (left) and [under polarized light](#) (right).

Solid particle nucleation (read: crystal formation) occurs most often when ice crystals and salt crystals come into contact. Note that in Figure 52, Figure 53, Figure 54, and Figure 55, where both the ice crystals and precipitated salts (NaCl and NaCl.2H₂O) are shown together in higher powered microscope images, it is nearly impossible to distinguish between the ice crystals and salts. To accurately determine the location and percent concentration of ice crystals, precipitated salt, and salt brine, advanced analysis and imaging techniques, such as cold stage RAMAN microscopy, were required (Malley et al., 2018).

In addition to crystal structures, bubbles in the ice crystals were observed and likely contained salt brine (Figure 65). Bubbles were observed at all temperatures where microscopic images were taken and in salt solution concentrations from 25 wt.% through 27 wt.%. This does not mean that bubbles were not present at other temperatures or salt solution concentrations. It only means that this effort found them where noted. The presence of salt brine-filled bubbles indicates that the solid phase of ice crystals and salt crystals is not uniform. Instead, it indicates that many phases can co-exist. **These images lend credibility to the concept that the ice formed in the presence of the salt brine is weaker than ice formed only in presence of pure water.**

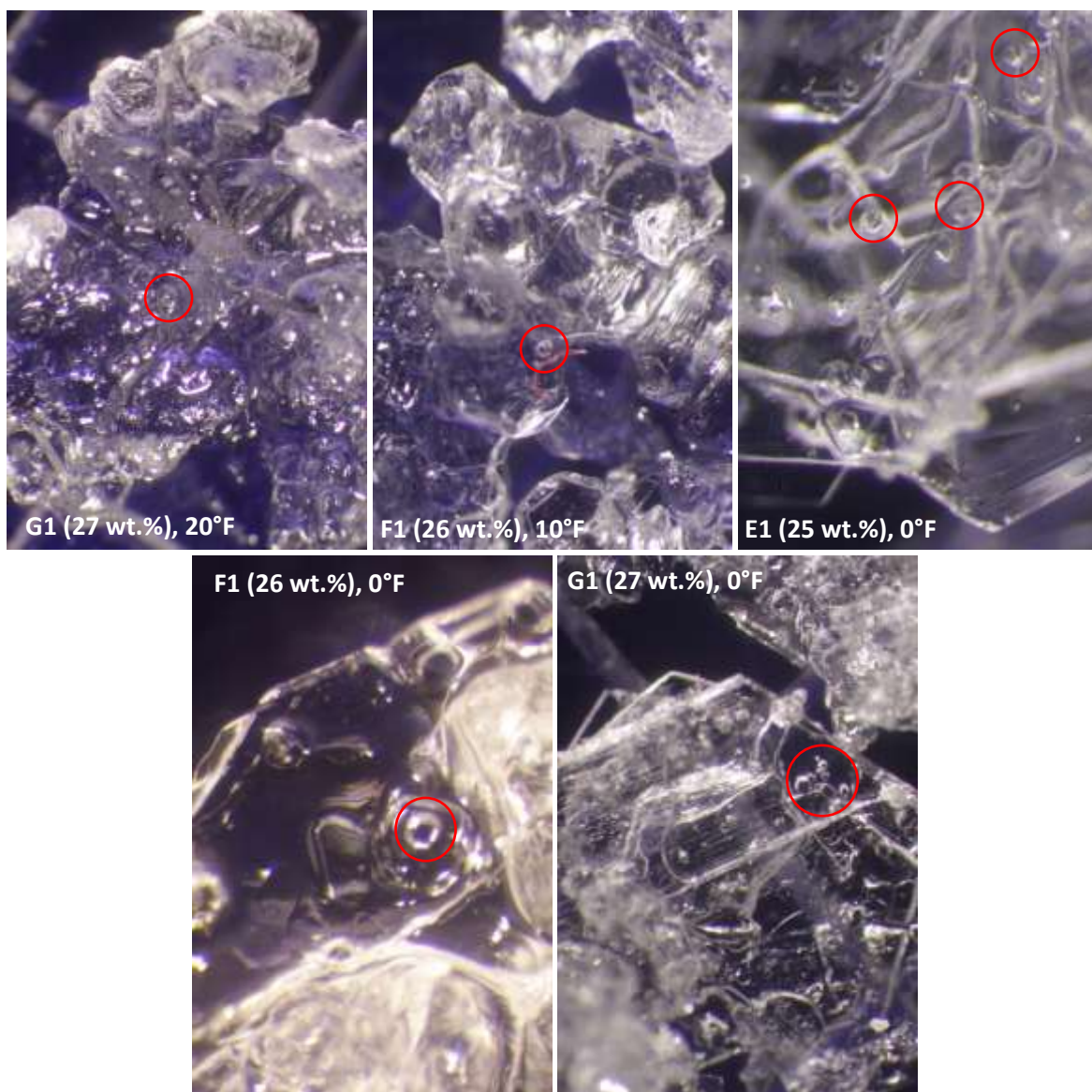


Figure 65. Microscopic images of ice crystals with bubbles (circled in red), likely filled with salt brine.

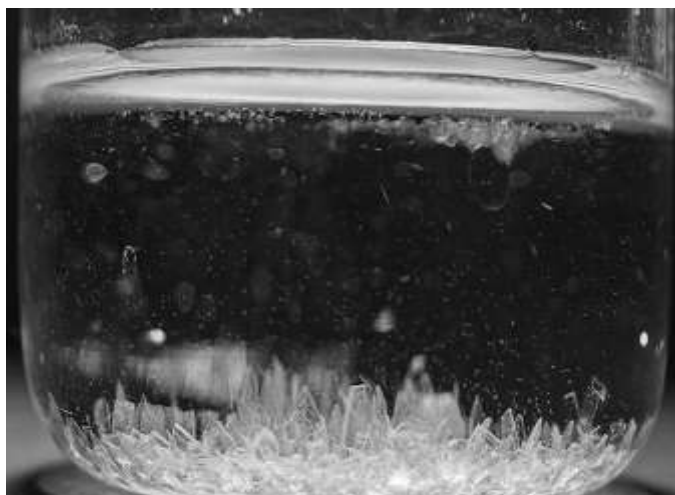


Figure 66. Brine solution showing crystals suspended in the brine solution and salt precipitated out at the bottom of the beaker. Test conditions: -6°F, solution H (28 wt.% NaCl).

Below 32°F, it is difficult to distinguish between NaCl and NaCl·2H₂O with the naked eye. Viewing the precipitate under a microscope or using advanced imaging techniques may provide additional information on the presence, and concentration, of each precipitate type.

Due to its low density, pure ice will float on the surface and be suspended in brine solution (Figure 66). As the pure ice crystals form, the water-salt (NaCl) balance in the brine solution shifts and excess salt precipitates out when the brine solution concentration increases above the 26.4% NaCl solubility limit (Figure 67). As more ice crystals form, more salt precipitates.



Figure 67. Brine solution showing both ice crystals suspended in the brine solution and salt precipitated out at the bottom of the beaker. Test conditions: 0°F, solution E (25 wt.% NaCl).

To further demonstrate this, timelapse photos were taken of 23.3 wt.% and 27 wt.% NaCl solutions at 5°F over the course of 285 minutes (4.75 hours). The 23.3 wt.% solution showed no ice crystal growth or salt precipitation over the course of the experiment (Figure 68). However, Figure 69 shows ice crystal formation, salt precipitation, and likely dihydrate salt formation, occurring in the 27 wt.% NaCl solution over the course of the experiment. A timelapse video of this experiment can be found at <https://youtu.be/rlbJdPes0jl>.

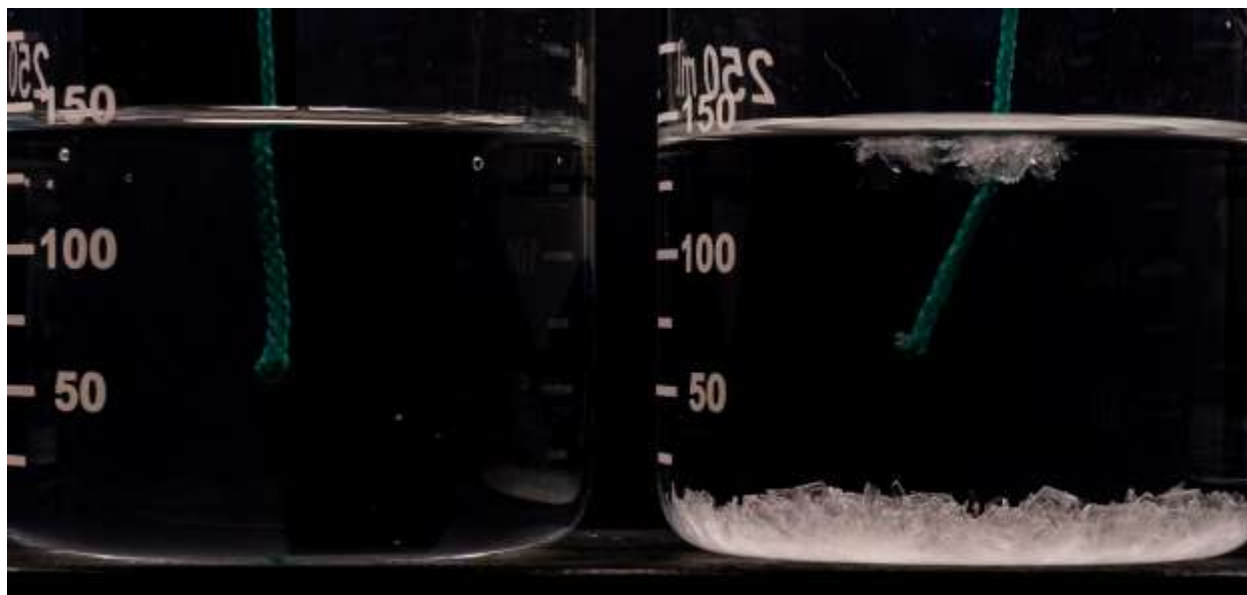


Figure 68. Ice crystal growth, salt precipitation, and potentially dihydrate salt formation in the 27 wt.% NaCl solution (right) compared with 23.3 wt.% NaCl solution with no ice crystal growth or salt precipitation at 5°F. Note that the string was added to serve as a nucleation point.

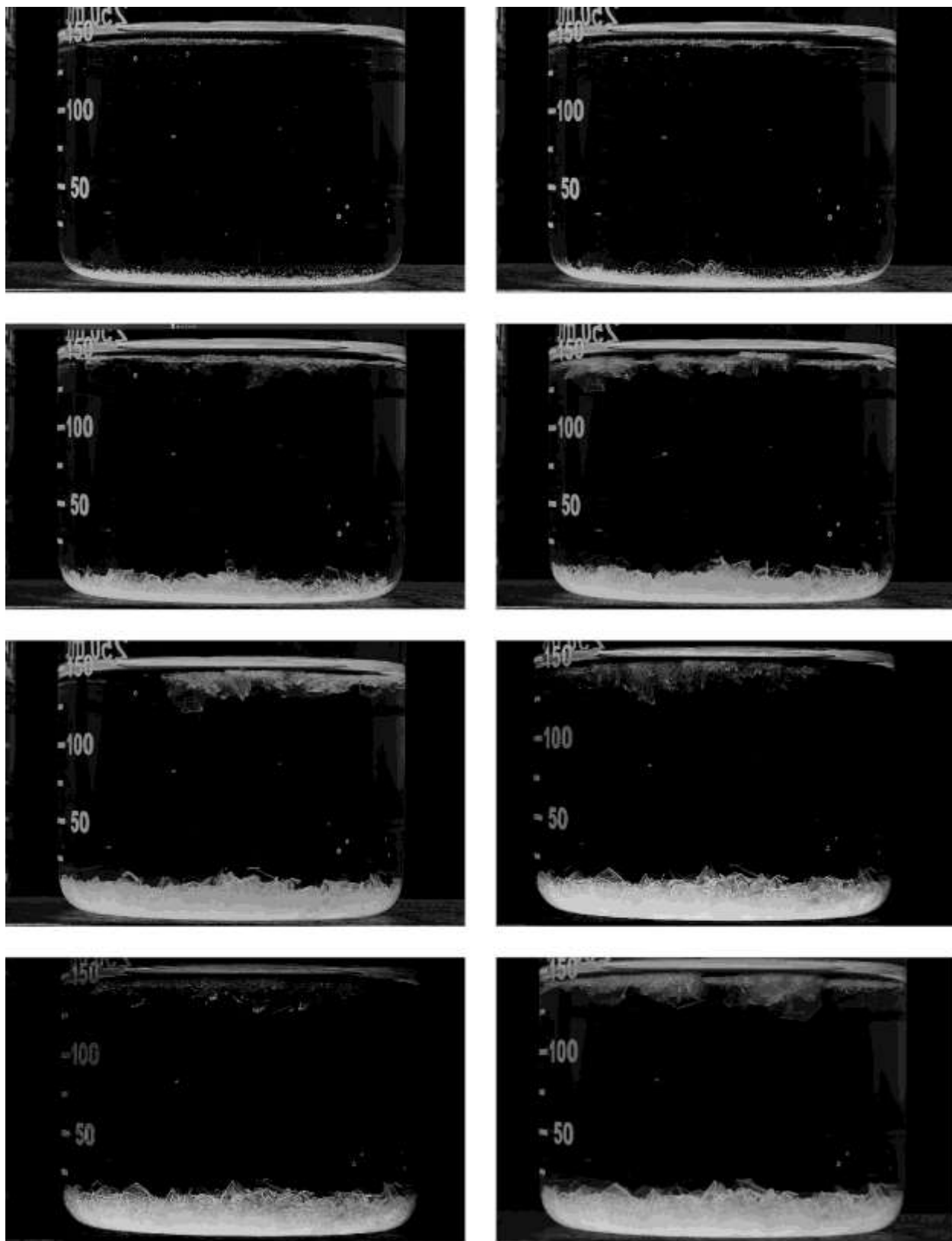


Figure 69. Time lapse images of ice crystal formation and salt precipitation occurring for 27 wt.% NaCl solution (starting top left, ending bottom right).

Friction Testing

Results

Eight different NaCl concentrations were tested on concrete and asphalt pavement samples at 15°F for a total of 16 tests. Table 15 provides a summary of testing variables including sample name, pavement type, NaCl brine solution concentration, pavement sample ID, NaCl brine solution application rate, snow density, and relative humidity of the cold chamber during testing. The density of the snow ranged from 0.17 to 0.35 g/mL, with an average of 0.28 g/mL. The relative humidity in the cold room during testing ranged from 13 to 60% and was influenced by the outside temperature, with the hotter parts of the day creating higher humidity levels within the cold lab.

Table 15. Summary of testing variables.

Sample Name	NaCl Solution (%)	Pavement Type	Pavement Sample ID	Application Rate (gal/in/mi)	Snow Density (g/mL)	Humidity (%)
C-21	21	Concrete	B2	45	0.3428	58
C-22	22	Concrete	B2	45	0.3062	41
C-23.3	23.3	Concrete	B4	45	0.3155	48
C-24	24	Concrete	B2	45	0.2903	16
C-25	25	Concrete	B5	45	0.3475	13
C-26	26	Concrete	B4	45	0.1699	50
C-27	27	Concrete	B3	45	0.3247	45
C-28	28	Concrete	B3	45	0.2043	51
A-21	21	Asphalt	A1	45	0.3294	60
A-22	22	Asphalt	A3	45	0.3031	41
A-23.3	23.3	Asphalt	A2	45	0.3333	25
A-24	24	Asphalt	A2	45	0.2948	51
A-25	25	Asphalt	A3	45	0.3034	42
A-26	26	Asphalt	A3	45	0.1722	49
A-27	27	Asphalt	A2	45	0.3052	45
A-28	28	Asphalt	A2	45	0.1997	52

The following section summarizes the results of pavement surface friction values during trafficking testing on both concrete and asphalt pavement types.

Concrete Pavement Samples

Pull-test Friction Values

The average range of control group pull-test friction values for concrete was 0.5 to 0.66 (Table 16). Over the course of the experiment, pull-test friction values generally decreased following application of NaCl solution, with only 21%, 23.3%, 25% increasing the friction values (Figure 70, Table 16). The 28 wt. % NaCl solution had the largest decrease in friction after application on the pavement.

After snow was compacted on the concrete samples, the average pull-test friction values ranged from 0.3 to 0.38 (Table 16). These values were not affected by the solution applications and but were influenced by the snow density and humidity of the cold lab, which will be discussed in more detail in the statistical analysis section. During trafficking, the average pull-test friction values ranged from 0.22 to 0.37, with the two lowest friction values (0.22 and 0.23) resulting from the 28 and 27 wt. % NaCl solutions, respectively. Whereas the highest average pull-test friction values were from the 22 and 25 wt. % NaCl solutions (with values of 0.37). After plowing, the average pull-test friction values ranged from 0.22 to 0.35, with the lowest friction value belonging to the 28 wt. % NaCl solution, and the highest value to the 25 wt. % NaCl solution.

Table 16. Summary of friction values from the pull-test measured on concrete pavement samples during trafficking testing.

Test	Pull Test Averages (μ) and Standard Deviation									
	Control		Application		Compacted		Trafficked		Plowed	
	Avg	StDev	Avg	StDev	Avg	StDev	Avg	StDev	Avg	StDev
C-21	0.621	0.048	0.667	0.029	0.348	0.046	0.300	0.022	0.252	0.005
C-22	0.575	0.081	0.510	0.028	0.256	0.005	0.365	0.062	0.282	0.065
C-23.3	0.495	0.091	0.610	0.062	0.320	0.024	0.322	0.047	0.269	0.032
C-24	0.611	0.026	0.555	0.070	0.323	0.061	0.330	0.073	0.272	0.007
C-25	0.553	0.041	0.572	0.094	0.322	0.016	0.369	0.062	0.346	0.039
C-26	0.657	0.047	0.555	0.010	0.384	0.004	0.309	0.034	0.245	0.069
C-27	0.580	0.010	0.555	0.042	0.296	0.050	0.229	0.064	0.305	0.045
C-28	0.680	0.056	0.507	0.069	0.336	0.060	0.217	0.023	0.223	0.047

Figure 70 shows the pull-test friction values recorded on the concrete samples over the course of the experiment. No clear trends in pull-test friction values can be observed.

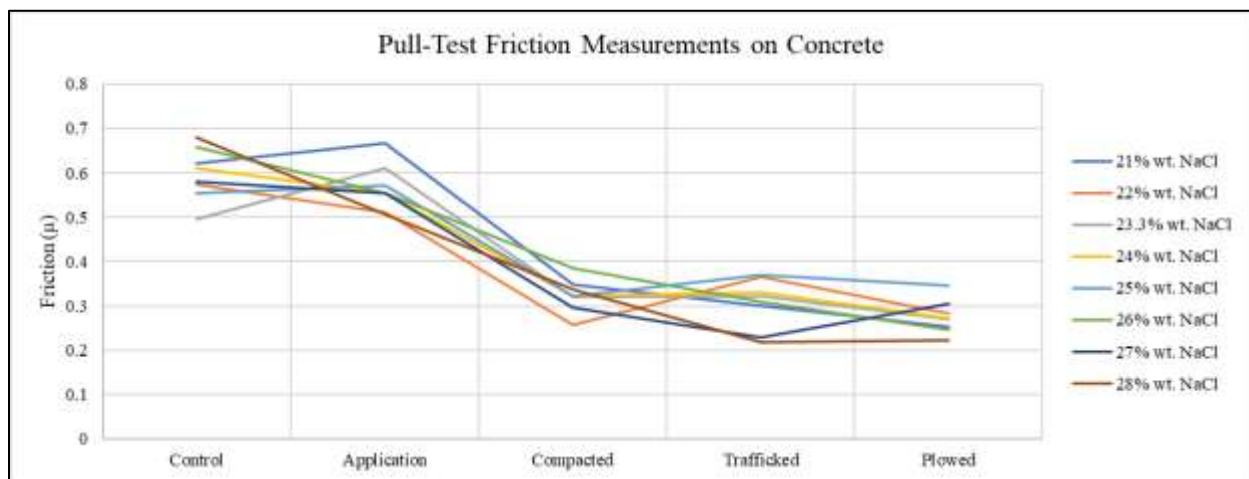


Figure 70. Friction values from the pull-test on concrete pavement samples during trafficking testing.

Teconer Friction Values

The Teconer friction data from the concrete samples generally showed slightly higher friction values over the course of the experiment (Table 17) than the pull-test friction values (Table 16). The average control friction values ranged between 0.66 and 0.81. Following NaCl solution application, average friction values were between 0.68 and 0.79, with all NaCl solutions, except the 22 wt. % NaCl solution, showing a decrease in friction after application to the concrete pavement. The 22 wt. % NaCl solution showed an increase in friction after application. The average friction values on the compacted snow ranged from 0.27 to 0.4. During trafficking, the average friction values remained relatively consistent and ranged from 0.28 to 0.38. The average friction values after plowing were all higher than the average pull-test friction values (Table 16 and Table 17), with the average Teconer friction values ranging between 0.44 and 0.53, with 22 wt. % NaCl solution having the lowest friction value and 27 wt. % NaCl solution having the highest friction value.

Table 17. Summary of friction values from the Teconer sensor measured on concrete pavement samples during trafficking testing.

Test	Teconer Friction Average (μ) and Standard Deviation									
	Control		Application		Compacted		Trafficked		Plowed	
	Avg	StDev	Avg	StDev	Avg	StDev	Avg	StDev	Avg	StDev
C-21	0.8053	0.0050	0.6833	0.1029	0.3652	0.0197	0.3688	0.0242	0.4883	0.0294
C-22	0.6594	0.0816	0.6942	0.0714	0.2678	0.0206	0.2835	0.0221	0.4420	0.0327
C-23.3	0.8051	0.0050	0.7443	0.0674	0.3650	0.0217	0.3529	0.0270	0.4615	0.0248
C-24	0.7819	0.0047	0.7341	0.0128	0.3995	0.0023	0.3560	0.0285	0.5183	0.0334
C-25	0.8086	0.0035	0.7713	0.0370	0.3524	0.0252	0.3479	0.0306	0.4570	0.0284
C-26	0.7935	0.0109	0.7754	0.0310	0.3798	0.0145	0.3814	0.0141	0.4613	0.0307
C-27	0.7853	0.0276	0.7743	0.0315	0.2691	0.0240	0.2899	0.0263	0.5388	0.0655
C-28	0.7961	0.0107	0.7836	0.0193	0.3998	0.0090	0.3817	0.0121	0.4582	0.0471

The Teconer friction values over the course of the experiment showed more consistency than the average pull-test friction values (Figure 70 and Figure 71).

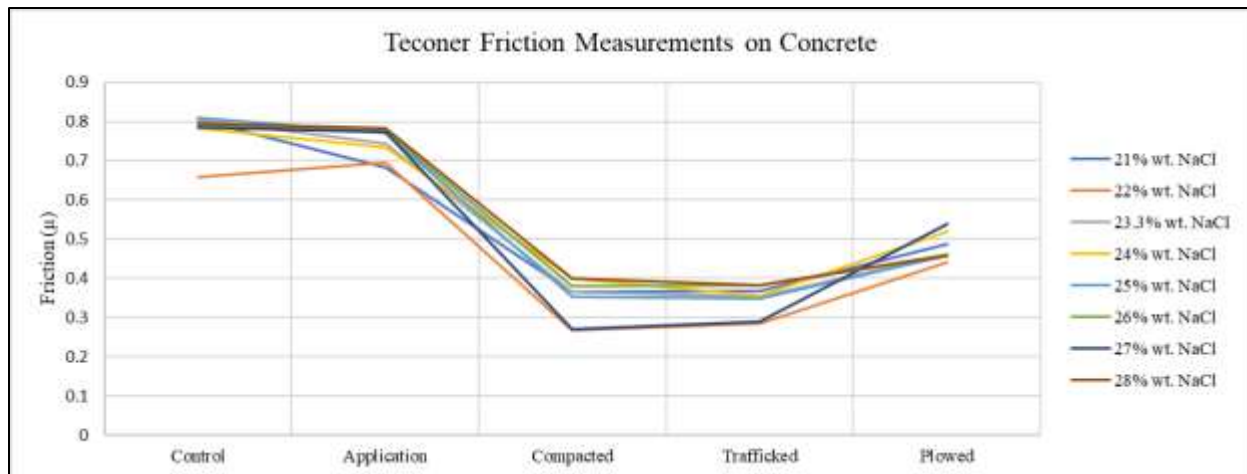


Figure 71. Friction values from the Teconer sensor on concrete pavement samples during trafficking testing.

Figure 72 shows the side-by-side comparison of all the NaCl solution concentration tests on concrete pavement following trafficking and after plowing. For images of samples post-trafficking, all showed some bare concrete, though some showed more than others and it appears that more snow stuck to pavement applied with the high NaCl solution concentrations (26-28 wt. % NaCl). A similar trend is noticeable in the side-by-side comparison of each concrete test after the snow was plowed off (Figure 72).

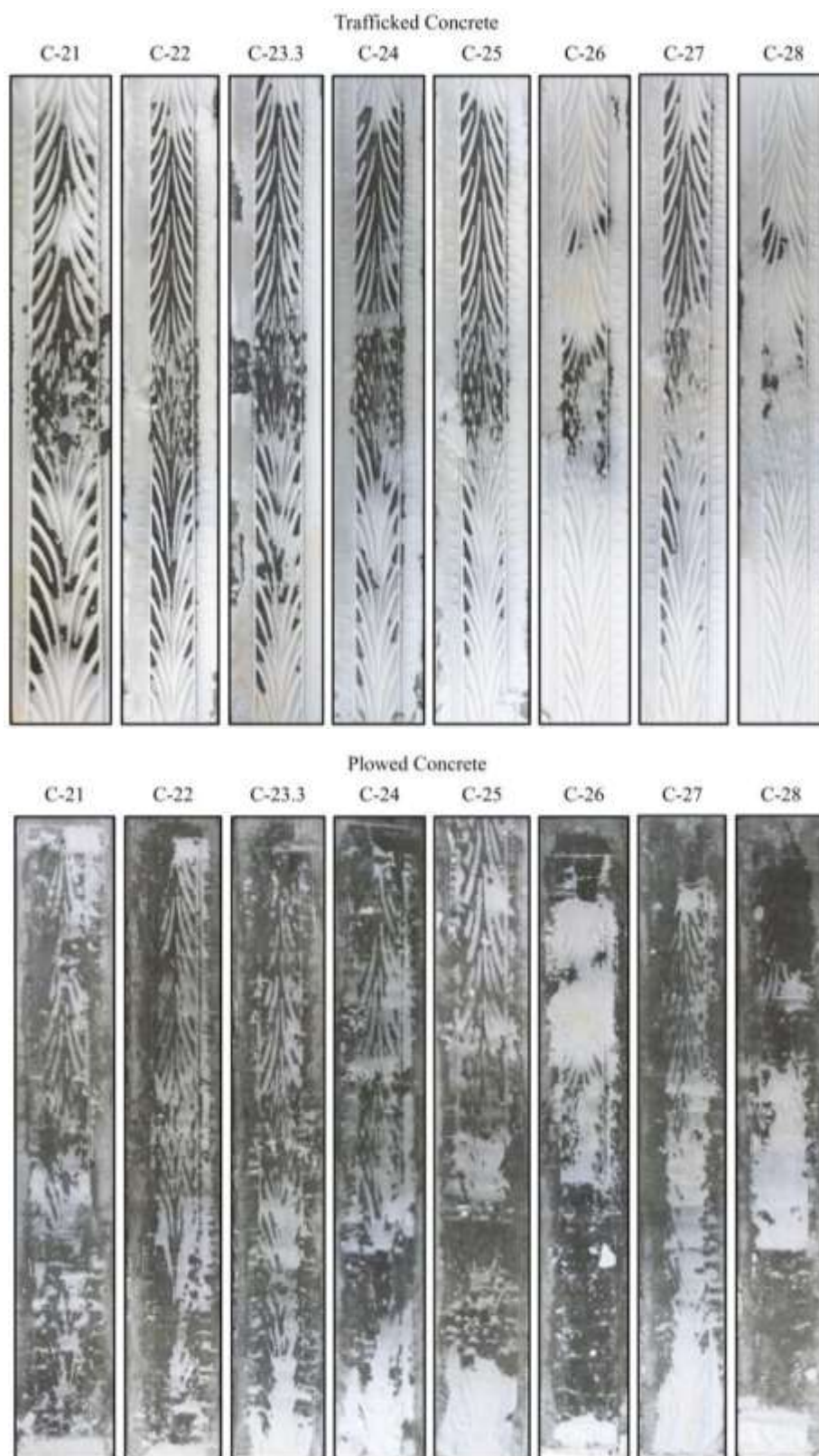


Figure 72. Images of concrete pavement samples after trafficking (top) and after plowing (bottom) for each NaCl solution.

Asphalt Pavement Samples

Pull-test Friction Values

For the pull-test, the control friction values ranged from 0.71 to 0.78, which is much higher than was measured on the concrete samples (Table 18). After the application of the NaCl solutions, pull-test friction values ranged from 0.58 to 0.66. All pull-test friction values measured after the NaCl solution was applied were lower than control pull-test friction values. Friction values measured on the compacted snow ranged from 0.15 to 0.34, with an average compacted pull-test friction value of 0.29. Pull-test friction values measured on the trafficked snow ranged from 0.11 to 0.33, with the lowest value corresponding with the 27 wt. % NaCl solution, and the highest friction value with the 22 wt. % NaCl solution. After the snow was plowed from the pavement, the pull-test friction values ranged from 0.17 to 0.3, with the highest friction value corresponding to the 22 wt. % NaCl solution and the lowest pull-test friction values to the 25 wt.% and 27 wt.% NaCl solutions (Table 18).

Table 18. Summary of friction values from the pull-test measured on asphalt pavement samples during trafficking testing.

Test	Pull Test Averages (μ) and Standard Deviation									
	Control		Application		Compacted		Trafficked		Plowed	
	Avg	StDev	Avg	StDev	Avg	StDev	Avg	StDev	Avg	StDev
A-21	0.775	0.001	0.584	0.091	0.313	0.084	0.286	0.066	0.270	0.034
A-22	0.706	0.059	0.597	0.096	0.341	0.045	0.331	0.009	0.300	0.029
A-23.3	0.740	0.019	0.620	0.032	0.295	0.042	0.280	0.006	0.262	0.014
A-24	0.739	0.092	0.655	0.071	0.298	0.048	0.263	0.035	0.289	0.072
A-25	0.773	0.032	0.656	0.010	0.305	0.037	0.145	0.015	0.165	0.026
A-26	0.750	0.070	0.636	0.034	0.340	0.017	0.291	0.072	0.255	0.031
A-27	0.743	0.093	0.662	0.046	0.153	0.066	0.109	0.040	0.182	0.040
A-28	0.741	0.073	0.577	0.080	0.269	0.007	0.254	0.029	0.276	0.045

Like the concrete pavement values, the asphalt pull-test friction values did not show a significant increase from trafficking to plowed measurements (Figure 73). Some of the NaCl solutions had higher friction values, while others had lower friction values.

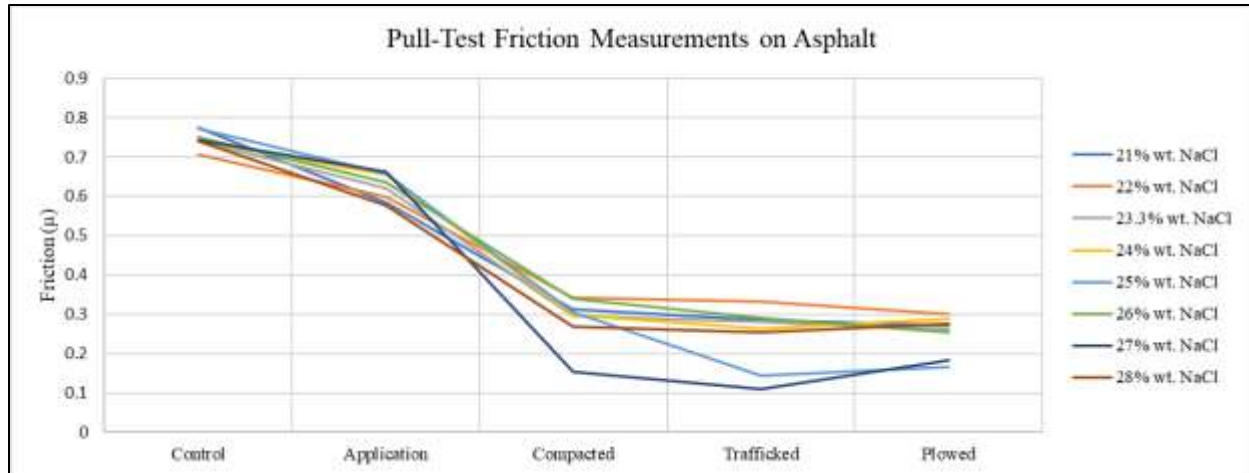


Figure 73. Friction values from the pull-test on asphalt pavement samples during trafficking testing.

Teconer Friction Values

The Teconer friction measurements from the asphalt samples were generally higher than the pull-test friction values from the same samples, similar to results from the concrete pavement tests. The Teconer friction measurements on the control asphalt samples ranged from 0.69 to 0.75 (Table 19). After the application of the NaCl solutions, the friction values ranged from 0.64 to 0.78, with the 23.3 and 25 wt. % NaCl solutions having higher friction values after anti-icer application. Teconer friction values measured on the compacted snow were relatively consistent and ranged from 0.25 to 0.38. Teconer friction values measured during trafficking ranged from 0.27 to 0.37, with the lowest friction value resulting from the 25 wt.% NaCl solution and the highest friction value from the 26 wt. % NaCl solution. After the snow was plowed from the asphalt samples, the Teconer friction values ranged from 0.33 to 0.54. Every NaCl solution concentration showed increased friction values from trafficking to plowing, except the 24 wt. % NaCl solution.

Table 19. Summary of friction values from the Teconer sensor measured on asphalt pavement samples during trafficking testing.

Test	Teconer Friction Average (μ) and Standard Deviation									
	Control		Application		Compacted		Trafficked		Plowed	
	Avg	StDev	Avg	StDev	Avg	StDev	Avg	StDev	Avg	StDev
A-21	0.7421	0.0523	0.7200	0.0459	0.3417	0.0253	0.3493	0.0270	0.3544	0.0418
A-22	0.7469	0.0448	0.6635	0.0460	0.2593	0.0208	0.2801	0.0250	0.3656	0.0340
A-23.3	0.7407	0.0514	0.7763	0.0420	0.3463	0.0256	0.3396	0.0259	0.4122	0.0930
A-24	0.7502	0.0272	0.7260	0.0339	0.3509	0.0256	0.3447	0.0315	0.3261	0.0382
A-25	0.7093	0.0184	0.7104	0.0103	0.2587	0.0154	0.2658	0.0186	0.3826	0.0282
A-26	0.7482	0.0276	0.7295	0.0415	0.3594	0.0229	0.3704	0.0191	0.4585	0.0448
A-27	0.6942	0.0542	0.6369	0.0608	0.2522	0.0148	0.2907	0.0230	0.3252	0.0471
A-28	0.7523	0.0259	0.7451	0.0301	0.3791	0.0143	0.3667	0.0193	0.5365	0.0470

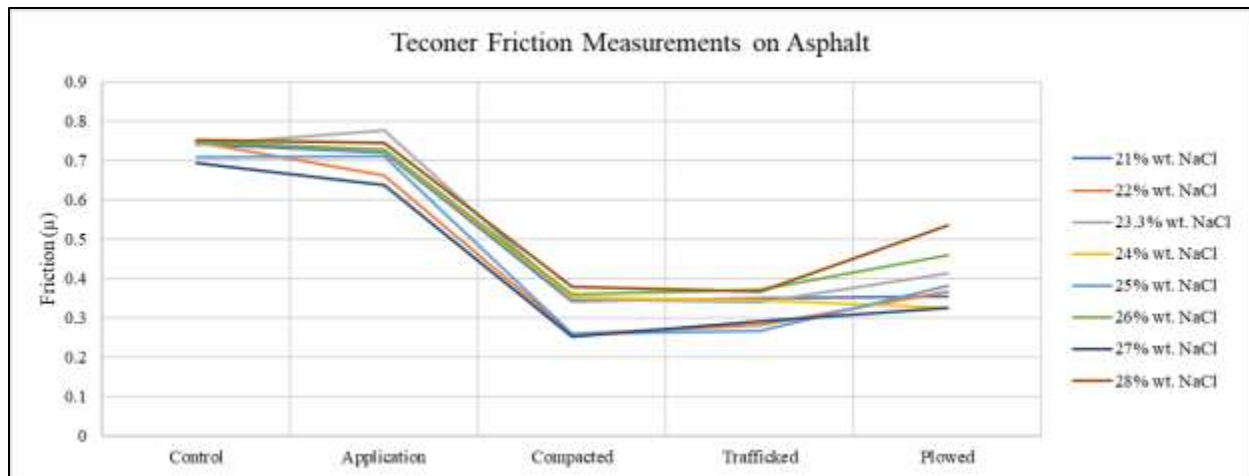


Figure 74. Friction values from the Teconer sensor on asphalt pavement samples during trafficking testing.

Figure 74 shows the Teconer friction values over the course of the experiment on asphalt samples and clearly shows the increase in friction values from trafficking to plowed.

Figure 75 shows a side-by-side comparison of all the asphalt pavement samples after trafficking (top) and after plowing (bottom) for all NaCl solutions. For every NaCl concentration except the 28 wt. % NaCl solution, some asphalt pavement was exposed after plowing. Overall, more snow cover can be seen in the middle section of the asphalt pavement samples where both tires trafficked the sample.

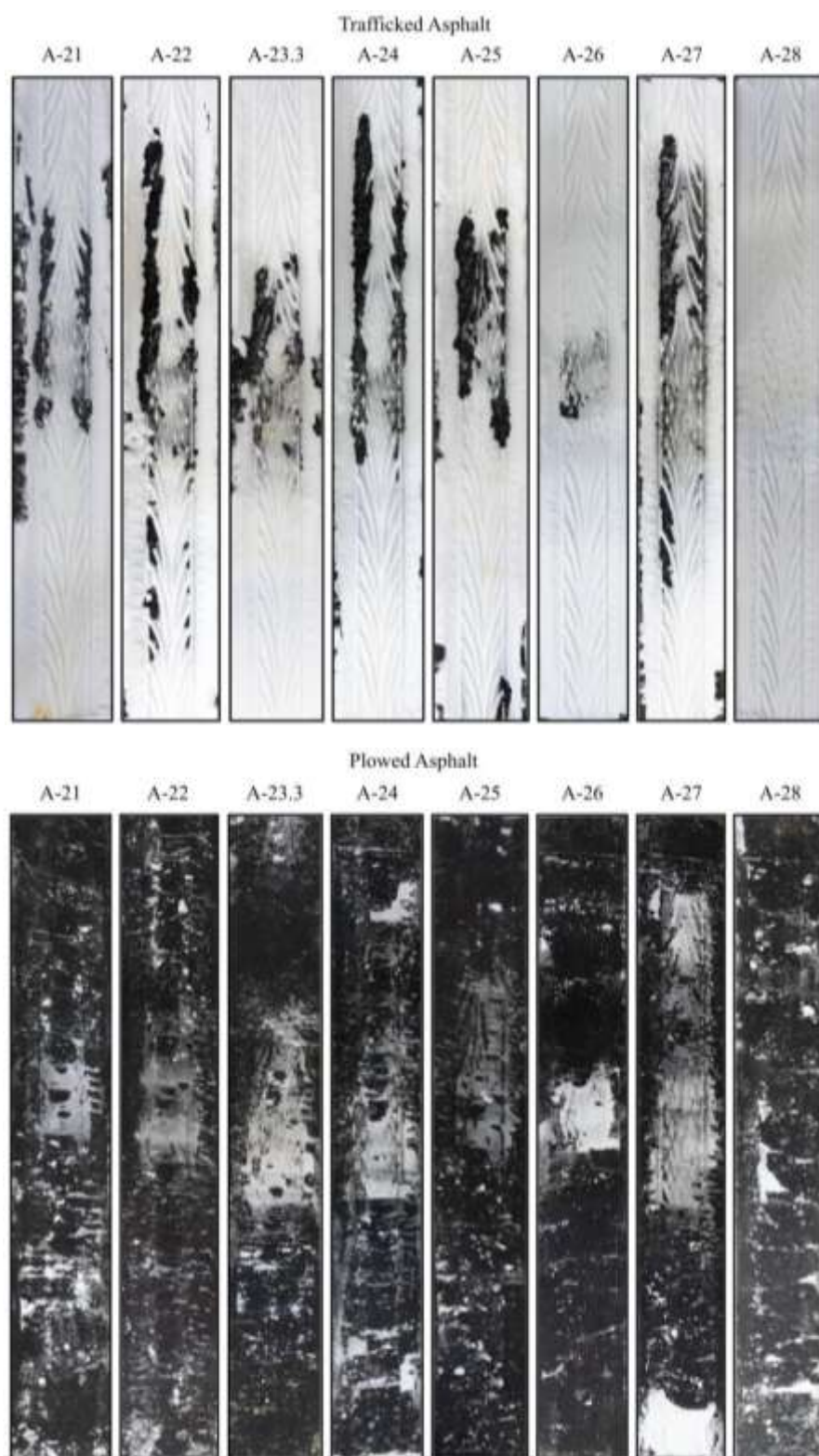


Figure 75. Images of asphalt pavement samples (top) after trafficking and (bottom) after plowing for each NaCl solution.

Statistical Analysis

Concrete

Pull-test Friction Values

A t-test comparison was used to evaluate the difference in pavement friction values after plowing. The analysis found there was no significant difference in plowed pull-test friction values between NaCl solution ($F(1,6) = 0.033$, $p\text{-value} = 0.862$). When the plowed pull-test friction values were compared to snow density, no statistical significance was found ($F(1,6) = 5.278$, $p\text{-value} = 0.061$) and when the plowed pull-test friction values were compared to humidity of the air during testing, no statistical significance was found ($F(1,6) = 5.14$, $p\text{-value} = 0.064$). The density of snow and humidity of the cold lab were found to be statistically significant variables so they should be considered influential factors because of their very low p-values.

Teconer Sensor Friction Values

There was a significant difference in the concrete pavement friction values after plowing when comparing different NaCl solutions. For example, the post-plowing concrete pavement friction for NaCl solution 21 wt.% was significantly different from all other NaCl solutions; it was significantly higher than 22 wt.%, 23.3 wt.%, 25 wt.%, 26 wt.%, and 28 wt.% and significantly lower than the 24 wt.% and 27 wt.% NaCl solutions.

The 22 wt.% NaCl solution had lower concrete pavement friction after plowing than all other solutions, but concrete pavement friction after plowing was only significantly lower when compared 21 wt.%, 24 wt.%, and 27 wt.%. At NaCl's eutectic concentration of 23.3 wt.%, concrete pavement friction after plowing was significantly lower than NaCl solutions 21 wt.%, 24 wt.%, and 27 wt.%. The 24 wt.% NaCl solution had significantly higher concrete pavement friction after plowing than NaCl solutions 21 wt.%, 22 wt.%, 23.3 wt.%, 25 wt.%, 26 wt.%, 27 wt.%, and 28 wt.%. The 25 wt.% NaCl solution had significantly lower concrete pavement friction after plowing than NaCl solutions 21wt.%, 24wt.%, and 27wt.%. The 26 wt.% NaCl solution had significantly lower concrete pavement friction after plowing than NaCl solutions 21 wt.%, 24 wt.%, and 27 wt.%. The 27 wt.% NaCl solution had significantly higher concrete pavement friction after plowing than the 21 wt.%, 22 wt.%, 23.3 wt.%, 24 wt.%, 25 wt.%, 26 wt.%, and 28 wt.% NaCl solutions (27 wt.% plowed friction was higher but not statistically significant). The 28 wt.% NaCl solution had significantly lower concrete pavement friction after plowing than NaCl solutions 21 wt.%, 24 wt.%, and 27 wt.%. When ranking the concrete pavement friction values from highest to lowest by NaCl solution concentration, the results are: 27 wt.%, 24 wt.% > 21wt.% > 22, 23.3, 25, 26, 28wt.%

Summary statics are provided in Table 26, Appendix B – Teconer Friction Statistical Results Tables.

Asphalt

Pull-test Friction Values

Like the concrete analysis, a t-test comparison was used to evaluate the difference in pavement friction values after plowing. The analysis found there was not a significant difference in plowed pull-test friction values between NaCl solutions ($F(1,6) = 1.203$, $p\text{-value} = 0.315$). When the plowed pull-test friction values were compared to snow density, no statistical significance was found ($F(1,6) = 0.125$, $p\text{-value} = 0.736$) and when the plowed pull-test friction values were compared to air humidity, no statistical significance was found ($F(1,6) = 0.151$, $p\text{-value} = 0.711$).

Teconer Sensor Friction Values

As in the concrete pavement Teconer friction results, there was a significant difference in asphalt pavement friction values after plowing when comparing different NaCl solutions. For example, the asphalt pavement friction for NaCl solution 21 wt.% was significantly lower when compared to asphalt pavement friction for NaCl solutions 23.3 wt.%, 25 wt.%, 26 wt.%, and 28 wt.%. The asphalt pavement friction after plowing for NaCl solutions 22 wt.% and 23.3 wt.% showed mix results; asphalt pavement friction for the NaCl solution 22 wt.% was significantly lower than NaCl solutions 23.3 wt.%, 26 wt.%, and 28 wt.%, but significantly higher than NaCl solutions 24wt.% and 27wt%. At the NaCl eutectic concentration of 23.3 wt.%, asphalt pavement friction after plowing was significantly higher than NaCl solutions 21 wt.%, 22 wt.%, 24 wt.%, and 27 wt.%, but was significantly lower than NaCl solutions 26 wt.% and 28 wt.%.

For the NaCl solution 24 wt.% lower asphalt pavement friction values after plowing were found compared to all other NaCl solution; but was significantly lower for NaCl solutions 22 wt.%, 23.3 wt.%, 25 wt.%, 26 wt.%, and 28 wt.%. For NaCl solutions 25 wt.% and 26 wt. % asphalt pavement friction after plowing showed mix results. While 25 wt.% asphalt pavement friction after plowing was significantly lower for NaCl solutions 26 wt.% and 28 wt.%, it was significantly higher than NaCl solutions 21 wt.%, 24 wt.%, and 27 wt.%. For NaCl solution 26 wt.% asphalt pavement friction after plowing was significantly lower than NaCl solution 28 wt.% but was significantly higher than NaCl solutions 21 wt.%, 22 wt.%, 23.3 wt.%, 24 wt.%, 25 wt.%, and 27 wt.%. The 27 wt.% NaCl solution had significantly lower asphalt pavement friction after plowing than NaCl solutions 22 wt.%, 23.3 wt.%, 25 wt.%, 26 wt.%, and 28 wt.%, whereas the 28 wt.% NaCl solution had significantly higher asphalt pavement friction after plowing than all other NaCl solutions.

When ranking asphalt pavement friction values after plowing from highest to lowest by NaCl solution, the results are: 28 wt.% > 26 wt.% > 23.3 wt.% > 22, 25 wt.% > 21, 24, 27 wt.%. For asphalt pavements, snow density appears to be a significant contributing factor to the test results.

Summary statistics are provided in Table 27, Appendix B – Teconer Friction Statistical Results Tables.

Asphalt versus Concrete

Pull-test Friction Values

In addition, the Tukey HSD analyzed 120 combinations between the 16 trafficking tests. Of all the combinations, only four reported p-values less than 0.05, or significantly different. Three of these were comparisons between asphalt and concrete samples, and only one of the comparisons was with the same pavement type: asphalt samples with 25 and 22 wt. % NaCl (mean diff. = -0.14, p-value = 0.03). There were an additional five comparisons that produced p-values between 0.05 and 0.1, two of which were comparisons between the same pavement type. In summary, some of the pull-test friction values after plowing showed a significant difference between concrete and asphalt pavement types but these results were inconsistent.

Teconer Friction Values

When comparing friction values after plowing on concrete and asphalt pavement samples for every solution, nearly all the comparisons were significant (p-values less than 0.05). This indicates that there was a statistically significant difference in friction values between concrete and asphalt pavement surfaces. The difference in friction values between concrete and asphalt pavements has been observed

in past research (Fay et al., 2018; Wåhlin et al., 2016), and many stationary and mobile non-contact friction sensor vendors suggest that the sensors be calibrated for each pavement type prior to data collection. The Teconer sensor is unique in that it is calibrated using a provided grey disc, so only one calibration is available for all pavement types.

Summary statistics are provided in Table 28, Appendix A.

Discussion

While past efforts by Akin et al., Muthumani et al., and Cuelho et al. were able to successfully report significant findings using the pull-test friction method (Akin et al., 2020 and [Clear Roads project 12-03](#); Muthumani et al. 2015 and [Clear Roads project 13-02](#); Cuehlo et al., 2010), the pull-test friction results from this experiment were inconsistent and did not point to any significant findings. This is likely due to the limited number of data points collected. The pull-test is measured at three random locations along the pavement sample, whereas the Teconer sensor takes a measurement every second at different points across the entire sample for an entire minute ($n = 60$). Because the Teconer sensor provides significantly more data for each sample, a more robust analysis was allowed. For this reason, the discussion focusses on the results on the Teconer sensor friction data. It is important to note that the Teconer sensor reports derived friction values based on remote sensing of the pavement temperature and surface condition.

Teconer friction values were generally higher than pull-test friction values throughout the experiment on both pavement types and they showed a notable increase in friction values after plowing for both pavement types, which was not observed in the pull-test friction values. The Teconer friction values were significantly different between concrete and asphalt pavement types. For asphalt pavements only, snow density appears to be a significant contributing factor to friction values.

When looking at the post-plowing concrete and asphalt friction values for all NaCl solutions, the results are not consistent. In fact, the results are almost exactly opposite for concrete and asphalt as shown in the rankings below (Figure 76 and Figure 77).

Concrete sample NaCl solution ranking (highest friction values on the left, lowest right)

27, 24 wt.% > 21wt.% > 22, 23.3, 25, 26, 28 wt.%

Asphalt sample NaCl solution ranking (highest friction values on the left, lowest right)

28 wt.% > 26 wt.% > 23.3 wt.% > 22, 25 wt.% > 21, 24, 27 wt.%

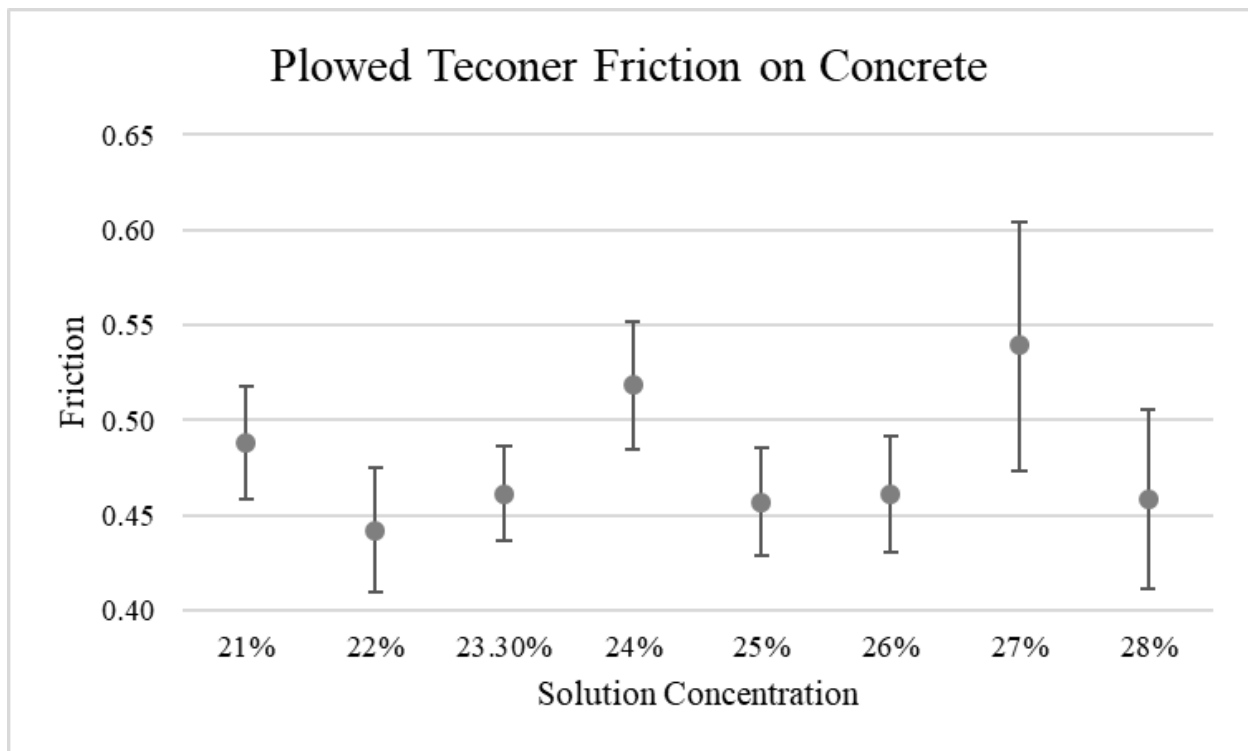


Figure 76. Teconer friction values after plowing for all NaCl solutions on concrete pavement samples.

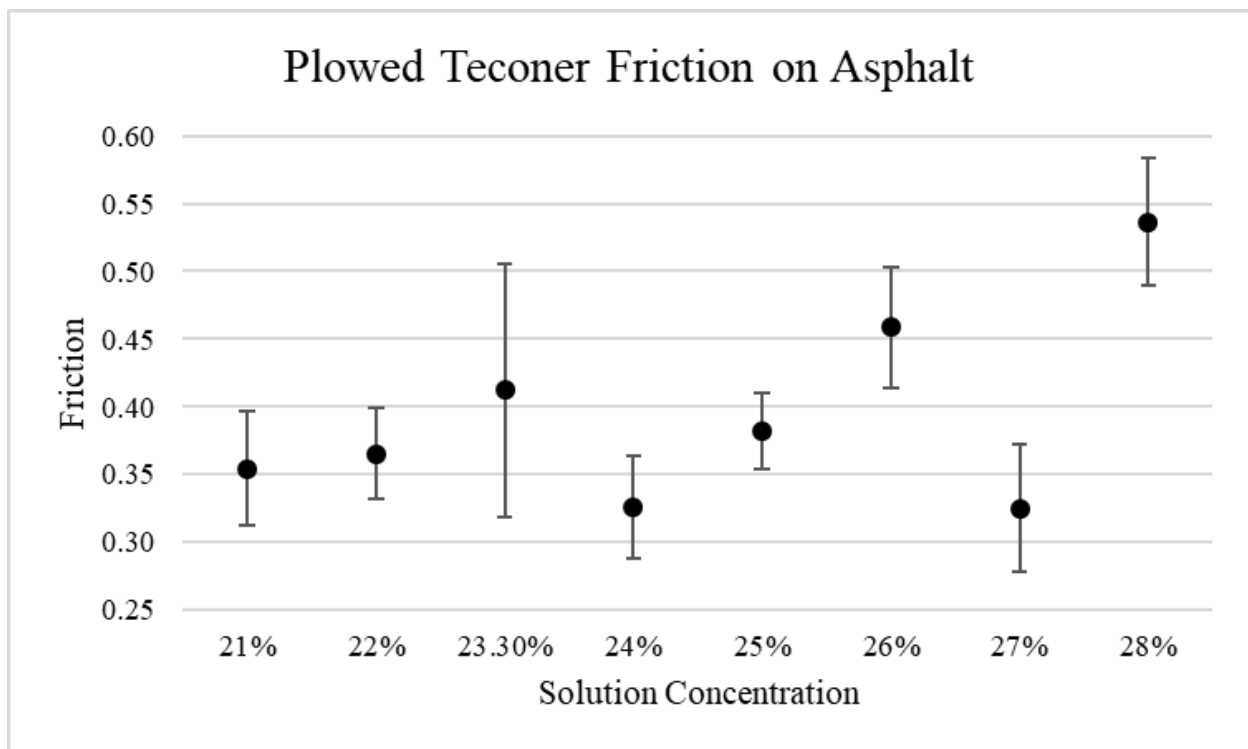


Figure 77. Teconer friction values after plowing for all NaCl solutions on asphalt pavement samples.

Observations made during the trafficking tests indicated that there were differences in how the NaCl solution behaved when applied to concrete versus asphalt pavement types. NaCl solutions applied to the concrete samples seemed to spread more evenly across the pavement surface and seep into micro-cracks, appearing to be absorbed, while the NaCl solutions applied to the asphalt samples formed into droplets (Figure 78). In addition, there was more texture on the surface of the asphalt samples compared to the concrete surface. These differences may influence the baseline friction values and amount of snow that is remaining on the pavement samples after trafficking and plowing for each pavement type.



Figure 78. Images of NaCl solution application on (left) concrete and (right) asphalt samples.

What can be stated is that more snow appeared to remain, after trafficking and plowing, on the concrete samples with the high NaCl solution concentrations (26-28 wt. % NaCl) than low NaCl concentrations, while no clear trends could be identified for the asphalt pavements.

It appears that the NaCl solutions melted the snow in contact with the pavement surface and caused dilution, decreasing the NaCl solution concentration. This likely created a scenario where the higher NaCl concentrations (26%, 27%, and 28%) were sufficiently diluted to closer to ideal NaCl solution concentrations (i.e., 23.3%) for deicing purposes.

The following conclusions may be drawn from the trafficking testing of various NaCl solutions on concrete and asphalt pavements:

- A significant difference in plowed friction values was observed between the concrete and asphalt pavements from the pull-test and Teconer sensor results.
- Snow density and humidity of the cold lab were found to be statistically significant variables in some instances and should be considered as influential factors.
- The Teconer sensor provided a more consistent and robust friction data set for analysis when compared with the pull-test method.
- While the results from the concrete and asphalt pavement are interesting on their own, the final friction values for each NaCl solution sample after plowing are almost opposite between the pavement types.

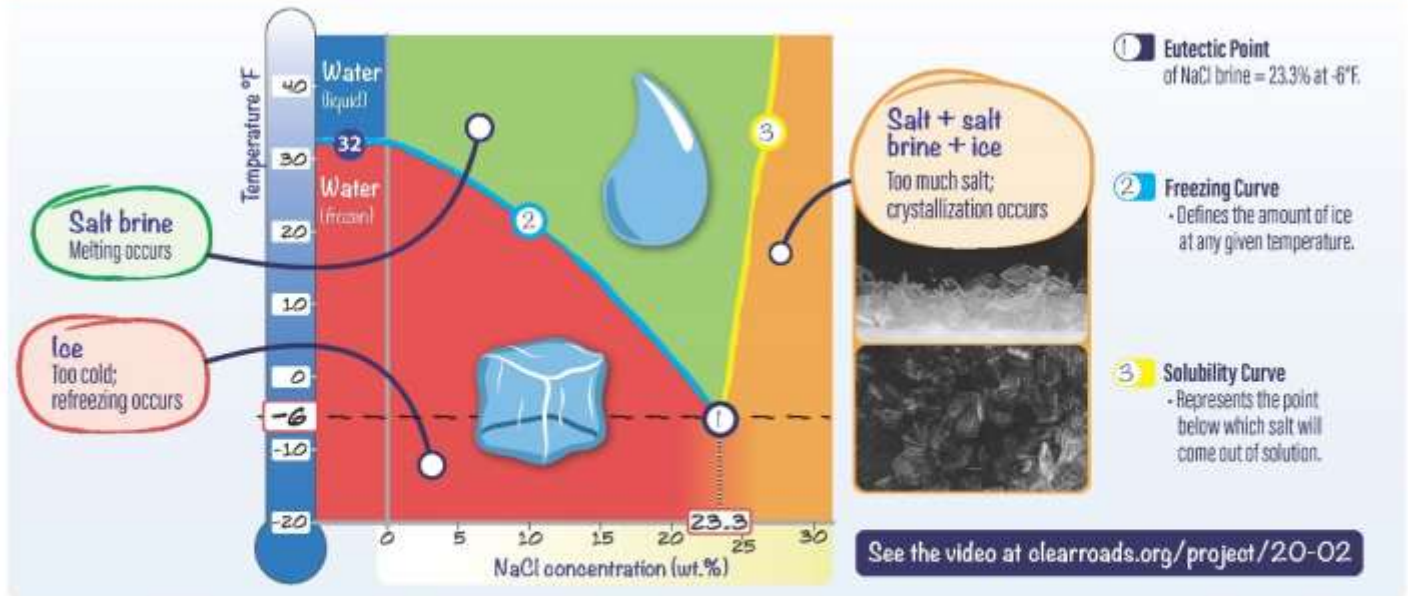
One Page Fact Sheet

The following one-page fact sheet was developed to help winter maintenance practitioners make informed decisions on the use of NaCl-based road salts at varying temperatures and concentrations. It focuses on understanding and applying the NaCl phase diagram.

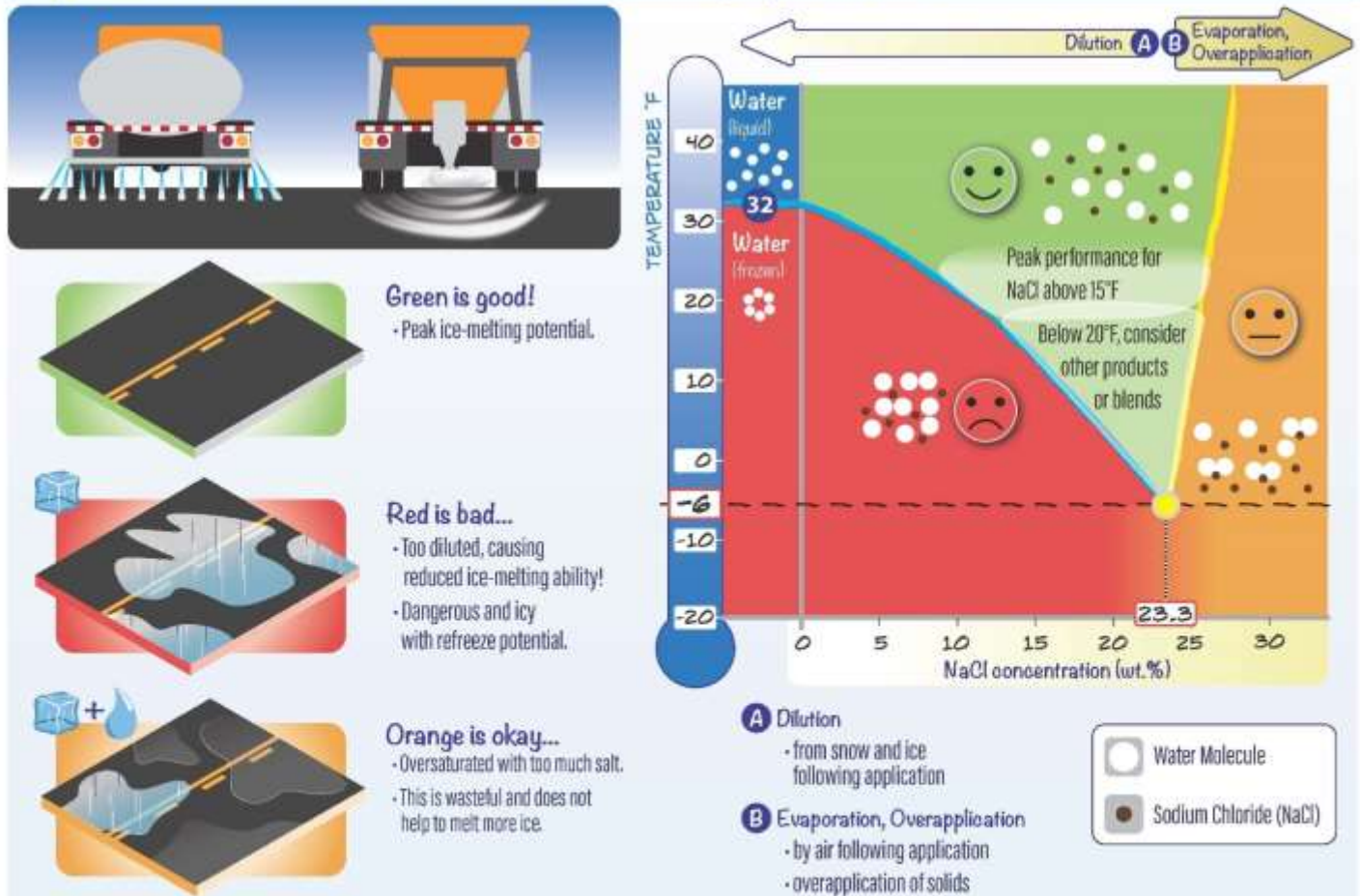
The one-page fact sheet can also be downloaded from the Clear Roads project website:

<https://clearroads.org/project/20-02/>

Understanding Salt Brine Concentration



Impact of brine concentration on anti-icing operations



Educational Video

An educational video was developed based on the content of the Understanding Salt Brine Concentration fact sheet to help winter maintenance practitioners answer the question *Can adding more salt ever make road conditions worse?* The 8:30 minute video can be found here https://youtu.be/xzrvOoJGH_w.

Conclusions

Salt phase diagrams are a great source of information for understanding the chemistry of NaCl solutions (brines) and provide key information such as the eutectic point and the solubility limit. Phase diagrams also help users identify which deicer type or deicer blend will meet their needs. While the published domain contains information on NaCl phase diagrams and eutectic curves, much of it is targeted at the scientific and engineering communities and lacks sufficient explanation of the concepts in language that can be widely understood. The project's [one page fact sheet](#) and [educational video](#) were developed to fill this gap.

Lab Testing Conclusions

Results from lab testing produced great images and video of ice and NaCl crystal formation, and potentially NaCl·2H₂O in solution.

Data gathered during the beaker test show a fairly accurate mirroring of the expected results based on the phase diagram. Due to the limited filtered ice crystal data collected, the inconsistent data due to differences in filtering methods, and the unknown quantity of NaCl crystals, precipitated NaCl, and NaCl·2H₂O incorporated in the filtrate, there was insufficient data available for a detailed analysis of the ice crystal mass. While this was an interesting exercise, better collection of detailed ice crystal formation results could provide significant information to advance this topic, specifically if an isothermal phase diagram can be generated. Possible method improvements could include increasing the time for ice crystal formation, refining a consistent filtering method, and using advanced imaging methods to determine the percent ice crystal versus NaCl crystal in the filtrate.

The presence of brine-filled bubbles in the ice crystals indicates that the solid phase of ice and NaCl crystals is not uniform. Instead, it shows that many phases can co-exist. This reinforces the concept that the ice formed in the presence of the salt brine is weaker than ice formed only in presence of pure water.

Results gathered from the beaker test (Table 9) show a high correlation with the salt phase diagram (Figure 9D), in terms of ice formation or any freezing in brine concentrations of 21% to 23% by weight. Precipitation was not observed for 24 wt. % at 15°F and 10°F. Based on the salt phase diagram, the brine concentrations beyond the eutectic point (24 wt. % to 28 wt. %) should not have shown any freezing (formation of ice) during the beaker test. The beaker test investigated isothermal cooling, which is not shown in the salt phase diagram, therefore our results could be different than what is depicted in the phase diagram.

When measuring pavement friction following the application of salt brine in various concentrations, the results varied between pavement type, salt concentration, and friction measurement technique. There is value in further refining this, or another, performance test method to assess the influence of salt brine concentration on pavement friction.

Future research in this field could use applied advance imaging techniques such as Raman microscopy, scanning electron microscopy (SEM), x-ray fluorescence (XFR), nuclear magnetic resonance (NMR) spectroscopy, and reflection infrared spectroscopy to better ascertain the chemistry and physics, and specifically the kinetics, of water, ice, salt, and salt brine interactions.

Knowledge Gap and Research Needs

The following knowledge gaps and research ideas were developed throughout this research effort.

- Humidity Study: conduct a detailed lab test that looks at the impacts of humidity on deicer friction values when the deicer is applied to various pavement types.
 - Apply brine solution to pavements, allow to dry, then slowly increase the humidity, measuring friction overtime with each increase in humidity.
- Utilize advanced imaging techniques to better understand ice and solid product structures and chemical composition at cold temperatures.
 - Cold stage RAMAN analysis of salt brine solutions (21 to 28 wt.% NaCl) to determine chemical composition of precipitated salt (NaCl, NaCl.2H₂O, etc.), the 3D structure of the ice and precipitated salt solids, and brine solution pockets, etc.
 - Cold stage RAMAN analysis of blended products such as salt brines with ag-based additives
- Investigate the impacts of NaCl.2H₂O precipitated solids on pavement friction values.
- The authors were unable to find an isothermal transformation (IT) salt phase diagram in the published domain. There could be a need to develop an IT salt phase diagram based, in part, on results of this effort.

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Appendix A – Literature Review Additional Information

NaCl Based Deicers Used for Melting Snow

Introduction

The following chapter provides information available from the published domain related to deicers composed of salt (NaCl, solid), salt brine (NaCl solution, liquid), and solid deicer pre-wet with salt brine. The chapter includes information on these deicers' compositions and performance.

Compositions and Ice Melting Performance of Salt Deicers

Laboratory Analysis

Goyal et al. (1989) developed an ice-melting test protocol. They used two variants of the blotter method (Blotter-S and Blotter-Z) and studied the effect of different variables - relative humidity, temperature, treatment time, etc., on the performance of salt and Qwiksalt (QS) deicers. QS is a mixture of salt, magnesium chloride ($MgCl_2$), water and a corrosion inhibitor, PCI (Goyal et al., 1989). The blotter method uses blotter paper to absorb the brine that forms as ice melts. The difference in the weight of the blotter paper is then used to find the ice melting capacity (IMC) for the deicer. Using the blotter method, they were able to show that deicer functionality requires ice melting and ice penetration to occur over time. The results of the blotter methods at two temperatures ($14^{\circ}F$ ($-10^{\circ}C$) and $-0.4^{\circ}F$ ($-18^{\circ}C$)) are shown in Figure 79. Units reported are net pounds of water collected per lane mile (PWLM) and low relative humidity (L RH) and high relative humidity (H RH) are labeled as such (Goyal et al., 1989). The study is limited to laboratory-based results and does not discuss the findings in the context of the field environment.

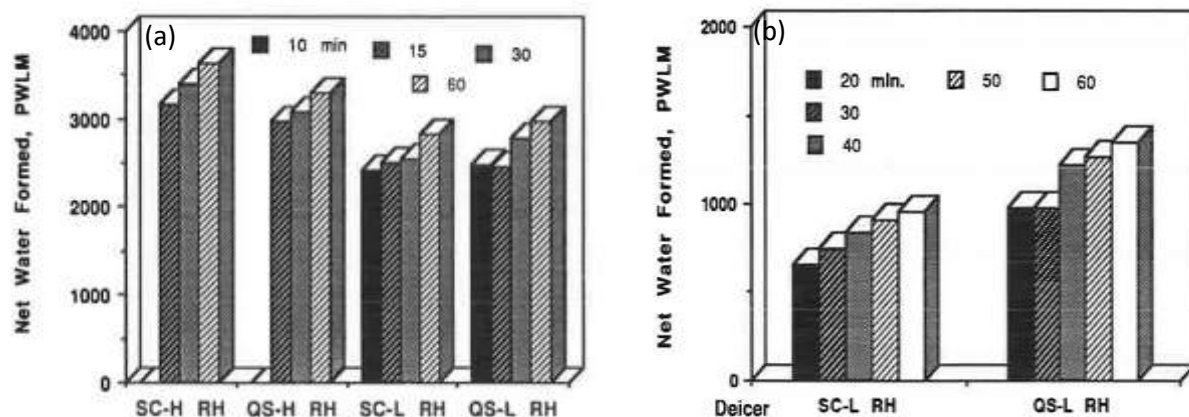


Figure 79. Ice melted by sodium chloride (SC) and QS at different humidity levels at $14^{\circ}F$ ($-10^{\circ}C$) (a) and $-0.4^{\circ}F$ ($-18^{\circ}C$) (b) (Goyal et al., 1989).

Chappelow et al. (1992) developed the SHRP ice melting test method. During the SHRP test, solid deicers are tested at application rates approximately three times higher than typical highway deicing applications. Therefore, the standard SHRP ice melting test applies the equivalent of 1,320 lb/lane-mile for solid deicers. Similarly high application rates are used for liquid deicers; the recommended application rate of 3.8 mL of liquid deicer is equivalent to approximately 144 gallons/lane-mile. From the SHRP ice melting test, the ice melting capacity (IMC) is measured as the amount of ice melted by deicers over time. This test should be performed three times (read: in triplicate) at a minimum for each deicer at

any desired temperature (Chappelow et al., 1992). Note that the error rate for this test method is highly variable and results vary significantly between labs (Nilssen et al., 2016). While the SHRP ice melting test is a good indicator of a deicer's ability to melt ice, the results of the test should be viewed with consideration of the error range and not as absolute values.

In a study conducted by Shi et al. (2013), commercial liquid deicers and reagent-grade solid (r,s) deicers were evaluated in terms of IMC and corrosion rates. The IMC test used was a modified version of the SHRP ice melting test (Shi et al., 2013) and the results are shown in Figure 80, where $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and NaCl (r,s) had the highest IMC in 60 min at both 30°F and 15°F, but $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ had the highest IMC in 60 min at 0°F. To study their corrosiveness, deicers were mixed with corrosion inhibitors. Corrosion measurements revealed that inhibited NaCl was the most corrosive deicer, with percent corrosion rates (pcr) of 36 to 41 as compared to inhibited CaCl_2 (pcr: 25-30) and MgCl_2 (pcr: 27-33) based deicers (Shi et al., 2013).

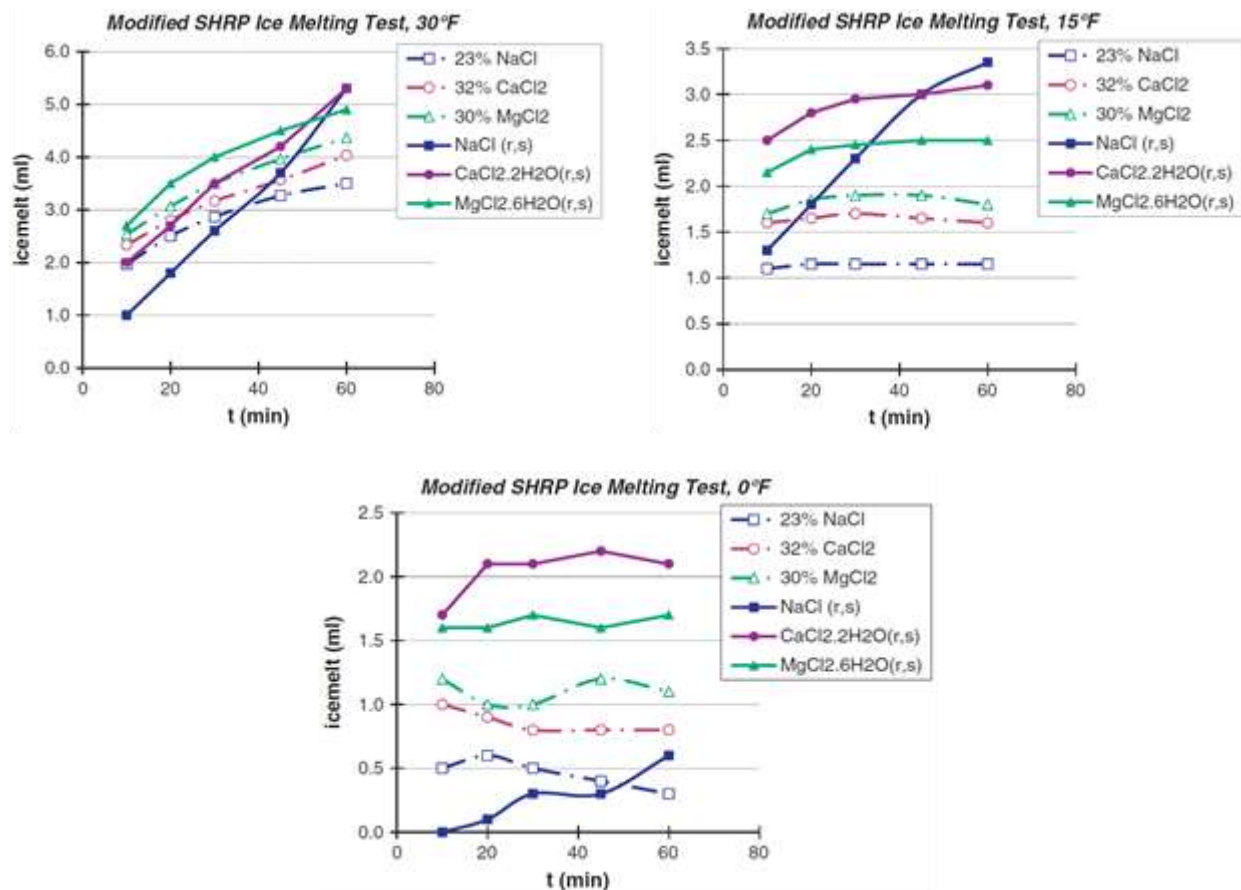


Figure 80. IMC versus time for liquid and solid deicers at various temperatures (Shi et al., 2013).

Koefod (2017) developed a novel method to evaluate the IMC of deicers. A key outcome of this study was to help winter maintenance personnel understand how important mixing is in determining the deicer melting performance (Koefod, 2017). Through his work, Koefod found that chemical deicing

might be better viewed as deicers dissolving rather than through the ice melting process. Koefod's method was determined to be more accurate than the standard SHRP method. The research also found that prewet salts can reduce the application rates needed for solid salt deicers as well as speed up the ice melting process. Koefod (2017) noted that prewet salts may also have a lower effective temperature than solid salts; the effective temperature for NaCl salt is typically around 15 to 20°F (-6 to -9°C), but when prewet may be lowered to 0°F (-18°C) (Koefod, 2017).

Another laboratory study showed that solid NaCl has a better IMC compared to other commercially available salts in solid hydrated forms (like $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) (Nilssen et al., 2018). Solid hydrated salts have lower IMCs because they contain more moisture than solid NaCl. The study also showed that using an improved calorimeter could increase the accuracy of measured IMC for NaCl (Figure 81, left images). Figure 81 (right side graph) shows the results of the IMC measured for 14 NaCl brine samples (red dots) plotted along with the theoretically calculated IMC for salt (the blue line) (Nilssen et al., 2018).

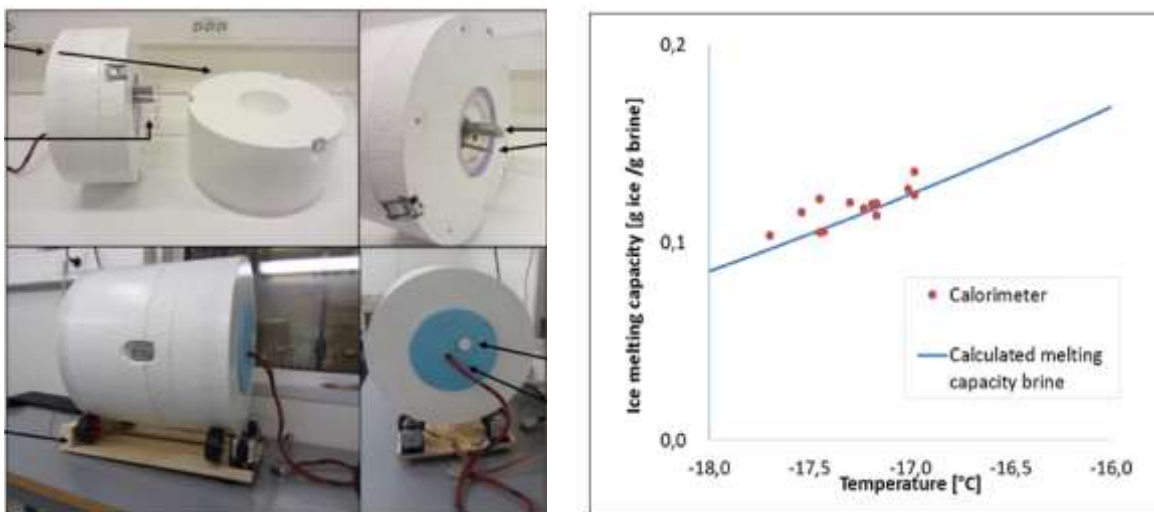


Figure 81. Improved calorimeter (left) and IMC results for salt (right) (Nilssen et al., 2018).

The research by Nilssen et al. (2018) showed that solid NaCl has a higher IMC not only compared to other commercial solid hydrated salts but mixtures of these hydrated salts with NaCl. Hydrated salts (for instance $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) were mixed with NaCl in an 80:20 ratio (NaCl/hydrated salt) with the results shown in Figure 82. On the other hand, the IMC results of salt brine and other liquid salt solutions showed that NaCl brine has the lowest IMC (Figure 83). The research revealed that adding additives (apart from sugar and potassium formate (KFO)) such as CaCl_2 and MgCl_2 to NaCl brine, increased the IMC for brine by as much as 144% (Figure 83) (Nilssen et al., 2018).

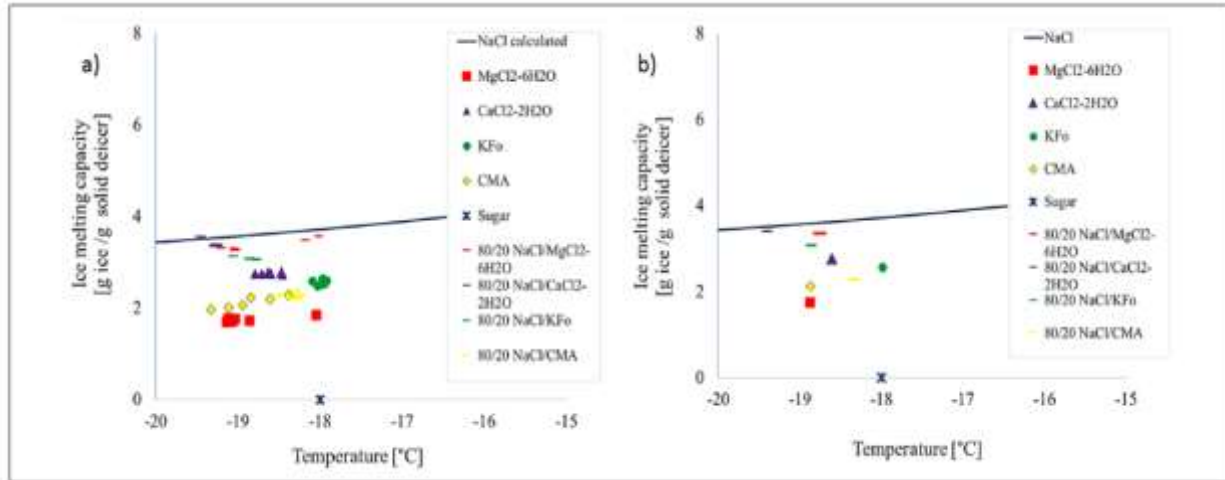


Figure 82. Calorimetry results for IMC of solid deicers (Nilssen et al., 2018).

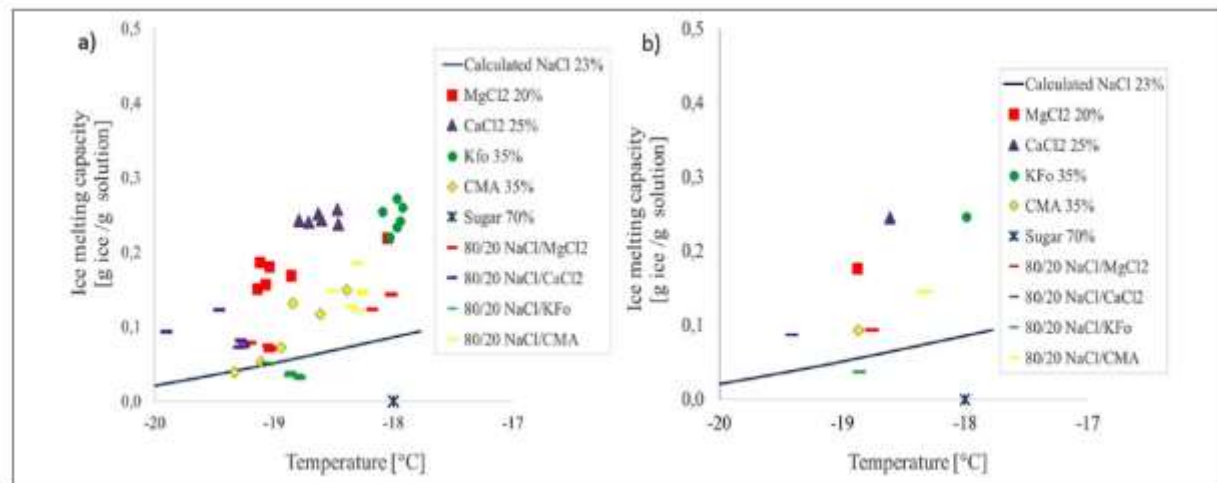


Figure 83. IMCs for brine and salt solutions/mixtures, (a) all data and (b) average (Nilssen et al., 2018).

Field Analysis

In a study by the Utah Department of Transportation (UDOT), 18 types of multiple linear regression analysis² were used to examine the effect of pavement type (concrete and asphalt) on deicer usage (Guthrie and Thomas, 2014). The deicers investigated included salt, Redmond salt, brine, wetted salt, magnesium chloride, pre-mix, and wetted pre-mix. The researchers also considered sand as a deicer; however, sand is an abrasive and has no deicing effect. The independent variables used were traffic/lane-mile, elevation, latitude, and concrete proportion (CP), or the amount of concrete pavement area given for a maintenance station. The dependent variables were the total amount of deicers per lane-mile and the value of each deicer per lane-mile. Regression analysis showed that CP was statistically significant in the presence of brine and wetted deicers, but it was not significant when dry deicers were applied. However, after modifying the models for traffic and pavement area, it was

² A linear regression analysis is a statistical approach to examine the behaviors of different independent variables, where the results are plotted graphically with dependent variable in a linear way.

concluded that the type of pavement has no effect on the amount of deicer used (Guthrie and Thomas, 2014).

Work by Fischel (2001) for Colorado Department of Transportation (CDOT) evaluated various chloride-based deicers, including NaCl, based on performance. The study reported which deicer types were used by different US states and noted the Clear Roads approved product list ([Qualified Product List \(QPL\)](#)) [formerly the Pacific Northwest Snowfighters (PNS) QPL] (Fischel, 2001). Though Fischel (2001) primarily discusses deicers used by CDOT and does not discuss deicer performance, the study does provide effective temperature values for NaCl based deicers (Table 20). The effective temperature reported matches the temperature at which the ending concentration (EC) of brine reaches 23.3 wt. %.

Table 20. Effective temperatures for different deicers (Fischel, 2001).

Chemical	Brand Name	Effective Temperature (°F)	Reference
30% Magnesium Chloride + 10% carbohydrates	Caliber™ M1000	-10°F	G. Leist, Envirotech, pers. Communication
30% Magnesium Chloride	FreezGard® with Shield LS	+5°F	G. Leist, Envirotech, pers. Communication
Magnesium Chloride	Ice Stop™CI	+5°F	Product Specification Sheet
Sodium Chloride	Ice Slicer®	0 to +5°F	Product Specification Sheet
Sodium Chloride	Rock Salt	+15°F	Chang et al 1994
Calcium Chloride	Liquidow* Armor*	-25°F	Dow Chemical Product Information Document ¹
Calcium Magnesium Acetate	CMA®	+20°F	K. Johnson, Cryotech, pers. communication
CMA25	CMA25®	+20°F	K. Johnson, Cryotech, pers. communication
CMA + Potassium Acetate	CMAK™	0°F	K. Johnson, Cryotech, pers. communication
Potassium Acetate	CF7®	-15°F	K. Johnson, Cryotech, pers. communication
Sodium Acetate	NAAC®	+5°F	K. Johnson, Cryotech, pers. communication

¹ – Dow Chemical Company Manual of Good Practice for Snow and Ice control with Dow Calcium Chloride Products (no date).

NA – Not available

Wåhlin et al. (2017) showed that by adding the liquid additives 30 wt. % of MgCl₂ and 32 wt. % of CaCl₂ to 23 wt. % NaCl brine, the freezing point of brine can be significantly lowered (Figure 84). The IMC was also calculated with brine plus additives and it was shown that IMC increases for two different temperatures: 28.4°F and 5°F (-2°C and -15°C). The research also discussed the freezing point depressions for various chloride-based deicer chemicals including NaCl (Wåhlin et al., 2017).

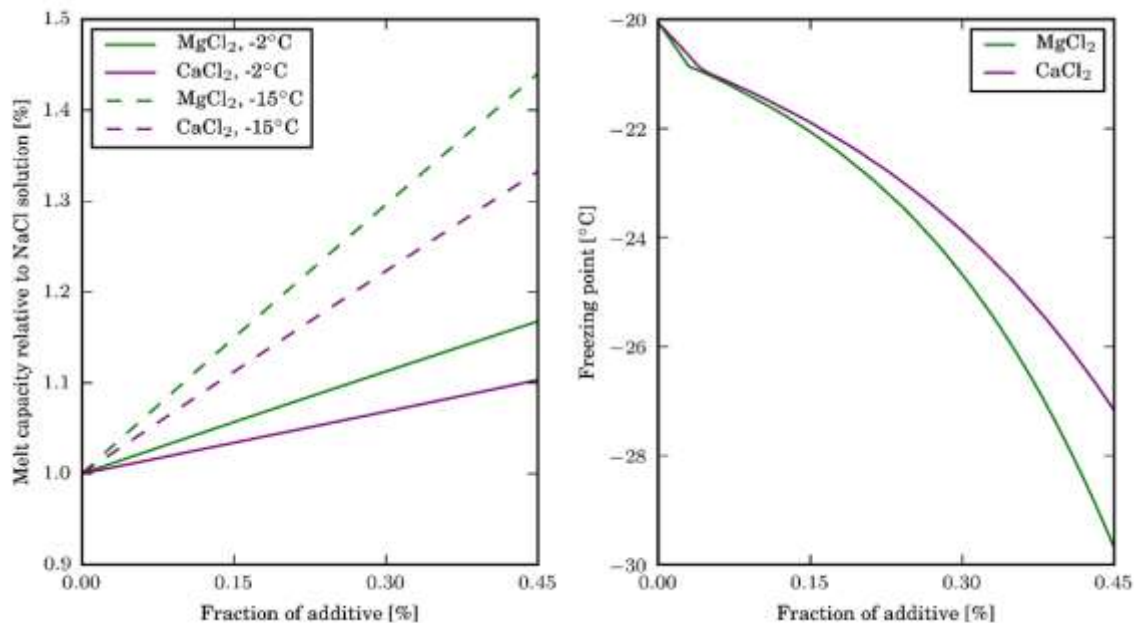


Figure 84. Effect of adding additives (from 0 to 45 wt. %) to salt brine (23 wt. % NaCl) (Wåhlin et al., 2017).

In South Korea, the test methods used to evaluate deicer performance are quite similar to the SHRP standard protocol (Chappelow et al., 1992), where they measure IMC, freeze-thaw impacts, metal corrosion, and fish toxicity under laboratory conditions using Korean standard deicing testing procedures (EL610) (Lee et al., 2017). Deicers shown in Table 21 were examined for their performance. Note that the “eco-labeled” deicers had chloride ions present but were completely different from the conventional chloride-based deicers and that the pre-wetted solid deicer had 70 % NaCl in 30 % CaCl₂ brine solution (Table 21). Ice melting performance of NaCl based deicers compared to eco-label deicers was tested at 23°F (-5°C) (Figure 85) and 10.4°F (-12°C) (Figure 86).

Table 21. Different deicers used in performance evaluation (Lee et al., 2017).

Content		Type	Ingredient
Salt (reagent)		Solid	NaCl
Deicer salt		Solid	NaCl
Calcium chloride		Solid	CaCl ₂
Pre-wetted salt		Solid	NaCl + CaCl ₂
Eco-label deicer	ES	Solid	CaCl ₂ + MgCl ₂ + organic acid
	BS	Solid	NaCl + organic acid
	BL	Liquid	MgCl ₂ + organic acid
	JL	Liquid	MgCl ₂ + organic-inorganic composite
	JMS	Solid	NaCl + MgCl ₂ + organic acid
	KS	Solid	NaCl + CaCl ₂ + organic-inorganic composite
	KL	Liquid	NaCl + CaCl ₂ + organic-inorganic composite
	SS	Solid	NaCl + CaCl ₂ + MgCl ₂ + CH ₃ CO ₂ Na
	SL	Liquid	NaCl + CaCl ₂ + MgCl ₂ + CH ₃ CO ₂ Na
	YL	Liquid	CaCl ₂ + organic acid

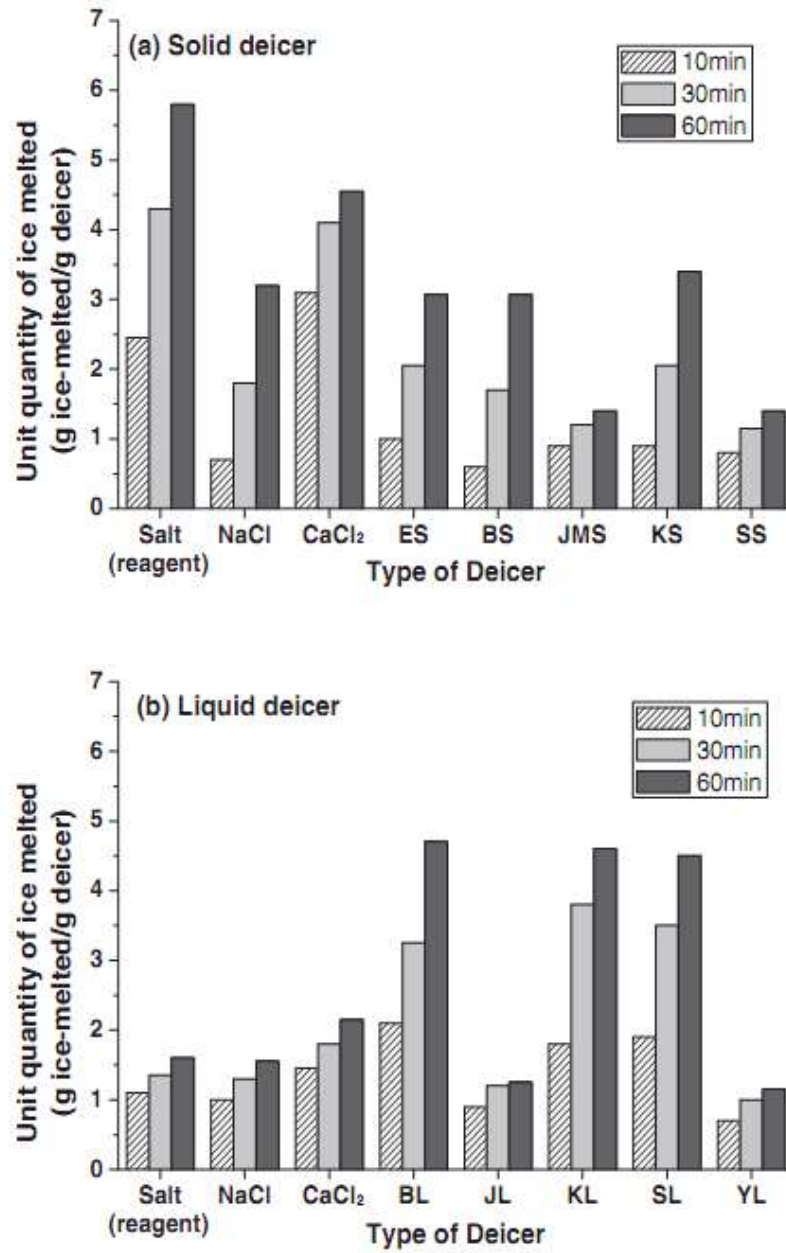


Figure 85. IMCs for solid and liquid deicers at 23°F (-5°C) (Lee et al., 2017).

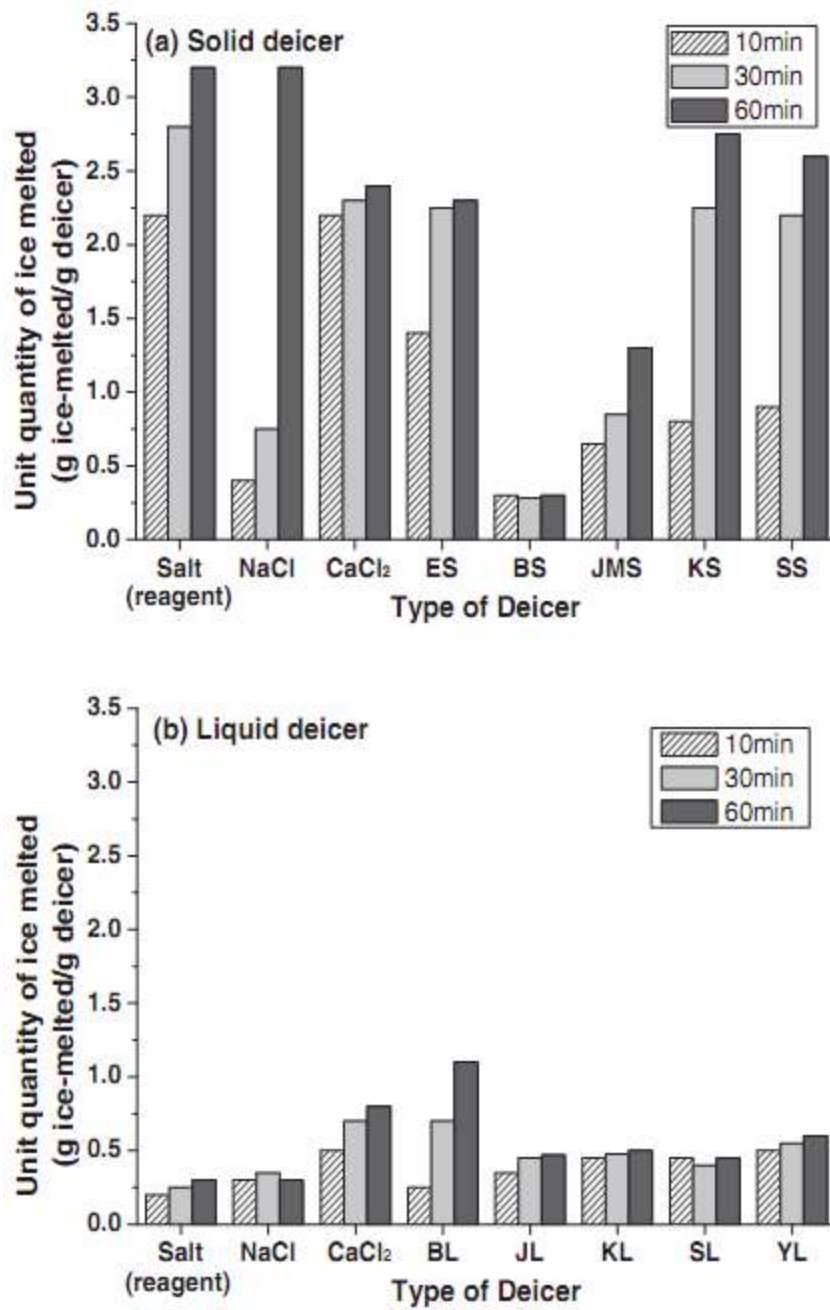


Figure 86. IMCs for solid and liquid deicers at 10.4°F (-12°C) (Lee et al., 2017).

The friction test results for all salts tested in this study showed that pre-wetted salt (solid NaCl in CaCl_2 solution) provided the best skid resistance (Figure 87)(Lee et al. (2017)).

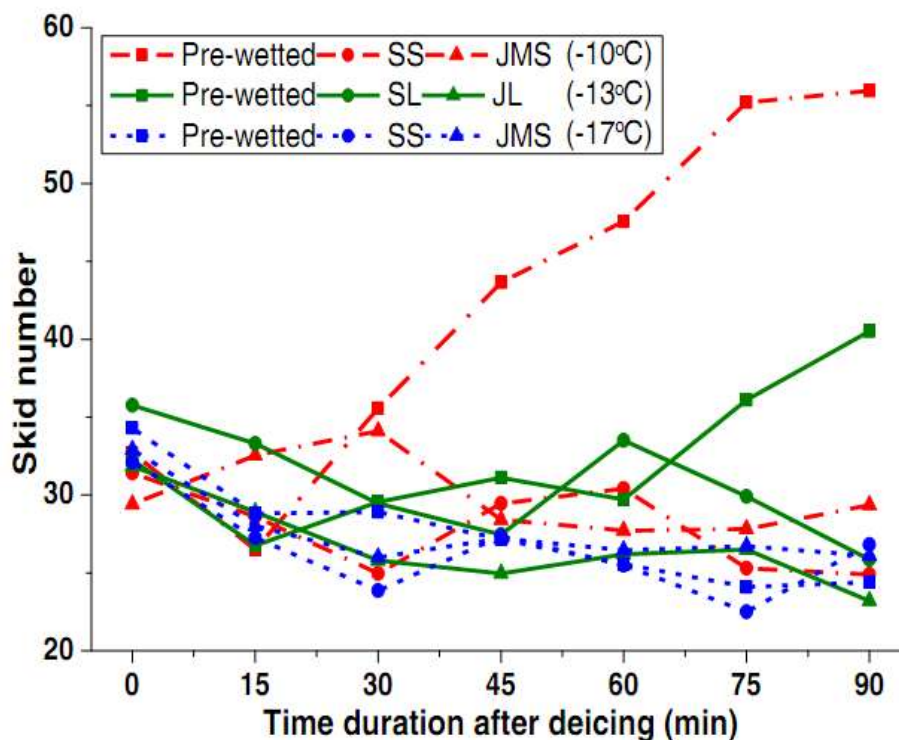


Figure 87. Friction results on road surface during snow-melting after deicers' application (Lee et al., 2017).

Conclusion

In this chapter, a brief overview of the salt-based deicers and their performance, mainly in terms of IMC, was provided. Some methods to improve the IMC for salt-based deicers were also shared. Results show that solid salt has the highest IMC, and the IMC for liquid salt solutions (brines) may be increased with additives. Calorimetry is an advanced method that can be used to accurately find IMC values, compared to other benchtop tests.

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Application Guidelines for Deicers

Introduction

This section discusses the guidelines for the application of deicers, primarily NaCl in solid, liquid, or pre-wetted form, on the roads. Every year U.S. state agencies collectively spend over \$2 billion on winter maintenance operations, plowing snow, and spreading deicers on roadways and use approximately 24.5 million metric tons (27 million US tons) of NaCl for deicing purposes (Lilek, 2017). Common methods used to treat snowy and icy roadways include deicing (the application of solid deicers after the storm begins), anti-icing (the application liquid deicers prior to a storm beginning), sanding (the application of abrasives to improve roadway friction), and plowing of snow and ice off the roadway. Deicing is typically the application of solid deicer on top of snow and ice and relies on melting and penetration of the deicer to aid in reducing or breaking the bond between, snow, ice, and pavement. Anti-icing is the application of liquid deicers to pavement, which prevents snow and ice from bonding with the road surface. Sanding improves friction on snow packed and icy roads, but it is temporary.

When solid deicers are applied, conditions like wind and traffic can remove a portion of the dry salt from the roadways. To minimize this issue, solid salts can be wetted (or pre-wetted) with various liquids. These pre-wetted salts melt the ice more quickly than solid salts, but also stay on the roads much longer. However, the overall IMCs for these forms of salts (discussed in Appendix A) are not as good as solid salt. It is necessary to understand the various application strategies when dealing with snow and ice to choose the best deicers. Factors like application rates, weather, and pavement conditions may affect the choice of deicer (solid, pre-wetted or liquid). Conversely, if a choice is already made, proper timing and application rates may have to be selected for successful snow and ice control operations.

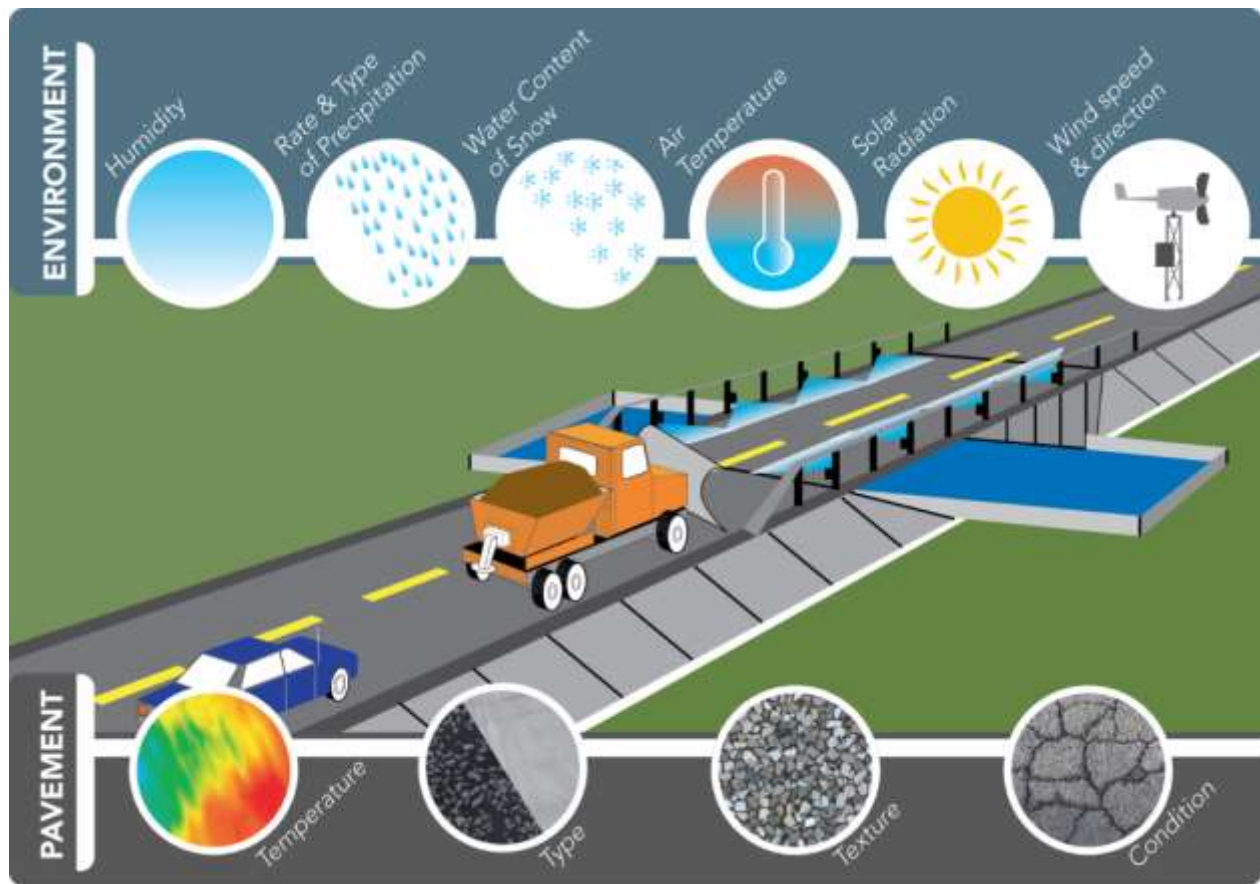


Figure 88. Illustration of environmental and pavement conditions that impact winter maintenance operations (N. Hetherington, WTI-MSU).

Figure 88 provides an illustration of the many environmental and pavement conditions that affect deicer performance and friction (between tires and road surface) on roadways. Muthumani et al. (2014) reported on many studies and their methods to assess each of these parameters (Figure 89) and used laboratory work to evaluate various chloride-based and agricultural blends of deicer using IMC measurement, ice penetration test, ice undercutting test, differential scanning calorimetry (DSC), and friction and bonding strength test. Some of these test methods can be used to guide snow-fighters in field applications (Muthumani et al., 2014). Application rates from several published research sources were also discussed in this study (Figure 89).

Reference	Purpose	Deicing or anti-icing: deicer type	Specific parameters (incorporated or simulated)		Pros	Cons
			Temperature	Precipitation, pavement, traffic, humidity, long short wave radiation, or wind		
Adams et al., 1989	Interfacial shear strength tests of ice formed on pavement	Anti-icing, concentrated solutions of South Dakota Deicer No. 2 (SD2), CMA, and NaCl.	Laboratory chamber at 23 and 5 °F (−3 and −15 °C)	32 °F (0 °C) distilled water poured in baffles rings to simulate freezing rain; on Portland cement concrete (PCC) substrates	•Each substrate accommodates two specimens allows eight test without opening the chamber door; •Four deicer application rates (100,200,300,400) were considered and compared; •Reference tests are conducted to make sure substrates are clean.	•Only considered one type of ice, could be more realistic if consider refrozen ice, atmospheric ice, and compacted snow ice; •One type of pavement
Adams et al., 1992	Residual anti-icing properties	Anti-icing, concentrated solutions of NaCl and CMA	Laboratory chamber at 24.8 °F (−4 °C)	Natural aged snow, sieved; on smooth bronze and granite coupons compacted snow with 31 psi for 10 min	•Natural snow more realistic than ice, but aged snow is different than fresh snow	•No measurement •Air and pavement were at same temperature •Only considered snow, no ice; •No macrotexture–lower application rates than field •Road force not measured—just temperature when snow sheared
Carlini, 2010	Anti-icing application rates	Anti-icing, NaCl, CaCl ₂ , MgCl ₂ , potassium acetate, Ag. by-product	Air (A), Pavement (P) Storm 1: A23°F (−5 °C), P32°F (0 °C); Storm 2: A14°F (−10 °C), P 14 °F (−10 °C); Storm 3: A30°F (−1.1 °C), P32° (0 °C)	Natural aged snow, sieved 60A in.; on asphalt and concrete pavements; surface ground smooth; compacted snow at 90 psi for 5 min	•Natural snow more realistic than ice, but aged snow is different than fresh snow; •Different air and pavement temperature	
Bernardo et al., 1996, 1998	Anti-icing properties	Anti-freezing resistance test, liquid runway deicer: urea-ethylene-glycol based, urea of potassium based and FRIGOL	Climate chamber at 23 °F (−5 °C) and substrate at 26.8 °F (−3 °C)	Freezing rate; on concrete plates, milled aluminum plates, polymer concrete and an epoxy-resin coated aluminum plate.	•Air and pavement were at different temperature •Weight is added to simulate the action of the plow trucks in airports.	•Only considered one type of ice, could be more realistic if consider refrozen ice, atmospheric ice, and compacted snow ice; •Tests not reproducible because the concrete substrate absorbs part of the deicer and some of the precipitation; •Only one type of pavement was tested; •Only one deicer application rate of
Nolan and Yim, 2003	Snapping resistance of different types of ice		Controlled cold room, temperatures at 30.2, 23,	Refrozen ice, atmospheric ice, and compacted snow ice; on concrete	•More realistic by using three types of ice.	
	on the pavement under different de-icing chemical application	Deicing, Solid NaCl, solid CaCl ₂ , and 27.35 by weight liquid NaCl.	−4 °F (−1, −3, −20 °C) to produce ice. Chemical tests conducted at a temperature of 23 °F (−5 °C)	specimens prepared using an Iowa DOT concrete mix design; overpacked snow under 63 psi for 10 min		•760 lbs per lane mile was considered, which is very heavy compared with usual application rate of 300–400 lbs/ lane mile.
Mullins et al., 1990	Deicers undermining and disbondment characteristics	Deicing, CaCl ₂ pellets, CaCl ₂ flakes, NaCl (2 products), KCl, pelletized urea, NaCl with traces of carbonylmethacrylonitrile, mixture of NaCl with KCl and urea, mixture of NaCl and urea, and CMA	Controlled temperatures: 0, 5, 10, 15, 20, 25 °F (−17.8, −15, −12.2, −9.4, −6.7, −3.9 °C)	Freezing chamber produced ice with surface partially milled with a metal iron; on concrete specimen according to ASTM specifications (ASTM C109- 84), lightly browned.	•Each specimen accommodates two disbondment blade tests	•Disbondment test was not standardized; •Only considered one type of ice, could be more realistic if consider refrozen ice, atmospheric ice, and compacted snow ice
Kirchman, 1992	Undercutting and disbondment characteristics	Deicing, pellets of equal weights of CaCl ₂ , NaCl, KCl, pelletized urea, CMA	Controlled temperatures: 0, 5, 10, 15, 20, 25 °F (−17.8, −15, −12.2, −9.4, −6.7, −3.9 °C)	Freezing chamber produced ice, surface partially milled with a metal iron; on lightly browned concrete slab		•Only considered one type of ice, could be more realistic if consider refrozen ice, atmospheric ice, and compacted snow ice
Tazawa et al., 1992	Interfacial bonding between ice and asphalt concrete	Anti-icing, water repellent agents: organic polysiloxane bonded with optical metal; dimethyl polysiloxane; dimethyl polysiloxane; siloxane water repellent agent; silane; fluorine contained resin; oleic acid; acetic acid ester; mixture of higher fatty acid, oleic naphthosulfonate, polyvinyl methacrylate; penetration primer; solvent and diluents; pulverized silicone polymer; reacted hydrophobic silica powder.	Temperature normally tested at 9.5, 5, 0.5 °F (−12.5, −15, −17.5 °C), some test at 14 and −4 °F (−10 °C and −20 °C).	Ice produced in a refrigerator; on asphalt concrete	•Three types of tests for measurement of debonding strength	•Only one type of ice is considered.
Schweizer, 1998	Behavior of agnew snow under shear to understand slab- anchorage formation	–	Controlled cold room, temperatures at 23 °F (−5 °C), 14 °F (−10 °C), and 5 °F (−15 °C).	Natural alpine snow	–	–

Figure 89. A summary of various experiments performed by different researchers (Muthumani et al., 2014).

Application strategies developed by Levelton Consultants (2007) include application rates for liquid, solid, and mixed deicers including pre-wet, and abrasives (Table 22). Blackburn et al. (2004) provides detailed application rates for solid, prewet solid, and liquid NaCl deicers (Figure 90). Application rates for deicers are normally specified in pound per lane-mile (lb/l-m) or kilogram per lane-kilometer (kg/l-km) and discharge rates are normally in lb/mile or kg/km. It is important to understand the difference between application and discharge rates to successfully choose the correct application rates for deicers. Table 23 provides the equivalent discharge and application rates for one and three lanes. Different application rates for several conditions (pavement and operational) are specified in this report (Blackburn et al., 2004). Blackburn et al. (2004) also discusses how application rates for other deicers can be found using salt-based deicers' application rates based on dilution potential, which is an important parameter when forming a basic guideline for any deicer use. Moreover, these salt application rates were used to find equivalent application rates for other deicers and are shown in Table 24 (Blackburn et al., 2004).

Table 22. Application rates of some commonly used deicers (Levelton Consultants, 2007).

Strategy/ Method	Materials	Pavement Temperature Ranges ¹	Application Rates ²
Anti-Icing	Liquid Chemicals, Solid Chemicals, Pre-wet Solid Chemicals	0° C to -12° C (32° F to 10° F)	18-110 Kg /Lane /Km (65 – 400 Lbs / Lane/ Mile)
Deicing	Pre-wet Solid Chemicals, Dry Solid Chemicals	0° C to -18° C (32° F to 0° F)	113 – 400 Kg /Lane /Km (200-700 Lbs / Lane/ Mile)
Abrasives	Pre-wet Abrasives, Dry Abrasives	No limits	225 – 2,700 Kg /Lane /Km (500-6,000 Lbs / Lane/ Mile)
	Abrasive/Salt Mixes	0° C to -18° C (32° F to 0° F)	225 – 2,700 Kg /Lane /Km (500-6,000 Lbs / Lane/ Mile)

¹ Source: (6)

² Source: (6, 7)

Pavement Temperature (°F)	Adjusted dilution potential	Ice pavement bond	Application rate	
			Solid (1) lb/LM	Liquid (2) gal/LM
Over 32° F	Low	No	90 (3)	40 (3)
		Yes	200	NR (4)
	Medium	No	100 (3)	44 (3)
		Yes	225	NR (4)
	High	No	110 (3)	48 (3)
		Yes	250	NR (4)
32 to 30	Low	No	130	57
		Yes	275	NR (4)
	Medium	No	150	66
		Yes	300	NR (4)
	High	No	160	70
		Yes	325	NR (4)
30 to 25	Low	No	170	74
		Yes	350	NR (4)
	Medium	No	180	79
		Yes	375	NR (4)
	High	No	190	83
		Yes	400	NR (4)
25 to 20	Low	No	200	87
		Yes	425	NR (4)
	Medium	No	210	92
		Yes	450	NR (4)
	High	No	220	96
		Yes	475	NR
20 to 15	Low	No	230	NR
		Yes	500	NR
	Medium	No	240	NR
		Yes	525	NR
	High	No	250	NR
		Yes	550	NR
15 to 10	Low	No	260	NR
		Yes	575	NR
	Medium	No	270	NR
		Yes	600	NR
	High	No	280	NR
		Yes	625	NR
Below 10°F	A. If unbonded, try mechanical removal without chemical. B. If bonded, apply chemical at 700 lb/LM. Plow when slushy. Repeat as necessary. C. Apply abrasives as necessary.			

NR = Not recommended.

Specific Notes:

1. Values for "solid" also apply to prewet solid and include the equivalent dry chemical weight in prewetting solutions.
2. Liquid values are shown for the 23-percent concentration solution.
3. In unbonded, try mechanical removal without applying chemicals. If pretreating, use this application rate.
4. If very thin ice, liquids may be applied at the unbonded rates.

General Notes:

5. These application rates are starting points. Local experience should refine these recommendations.
6. Prewetting chemicals should allow application rates to be reduced by up to about 20% depending on such primary factors as spread pattern and spreading speed.
7. Application rates for chemicals other than sodium chloride will need to be adjusted using the equivalent application rates shown in Table A-6.
8. Before applying any ice control chemical, the surface should be cleared of as much snow and ice as possible.

Figure 90. Application rates for solid, prewet solid, and liquid sodium chloride deicers (Blackburn et al., 2004)

Table 23. Correspondence between discharge and application rates (Blackburn et al., 2004).

Discharge rate in lb/mi (kg/km)	Application rate in lb/LM (kg/Lkm)		
	Number of lanes being treated		
	1	2	3
100 (28)	100 (28)	50 (14)	33 (9)
200 (56)	200 (56)	100 (28)	67 (19)
300 (84)	300 (84)	150 (42)	100 (28)
400 (112)	400 (112)	200 (56)	133 (37)
500 (140)	500 (140)	250 (70)	167 (47)
600 (168)	600 (168)	300 (84)	200 (56)
700 (196)	700 (196)	350 (98)	233 (65)
800 (224)	800 (224)	400 (112)	267 (75)

Table 24. Equivalent rates of applying five commonly used deicers (Blackburn et al., 2004).

Temperature (°F)	NaCl		CaCl ₂		MgCl ₂		KAc		CMA	
	100%*	23%*	90-92%*	32%*	50%*	27%*	100%*	50%*	100%*	25%*
	Solid lb/LM	Liquid gal/LM	Solid lb/LM	Liquid gal/LM	Solid lb/LM	Liquid gal/LM	Solid lb/LM	Liquid gal/LM	Solid lb/LM	Liquid gal/LM
31.5	100	45	109	32	90	31	159	30	159	69
31	100	46	111	32	91	32	161	31	161	72
30.5	100	47	111	33	91	32	155	30	155	71
30	100	48	107	33	94	33	158	31	158	74
29	100	49	109	34	91	33	155	31	155	79
28	100	52	109	34	91	33	152	31	152	81
27	100	54	109	35	90	34	153	31	153	86
26	100	56	104	34	96	36	161	33	161	95
25	100	57	102	34	99	35	167	35	167	108
24	100	61	108	38	102	41	167	35	167	114
23	100	62	112	41	102	41	164	35	164	117
22	100	65	110	41	102	42	160	35	160	121
21	100	68	107	40	101	42	155	35	155	125
20	100	70	108	42	98	42	150	34	150	129
15	100	90	103	44	96	44	142	34	142	170
10	100	120	101	49	95	47	138	35	138	265
5	100	165	104	57	96	51	139	37	139	630

NaCl: Sodium chloride.

CaCl₂: Calcium chloride.

MgCl₂: Magnesium chloride.

KAc: Potassium acetate.

CMA: Calcium magnesium acetate.

* Typical percent concentrations of the solid and liquid forms with the balance being largely water.

General Notes:

1. The above application rates are normalized to 100 lb/LM of dry solid NaCl. The application rates corresponding to a dry solid NaCl rate other than 100 lb/LM are determined by multiplying the equivalent chemical application rates for a given temperature by the ratio of the desired dry solid NaCl rate to 100 lb/LM. For example, if a 200 lb/LM of dry solid NaCl application rate were recommended at a temperature of 20°F, then switching to a 90 to 92 percent concentration of solid CaCl₂ would require a slightly higher application rate of 216 lb/LM.
2. The above application rate data were derived from the freezing point (ice melting) data of the five chemical solutions. As such, the data are more conservative (larger) than field data would suggest for anti-icing operations.

The method of deicer application can have a significant impact on the amount of deicing product that remains on the road. For example, approximately 90 % of applied salt brine is retained on the roadways as compared to only 16 to 77% when dry solids or pre-wetted solids are applied (Levelton Consultants, 2007; Michigan DOT, 2012). The lowest retention of deicer on pavement is associated with dry solid application using vehicles traveling at 45 miles per hour (mph) (Michigan DOT, 2012) while the highest retention of deicer on pavement is associated with pre-wet solid application by vehicles traveling 25 mph (Michigan DOT, 2012). Deicer selection is often based on regional temperatures.

Informed decisions about deicer temperature performance were made using eutectic temperatures from phase diagrams. Levelton Consultants (2007) provided a formula for deicer selection based on the performance index (PI).

$$PI = (BC/EC) - 1 \quad (\text{Eq. 8})$$

Where BC is the beginning concentration and EC is the end concentration for a deicer at a certain temperature.

Many studies have reported the effective temperature of NaCl to be 21°F (-6°C). When temperatures are below the functionality of salt, other deicers that perform at these lower temperatures may be needed. Work by Luker et al. (2004) reported the proportion of time when the temperature in Norway was below the effective temperature of NaCl (21°F (-6°C)) (Table 25). The high percentage of colder temperatures identified for December and January led Luker et al. (2004) to recommend the use of MgCl₂, which provides improved deicing performance at colder temperatures but also allows for the less expensive NaCl to be used as much as is feasible.

Table 25. Percentage of the year (monthly basis) for which MgCl₂ would be required (Luker et al., 2004).

Month	Portion of the Time Below -6°C
November	5%
December	39%
January	41%
February	15%
March	1%
November–March	19%

Luker et al. (2004) also provided guidelines for the application of solid, prewet solid, and liquid chloride-based deicers on roadways (Figure 91). Application rates for NaCl increase as temperature decreases, particularly when there is a bond between ice and pavement (Figure 91). When there is no bond present, mechanical snow removal (read: plowing) should be tried first (Luker et al., 2004). Luker et al. (2004) also provided application rates for the solid and liquid deicing products (NaCl, CaCl₂, MgCl₂, KAc, and CMA) based on temperature (Figure 92).

Pavement Temperature (°F)	Adjusted Dilution Potential	Ice Pavement Bond	Application Rate	
			Solid (1) lb/LM	Liquid (2) gal/LM
Over 32	Low	No	90 (3)	40 (3)
		Yes	200	NR (4)
	Medium	No	100 (3)	44 (3)
		Yes	225	NR (4)
		No	110 (3)	48 (3)
30–32	High	Yes	250	NR (4)
	Low	No	130	57
		Yes	275	NR (4)
	Medium	No	150	66
		Yes	300	NR (4)
25–30	High	No	160	70
	Low	Yes	325	NR (4)
		No	170	74
	Medium	Yes	350	NR (4)
		No	180	79
20–25	High	Yes	375	NR (4)
	Low	No	190	83
		Yes	400	NR (4)
	Medium	No	200	87
		Yes	425	NR (4)
15–20	High	No	210	92
	Low	Yes	450	NR (4)
		No	220	96
	Medium	Yes	475	NR
		No	230	NR
10–15	High	Yes	500	NR
	Low	No	240	NR
		Yes	525	NR
	Medium	No	250	NR
		Yes	550	NR
Below 10°F	High	No	260	NR
	Low	Yes	575	NR
		No	270	NR
	Medium	Yes	600	NR
		No	280	NR
	High	Yes	625	NR
A. If unbonded, try mechanical removal without chemical.				
B. If bonded, apply chemical at 700 lb/L-M. Plow when slushy. Repeat as necessary.				
C. Apply abrasives as necessary.				

NR = not recommended; LM = lane-mile.

Specific notes:

1. Values for “solid” also apply to prewet solid and include the equivalent dry chemical weight in prewetting solutions.
2. Liquid values are shown for the 23-percent concentration solution.
3. In unbonded, try mechanical removal without applying chemicals. If pretreating, use this application rate.
4. If very thin ice, liquids may be applied at the unbonded rates.

General notes:

5. These application rates are starting points. Local experience should refine these recommendations.
6. Prewetting chemicals should allow application rates to be reduced by up to about 20% depending on such primary factors as spread pattern and spreading speed.
7. Application rates for chemicals other than sodium chloride will need to be adjusted using the guidance in Table 5.
8. Before applying any ice control chemical, the surface should be cleared of as much snow and ice as possible.

Figure 91. Application rates for different forms of NaCl based deicer (Luker et al., 2004).

Temperature Range (°F)	NaCl		CaCl ₂		MgCl ₂		KAc		CMA	
	23%		32%		27%		50%		25%	
	Solid	Liquid	Solid	Liquid	Solid	Liquid	Solid	Liquid	Solid	Liquid
	lb/LM	gal/LM	lb/LM	gal/LM	lb/LM	gal/LM	lb/LM	gal/LM	lb/LM	gal/LM
30–32	50	22	56	16	47	17	79	15	82	35
	100	44	111	32	94	33	158	30	164	70
	150	66	167	47	141	50	237	44	246	105
	200	87	222	63	188	66	316	59	328	140
	250	109	278	79	235	83	395	74	410	174
28–30	50	22	53	15	45	16	75	14	85	36
	100	44	106	30	90	32	150	28	169	72
	150	66	159	45	135	48	225	42	254	108
	200	87	212	60	180	64	300	56	338	144
	250	109	265	75	225	80	375	70	423	180
26–28	50	22	51	14	43	15	71	13	87	37
	100	44	102	29	86	30	142	27	174	74
	150	66	153	43	129	46	213	40	261	110
	200	87	204	58	172	61	284	53	348	148
	250	109	255	72	215	76	355	66	435	185
24–26	50	22	49	14	41	14	67	13	90	38
	100	44	98	28	87	29	134	25	179	76
	150	66	147	42	123	43	201	38	269	114
	200	87	196	56	164	58	268	50	358	152
	250	109	245	70	205	72	335	63	448	191
22–24	50	22	47	13	39	14	63	12	92	39
	100	44	94	27	78	28	125	23	184	78
	150	66	141	40	117	41	188	35	276	117
	200	87	188	53	156	55	250	47	368	157
	250	109	235	67	195	69	313	59	460	196
20–22	50	22	45	13	37	13	59	11	95	40
	100	44	89	25	74	26	117	22	189	80
	150	66	134	38	111	39	176	33	284	121
	200	87	178	51	148	52	234	44	378	161
	250	109	223	63	185	65	293	55	473	201

NaCl: Sodium chloride
 CaCl₂: Calcium chloride
 MgCl₂: Magnesium chloride
 KAc: Potassium acetate
 CMA: Calcium magnesium acetate
 LM: Lane mile

Figure 92. Application rates for five different deicing chemicals (Luker et al., 2004)

Location	Product	Application Rate (lb/LM)	Condition	Information Source
Germany	Salt, solid	130–260	Normal Treatment	Litzka (2002), Lefebvre (1993)
	Salt, solid	260–520	Problem areas	
Italy	Salt, solid	130–260	Preventive Treatment	Litzka (2002), Lefebvre (1993)
	Salt, solid	130–390	Normal Treatment	Litzka (2002), Lefebvre (1993)
	CaCl ₂ flakes	130–260	Normal Treatment	Lefebvre (1993)
	CaCl ₂ flakes	65–130	Preventive Treatment	Lefebvre (1993)
Belgium	Salt, solid	260–390	Normal Treatment	Lefebvre (1993)
	CaCl ₂ flakes	260–390	Normal Treatment	
	CaCl ₂ flakes	90–260	Preventive Treatment	
Denmark	Salt, solid	>130	Normal Treatment	Lefebvre (1993)
	Salt, solid	65–130	Preventive Treatment	
France	Salt, solid	260–390	Normal Treatment	Lefebvre (1993)
	Salt, solid	130–195	Preventive Treatment	
	CaCl ₂ flakes	260–390	Normal Treatment	
Japan	Salt, solid	<1300	Normal Treatment	Lefebvre (1993)
	Salt, solid	>130	Preventive Treatment	
	CaCl ₂ flakes	130–650	Normal and Preventive Treatment	
Netherlands	Salt, solid	65–260	Normal Treatment	Lefebvre (1993)
	CaCl ₂ liquid	16% prewet to solid salt	Not specified	
United Kingdom	Salt, solid	260–520	Normal Treatment	Lefebvre (1993)
	Salt, solid	130–260	Preventive Treatment	
Sweden	Salt, solid	260	Normal Treatment	Lefebvre (1993)
	Salt, solid	65–130	Preventive Treatment	
Switzerland	Salt, solid	195–260	Normal Treatment	Lefebvre (1993)
	Salt, solid	130–195	Preventive Treatment	
	CaCl ₂ flakes	195–520	Normal Treatment	
	CaCl ₂ flakes	195–390	Preventive Treatment	

Figure 93. Application rates of several common deicers used internationally (Akin et al., 2018)

Akin et al. (2018) studied the behavior of various deicers on porous and permeable pavements (PPPs). As a part of this effort, they reported the international application rates for various solid and liquid deicers (Figure 93).

Klein-Paste and Dalen (2018) discussed the use of plowing and sanding in winter maintenance operations in detail. They noted that plow trucks with high rake angles for the cutter edge may plow snow with ease, and are suitable for heavy snowfall, but could damage the pavement. They also noted that sand particles improve friction by indirectly aiding the interlocking of rubber tires with the pavement. When snow is present on the road, they noted that the friction would be dependent on the temperature of ice (Klein-Paste and Dalen, 2018), where at very low temperatures, traffic compaction of snow and ice could significantly reduce friction. They developed Figure 94 to illustrate weather, traffic, and winter operations factors that influence pavement conditions.

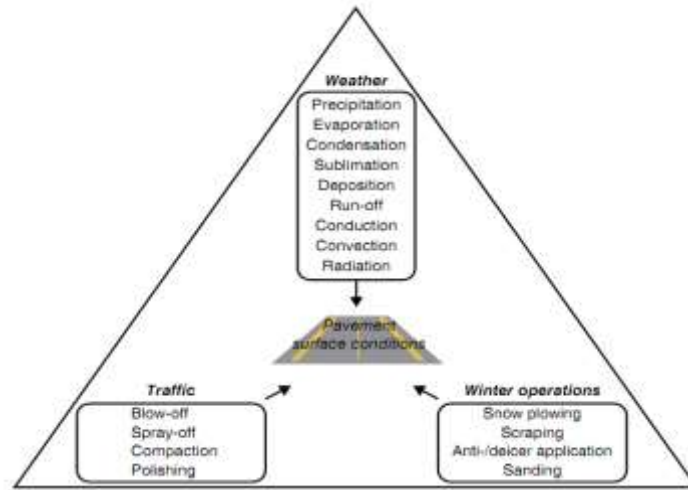


Figure 94. Factors that may affect surface conditions on a pavement (Klein-Paste and Dalen, 2018).

Klein-Paste and Wåhlin (2013) investigated the influence of anti-icers on ice. They found that a brine fraction (F_b) of 0.4 exerts a significant influence over ice formation, sufficiently weakening the ice. The following equations 9 & 10 were used to derive F_b .

$$F_b(T) = c/c_f(T) \quad (\text{Eq. 9})$$

Where c is the initial concentration of the solute prior to freezing, c_f is the concentration where equilibrium is reached, and $c_f(T)$ is given by the freezing curve in the phase diagram.

$$C_{min} = F_{b \min} c_f(T_p) \quad (\text{Eq. 10})$$

Where c_{min} is the theoretical minimum salt concentration, $F_{b \min}$ is the minimum brine fraction, and T_p is the pavement temperature.

When applying the brine fraction to field application of deicers, it was estimated that 60% less deicer is needed to achieve a sufficiently weakened ice layer, when compared to application rates based on freezing points.

Washington State University (WSU) (2019) illustrated several deicer application parameters including material application rates and strategies, equipment used for removing snow, weather effects, and other factors that should not be overlooked when choosing a suitable salt deicer. They noted that application rates may vary for the deicers that are either in solid or pre-wetted form and provide strategies for deicing, anti-icing, and use of abrasives, as well as application rates for light, moderate, and heavy snow conditions, and other weather condition-based rates. Application rates are provided for varying snowfall rates and precipitation types, temperatures, and road surface conditions which can be found on pages 3—33 of the Material Application Methodologies Guidebook: https://clearroads.org/wp-content/uploads/dlm_uploads/Guidebook_CR15.01_FINAL_7-28-19.pdf.

Conclusion

Research has identified factors that may influence the decision of which deicer type to use, including weather conditions, deicer application strategies, pavement type and condition, and application rates. Laboratory testing was used to mimic field conditions to better understand the influence of these parameters on deicer performance, and to identify methods that assess road conditions, such as friction, bonding strength, and retention of deicers. Key takeaways, including application rates, may and should vary depending on the form of deicer used (abrasive, pre-wet, or liquid), the type of deicer, pavement type, road condition, and environmental conditions such as air temperature and relative humidity.

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Appendix B – Teconer Friction Statistical Results Tables

In Table 26, Table 27, and Table 28 the first column on the left is the sample comparison, the second column is the difference in the mean for frictions values after plowing (i.e., mean of C22 friction minus mean of C21 friction – so if the difference is negative, the second sample has a higher friction value (Table 26)). The third and fourth columns from the left are the lower (lwr) and upper (upr) limits of a 95% confidence interval for true difference in means, and the fifth column is the p-value. P-values were assigned significance at 0.05 or less. Note that significant results, or P-values ≤ 0.05 are bolded.

Table 26. Summary statistics from after plowed Teconer friction values on concrete.

Samples IDs Compared	Difference	lwr	upr	p adj
C22-C21	-0.0473	-0.0691	-0.0255	0.0000
C23.3-C21	-0.0293	-0.0511	-0.0075	0.0013
C24-C21	0.0283	0.0065	0.0501	0.0022
C25-C21	-0.0331	-0.0550	-0.0113	0.0001
C26-C21	-0.0311	-0.0530	-0.0093	0.0004
C27-C21	0.0450	0.0232	0.0668	0.0000
C28-C21	-0.0361	-0.0580	-0.0143	0.0000
C23.3-C22	0.0180	-0.0038	0.0398	0.1923
C24-C22	0.0756	0.0538	0.0974	0.0000
C25-C22	0.0141	-0.0076	0.0359	0.4979
C26-C22	0.0161	-0.0056	0.0379	0.3197
C27-C22	0.0923	0.0705	0.1141	0.0000
C28-C22	0.0111	-0.0106	0.0329	0.7743
C24-C23.3	0.0576	0.0358	0.0794	0.0000
C25-C23.3	-0.0038	-0.0256	0.0179	0.9994
C26-C23.3	-0.0018	-0.0236	0.0199	0.9999
C27-C23.3	0.0743	0.0525	0.0961	0.0000
C28-C23.3	-0.0068	-0.0286	0.0149	0.9803
C25-C24	-0.0615	-0.0833	-0.0397	0.0000
C26-C24	-0.0595	-0.0813	-0.0377	0.0000
C27-C24	0.0166	-0.0051	0.0384	0.2810
C28-C24	-0.0645	-0.0863	-0.0427	0.0000
C26-C25	0.0020	-0.0198	0.0238	0.9999
C27-C25	0.0781	0.0563	0.0999	0.0000
C28-C25	-0.0030	-0.0248	0.0188	0.9999
C27-C26	0.0761	0.0543	0.0979	0.0000
C28-C26	-0.0050	-0.0268	0.0168	0.9970
C28-C27	-0.0811	-0.1029	-0.0593	0.0000

Table 27. Summary statistics from after plowed Teconer friction values on asphalt.

Sample ID Comparison	Difference	lwr	upr	p adj
A22-A21	0.0081	-0.0201	0.0365	0.9879
A23.3-A21	0.0521	0.0238	0.0805	0.0000
A24-A21	-0.0245	-0.0528	0.0038	0.1466
A25-A21	0.0323	0.0040	0.0607	0.0129
A26-A21	0.1080	0.0797	0.1363	0.0000
A27-A21	-0.0235	-0.0518	0.0048	0.1871
A28-A21	0.1857	0.1573	0.2140	0.0000
A23.3-A22	0.0440	0.0157	0.0723	0.0001
A24-A22	-0.0327	-0.0610	-0.0043	0.0114
A25-A22	0.0242	-0.0042	0.0525	0.1593
A26-A22	0.0998	0.0715	0.1282	0.0000
A27-A22	-0.0317	-0.0600	-0.0033	0.0164
A28-A22	0.1775	0.1492	0.2058	0.0000
A24-A23.3	-0.0767	-0.1050	-0.0483	0.0000
A25-A23.3	-0.0198	-0.0482	0.0085	0.3960
A26-A23.3	0.0558	0.0275	0.0842	0.0000
A27-A23.3	-0.0757	-0.1040	-0.0473	0.0000
A28-A23.3	0.1335	0.1052	0.1618	0.0000
A25-A24	0.0568	0.0285	0.0852	0.0000
A26-A24	0.1325	0.1042	0.1608	0.0000
A27-A24	0.0010	-0.0273	0.0293	1.0000
A28-A24	0.2102	0.1818	0.2385	0.0000
A26-A25	0.0757	0.0473	0.1040	0.0000
A27-A25	-0.0558	-0.0842	-0.0275	0.0000
A28-A25	0.1533	0.1250	0.1817	0.0000
A27-A26	-0.1315	-0.1598	-0.1032	0.0000
A28-A26	0.0777	0.0493	0.1060	0.0000
A28-A27	0.2092	0.1808	0.2375	0.0000

Table 28. Summary statistics from after plowed Teconer friction values comparing asphalt to concrete for all NaCl solutions.

Sample ID Comparison	Difference	lwr	upr	p adj
C21-A21	0.1435	0.1150	0.1720	0.0000
C22-A21	0.0962	0.0676	0.1247	0.0000
C23.3-A21	0.1142	0.0856	0.1427	0.0000
C24-A21	0.1718	0.1433	0.2004	0.0000
C25-A21	0.1103	0.0818	0.1389	0.0000
C26-A21	0.1123	0.0838	0.1409	0.0000
C27-A21	0.1885	0.1600	0.2170	0.0000
C28-A21	0.1073	0.0788	0.1359	0.0000
C21-A22	0.1353	0.1068	0.1639	0.0000
C22-A22	0.0880	0.0595	0.1165	0.0000
C23.3-A22	0.1060	0.0775	0.1345	0.0000
C24-A22	0.1637	0.1351	0.1922	0.0000
C25-A22	0.1022	0.0736	0.1307	0.0000
C26-A22	0.1042	0.0756	0.1327	0.0000
C27-A22	0.1803	0.1518	0.2089	0.0000
C28-A22	0.0992	0.0706	0.1277	0.0000
C21-A23.3	0.0913	0.0628	0.1199	0.0000
C22-A23.3	0.0440	0.0155	0.0725	0.0000
C23.3-A23.3	0.0620	0.0335	0.0905	0.0000
C24-A23.3	0.1197	0.0911	0.1482	0.0000
C25-A23.3	0.0582	0.0296	0.0867	0.0000
C26-A23.3	0.0602	0.0316	0.0887	0.0000
C27-A23.3	0.1363	0.1078	0.1649	0.0000
C28-A23.3	0.0552	0.0266	0.0837	0.0000
C21-A24	0.1680	0.1395	0.1965	0.0000
C22-A24	0.1207	0.0921	0.1492	0.0000
C23.3-A24	0.1387	0.1101	0.1672	0.0000
C24-A24	0.1963	0.1678	0.2249	0.0000
C25-A24	0.1348	0.1063	0.1634	0.0000
C26-A24	0.1368	0.1083	0.1654	0.0000
C27-A24	0.2130	0.1845	0.2415	0.0000
C28-A24	0.1318	0.1033	0.1604	0.0000
A26-A25	0.0757	0.0471	0.1042	0.0000
A27-A25	-0.0558	-0.0844	-0.0273	0.0000
A28-A25	0.1533	0.1248	0.1819	0.0000
C21-A25	0.1112	0.0826	0.1397	0.0000
C22-A25	0.0638	0.0353	0.0924	0.0000
C23.3-A25	0.0818	0.0533	0.1104	0.0000
C24-A25	0.1395	0.1110	0.1680	0.0000
C25-A25	0.0780	0.0495	0.1065	0.0000
C26-A25	0.0800	0.0515	0.1085	0.0000
C27-A25	0.1562	0.1276	0.1847	0.0000
C28-A25	0.0750	0.0465	0.1035	0.0000
C21-A26	0.0355	0.0070	0.0640	0.0022
C22-A26	-0.0118	-0.0404	0.0167	0.9893
C23.3-A26	0.0062	-0.0224	0.0347	1.0000
C24-A26	0.0638	0.0353	0.0924	0.0000
C25-A26	0.0023	-0.0262	0.0309	1.0000
C26-A26	0.0043	-0.0242	0.0329	1.0000
C27-A26	0.0805	0.0520	0.1090	0.0000
C28-A26	-0.0007	-0.0292	0.0279	1.0000
C21-A27	0.1670	0.1385	0.1955	0.0000
C22-A27	0.1197	0.0911	0.1482	0.0000
C23.3-A27	0.1377	0.1091	0.1662	0.0000
C24-A27	0.1953	0.1668	0.2239	0.0000
C25-A27	0.1338	0.1053	0.1624	0.0000
C26-A27	0.1358	0.1073	0.1644	0.0000
C27-A27	0.2120	0.1835	0.2405	0.0000
C28-A27	0.1308	0.1023	0.1594	0.0000
C21-A28	-0.0422	-0.0707	-0.0136	0.0001
C22-A28	-0.0895	-0.1180	-0.0610	0.0000
C23.3-A28	-0.0715	-0.1000	-0.0430	0.0000
C24-A28	-0.0138	-0.0424	0.0147	0.9550
C25-A28	-0.0753	-0.1039	-0.0468	0.0000
C26-A28	-0.0733	-0.1019	-0.0448	0.0000
C27-A28	0.0028	-0.0257	0.0314	1.0000
C28-A28	-0.0783	-0.1069	-0.0498	0.0000