**MT8698**

# Developing Renewable Agro-Based Anti-Icers for Sustainable Winter Road Maintenance Operations

**Mehdi Honarvar Nazari**[1], Ph.D., S.M. ASCE**, Xianming Shi**[2], Ph.D., P.E. M. ASCE

1. Graduate Research Assistant in Civil Engineering, Ph.D. in Metallurgical and Materials Engineering, Laboratory of Corrosion Science and Electrochemical Engineering, Dept. of Civil and Environmental Engineering, P. O. Box 642910, Washington State University, Pullman, WA 99164-2910; Email: m.honarvarnazari@wsu.edu
2. Associate Professor, Laboratory of Corrosion Science and Electrochemical Engineering, Department of Civil and Environmental Engineering, P. O. Box 642910, Washington State University; Pullman, WA 99164-2910; Phone: (509) 335-2576; Email: xianming.shi@wsu.edu (corresponding author)

**ABSTRACT**

This work evaluated the performance and impacts of several agro-based anti-icers along with two traditional chloride-based anti-icers (23 wt.% NaCl brine and its beet juice blend). A statistical design of experiments (central composite design) was employed for developing anti-icing liquids consisting of cost-competitive chemicals such as renewable agro-based compounds (e.g., Concord grape extract and glycerin), sodium chloride, sodium metasilicate, and sodium formate. The following experimentally obtained parameters were examined as a function of the formulation design: ice-melting capacity at −3.9°C, splitting strength of Portland cement mortar samples after 10 freeze-thaw/deicer cycles, corrosion rate of C1010 carbon steel after 24-hour immersion, and impact on low temperature performance of asphalt binder. One viable formula ("best performer") was tested for thermal properties by measuring its differential scanning calorimetry (DSC) thermograms, and other properties (friction coefficient on anti-iced asphalt pavement, pH, oxygen demands). These laboratory data shed light on the selection and formulation of innovative agro-based snow- and ice-control chemicals that can significantly reduce the costs of winter road maintenance operations.

*Keywords:*

Agro-based anti-icer; ice-melting; freeze-thaw; bending beam rheometer (BBR); corrosivity; DSC; chemical oxygen demand (COD); biochemical oxygen demand (BOD)

## 1. INTRODUCTION

The U.S. spends approximately $2.3 billion each year to keep highways free of snow and ice, and the highway winter maintenance operations cause considerable damages to infrastructure and the natural environment and add at least $5 billion to this cost (Fay et al. 2013). Roadway deicers contain mainly chloride salts, which are the most common freezing point depressants used for snow/ice control operations. The chloride salts are persistent in the environment, posing a significant risk to infrastructure (Dang et al. 2016; Farnam et al. 2015; Shi et al. 2010; Xie et al. 2017), motor vehicles (Honarvar Nazari et al. 2017; Li et al. 2013; Nazari and Shi 2018; Shi et al. 2013), and the natural environment over time (Corsi et al. 2015; Fay and Shi 2012; Honarvar Nazari et al. 2015; Pieper et al. 2018).

Bio-based deicers have been introduced to tackle the negative effects of chloride-based deicers and improve their performance. However, there are gaps in the studies related to these materials. Many of these studies did not report the constituents of the bio-based materials that they have used. This makes it nearly impossible for other researchers to repeat the experiments using similar compounds. Some studies used commercial bio-based products with some unknown compounds, and other studies used either raw bio-based materials (e.g., beet juice), waste of industrial processes (e.g., desugared molasses), or commercial organic chemicals. These may work effectively for winter road maintenance operations, but can induce acute impacts to the receiving environment, particularly due to potential toxicological effects and high oxygen demand of the organic compounds (Corsi et al. 2012; Shi et al. 2017). Yet another factor rarely investigated is the effect of aging on the performance of bio-based materials.

In this context, there is an urgent need to introduce more eco-friendly materials for winter road maintenance operations along with a more comprehensive evaluation of the multiple aspects of agro-based additives and formulations. Such evaluation should cover the important dimensions of deicer performance and impacts (especially those on the natural environment and transportation infrastructure) and focus on the guiding principles of sustainability.

This exploratory study aimed to develop more sustainable anti-icing formulations for snow and ice control on highways, using a Concord grape extract, glycerin, sodium metasilicate, and sodium formate. These formulations are expected to feature improved ice-melting capacity and corrosion inhibition performance, with less impact on the durability of cement mortar, asphalt pavement, and the environment. In this regard, all results have been compared with 23% NaCl solution and a currently popular “green” anti-icer (i.e., a blend of sugar beet juice with 23% NaCl brine) used in winter road maintenance operations.  In addition, this work examines the effect of aging on the performance of the bio-based anti-icers.

## 2. EXPERIMENTAL

### *2.1. Materials*

To prepare the anti-icer formulations, we used deionized water, reagent-grade sodium chloride, sodium metasilicate, and sodium formate, commercial-grade glycerin (Nature's Oil, Streetsboro, Ohio), and laboratory developed Concord grape extract. Each formulation had the same amount of sodium chloride (18.4 wt.%) and various amounts of other constituents.

It should be mentioned that all of the reagent-grade chemicals used in this research were purchased from Fisher Scientific (Fair Lawn, New Jersey), Sigma Aldrich (St. Louis, Missouri), and J. T. Baker (Phillipsburg, New Jersey).

### *2.2. Statistical Design of Experiments*

In order to minimize the number of experiments needed to explore a large domain of unknown factors and interactions, we used a scheme of statistical design of experiments known as central composite design. For instance, if we planned to investigate four influential factors, each varying at five different levels, without experimental design, there would be a total of $4^4$ (= 256) experiments. With central composite design, however, we could choose to conduct only 21 experiments, the data from which should be sufficient to reasonably illustrate the inherent relations between the influential factors and the target factors.

Using central composite design, we chose four factors of $X_1$, $X_2$, $X_3$, and $X_4$ as the weight percent of Concord grape extract, glycerol, sodium formate, and sodium metasilicate, respectively. The weight percent range of 0–6 g was chosen for $X_1$–$X_3$, and 0–4.5 g for $X_4$. The anti-icer formulations were investigated by adopting the design parameters and associated target attributes, shown in Table 1.

### *2.3. Preparation of the Concord grape extract*

For preparation of the extract, the as-received Concord grape waste powder (FruitHealth, Grandview, Washington) was milled to get a more homogenous powder. Then, 30 g of the powder was chosen for chemical and biological degradation. For chemical degradation, 30 g of the Concord grape powder, 120 g of urea, 0.5 g of $Ca(OH)_2$, and 3 g of NaOH were added to 200 mL of deionized water. The solution was stirred vigorously for 30 min, then placed in the refrigerator at -20°C overnight. The iced solution was removed from the refrigerator and put in room temperature for some hours until a slurry of ice and liquid was achieved. The solution was then stirred vigorously for 30 min, during which 250 mL of water was added gradually. For biological degradation, the pH of the prepared solution was adjusted to around 8.5 by adding $HNO_3$ and NaOH. A mixture of $KH_2PO_4$, $NaH_2PO_4.H_2O$, and $MgSO_4.7H_2O$ with the molar ratios of 7, 10.7, and 1, respectively, and total weight of less than 4 g was added to the solution to create an appropriate environment for the growth of bacteria. Next, 100 mL of *Bacillus megaterium* bacteria (NRRL B-14308) was added to the solution, and the solution was put in the shaker for 21 days to complete the biodegradation process (i.e., "natural fermentation").

It should be mentioned that all of the chemicals used in this section were reagent-grade. In addition, the freeze-dried *Bacillus Megaterium* bacteria was purchased from Ward's Science (Rochester, New York).

### *2.4. Freeze-thaw /deicer exposure of cement mortar*

The effects of anti-icers on concrete were assessed by conducting a freeze-thaw test of Portland cement mortar (PCM) samples in the presence of anti-icers, following the SHRP (Strategic Highway Research Program) H205.8 test method (Chappelow et al. 1992) with minor modifications. The test evaluates the combined effects of liquid chemicals and freeze-thaw cycling on the structural integrity of specimens of non-air-entrained mortar. Mortar samples were prepared in 5.1 cm × 10.2 cm poly (vinyl chloride) piping with a volume of 52.5 $cm^3$. The mortar mix design had a water-to-cement ratio of 0:5, sand-to-cement ratio of 3:1, and water reducer of 1.5 mL. The cement used was Portland cement type I-II; the sand used was a Sakrete multipurpose sand (Sakrete Inc., Cincinnati, Ohio). Samples were cured in water for the first 24 h before being placed in a container with 100% relative humidity. The dry weight of each sample at 28 days was recorded before the sample was placed on a sponge inside a dish containing 310 mL of diluted (3%) anti-icer solution. The dish was covered in plastic wrap to press the mortar samples into the sponge and to prevent evaporation of anti-icer solutions. Three mortar specimens were tested in each anti-icer solution. 23% NaCl brine solution and beet juice blend or more specifically beet juice/salt brine blend (80% (v/v) 23% NaCl solution + 20% (v/v) beet juice) were used as the controls. A thermocouple was embedded in one of the control mortar samples to monitor temperatures during freeze-thaw cycling. The sealed dishes were placed in the freezer for 16 to 18 h, at -20.8 ± 0.2°C, and afterward were placed in a laboratory environment for 6 to 8 h, at 23.2 ± 0.2°C. The cooling rate in the freezer and the heating rate in the laboratory environment were about 0.06°C/min and 0.07°C/min, respectively. This cycle was repeated for 10 days. The test specimens were removed from the dish, and the scaled-off materials were removed using a plastic brush. The specimens were air-dried overnight before the final weight of each was recorded. Most of the samples showed weight gain in spite of scaling, which demonstrates the absorption of anti-icers by most of the specimens. Therefore, weight loss data were not used for evaluating the effectiveness of the anti-icer solutions.

### *2.5. Ice-melting test*

The SHRP ice-melting test method is used for measuring the quantity of ice melted by deicers over time. In this test, liquid or solid deicers are uniformly spread over the prepared ice, and the melted liquid is removed for volume measurements (Chappelow et al. 1992). A modified SHRP test using 1.4 mL anti-icer, 48 mL distilled deionized water, and a 150 × 20 mm (5.9 in.: diameter × 0.8 in.: depth) polystyrene petri dish was conducted to measure the ice-melting capacity of the anti-icer at -9.4°C (-9.4°C). The anti-icer was applied evenly over the ice surface with a syringe. After 10, 20, 30, 45, and 60 min, the liquid volume was removed and volumetrically measured with a calibrated syringe. Another parallel series of tests were conducted in a 3.65 m × 4.27 m state-of-the-art temperature-regulated environmental chamber, following the same procedure. The tests were conducted at -3.9°C. To ensure statistical reliability, duplicate tests were performed for each combination of anti-icer type.

### *2.6. Low-temperature behavior of asphalt pavement*

A customized test protocol was used to assess the effect of anti-icers on the low-temperature behavior of asphalt pavement. A bending beam rheometer (BBR) was used for this purpose. Asphalt binder (PG 64-28 from Western States Asphalt, Spokane, Washington) was first aged in a rolling thin-film oven to simulate the aging of hot-mix asphalt concrete during mixing and placement of the asphalt pavement. The asphalt binder was then placed in a pressure-aging vessel with the air pressure of 2.10 MPa for 20 h to simulate the long-term field oxidative aging conditions (Bahia and Anderson 1993). The asphalt binders were moved to a can, and 4 mL of anti-icer solution was applied for each 40 g of binder, after which the cans were put in an oven at 80°C for 1 h, followed by 2 h at 155°C and atmospheric pressure. Finally, beams were molded and tested in the BBR.

### *2.7. Corrosion behavior of carbon steel*

The corrosion caused by anti-icers to C1010 carbon steel (ASTM A569) was assessed using the linear polarization resistance (LPR) technique. Measurements for this technique were carried out in a PARSTAT-MC multichannel potentiostat-galvanostat (Princeton Applied Research, Oak Ridge, Tennessee), coupled with a three-electrode electrochemical cell for each channel. Before testing, the steel coupons were wet-polished using 60 to 1500 grit silicon carbide papers, and washed with ethanol and distilled deionized water. For each anti-icer, at least two steel coupons were exposed to anti-icer for 24 h. The LPR measurement "is the only corrosion monitoring method that allows corrosion rates to be measured directly, in real time" (Metal Samples 2018). This electrochemical technique provides an alternative to the gravimetric method in rapidly assessing the corrosivity of solutions. The corrosivity of each anti-icer was reported as $\mu A/cm^2$.

### *2.8. DSC thermogram test*

The DSC (differential scanning calorimetry) thermogram test is a laboratory method used to quantify deicer performance. The test measures the energy necessary to maintain a near-zero temperature difference between the test substance (deicer) and an inert reference material, with the two subjected to an identical temperature program. The heat-flow measurements indicate phase transitions, energy changes, and kinetics. The DSC measurement used in this research required 5–10 mg of the sample, which was sealed in an aluminum capsule, using a heating rate of 2.6 °C/min.

### *2.9. pH measurements*

The pH of samples was measured using a Milwaukee MW100 portable pH meter with 0.1 pH resolution (Milwaukee Instruments, Rocky Mount, North Carolina). Before running the experiments, the pH probe was calibrated using the buffer solutions with the pHs of 4 and 7, respectively based on the instrument manual. For the measurement, the pH probe was placed in the test solution until the measured pH value was stable.

### *2.10. Friction test of anti-iced asphalt pavement*

For measuring the friction of asphalt pavement, the pavement sample was placed in a conditioning room with the temperature of -9.4 °C and the relative humidity of 80% for overnight. To achieve a 58.8 L/lane-km application rate for anti-icing, a given amount of anti-icer (293 µL) was applied over 182.4 $cm^2$ surface area of the pavement using a pipet in 13 drops (each drop 22.6 µL). After evaporating the water of the applied anti-icer using a dryer, the sample was returned to the conditioning room. Then, it was allowed to stay in the freezer for one hour. After that, to simulate the "black ice" scenario, a given amount of deionized water (728.5 µL) was applied on the surface of sample using a pipet in 13 drops (each drop 56 µL) exactly at the same spots of the applied anti-icer, over a duration of approximately 60 seconds. The mentioned amount of water was chosen as a result of trial and errors, in order to reach a layer of ice on the surface. For simulation of the plowing process, a sharp metallic object was used to level the ice with pavement surface. As a result, a thin layer of ice remained on the surface of the pavement sample. The surface friction was then measured using a static friction tester, which had a 0.64 cm thick, 10.16 $cm^2$ neoprene rubber contact surface (durometer rating of 30A). The apparatus was pulled horizontally across the pavement surface, and the force needed to overcome static friction was measured with a spring scale. The coefficient of static friction was defined as the ratio of the horizontal pulling force to the weight of the friction tester.

### *2.11. COD measurements*

The best-performer sample and beet juice/salt brine blend were used for the COD (chemical oxygen demand) test. Both solutions were diluted to a ratio of 1000:1 by adding deionized water.

Then 2 mL of the diluted solution was added to COD Standard Solution containing potassium dichromate as a strong oxidizing agent. The mixture was heated at 150°C for 2 h. After the mixture cooled to room temperature, the mg/L COD was measured at the wavelength of 420 nm using a Genesys 20 spectrophotometer (Thermo Electron Corporation, Waltham, Massachusetts).

### *2.12. $BOD_5$ measurements*

The "best performer" anti-icer and beet juice/salt brine blend were used for BOD (biochemical oxygen demand) test. For sample dilution, 45 mL of each sample was measured in a graduated cylinder. It was then transferred to a BOD bottle with the total volume of 300 mL. The remaining volume of the BOD bottle was filled with aerated dilution water. For calculating the dilution factor, the dilution volumes were recorded. Same dilution procedure was repeated three times for each sample. In addition, three bottles just filled with aerated dilution water were used as control. After measuring $DO_0$ (t = 0) using a calibrated dissolved oxygen (DO) meter, the bottles were labeled and placed in the 20°C incubator for 5 days. At day-five, the DO was measured in the incubated bottles using the DO meter ($DO_5$). The $BOD_5$ was calculated using following equation.

$$BOD_5\left(\frac{mg}{L}\right) = \frac{DO_0 - DO_5}{P} \qquad (1)$$

Where, $DO_0$ and $DO_5$ are dissolved oxygen concentrations (mg/L) at t of 0 and 5 days. $P$ is the decimal volumetric fraction of sample used (dilution fraction) which is 0.15.

## 3. RESULTS AND DISCUSSION

### *3.1. Ice-Melting Capacity of Anti-Icers*

Figure 1 shows the 20 min ice-melting capacity of selected anti-icers at -3.9°C. The differences in ice-melting capacities of 23% NaCl and beet juice/salt brine blend with mixture 20 were significant (equal or more than 0.2 mL brine/g anti-icer), which indicates the advantage of the use of mixture 20 over them. Figure 2 shows the 60 min ice-melting capacity of selected anti-icers at -3.9°C. No sample had an ice-melting capacity of at least 0.2 unit more than both 23% NaCl and beet juice/salt brine blend. The best sample (sample 10) could outperform 23% NaCl by more than 0.2 unit and beet juice/salt brine blend by 0.13 unit. This made it a potential candidate for roadway anti-icing, instead of using the controls (23% NaCl brine and the beet juice/salt brine blend). Considering ice-melting capacity at both 20 min and 60 min, mixture 10 had a relative advantage over the controls. A similar conclusion on the better performance of bio-based materials over 23% NaCl solution was reported by other researchers (Hossain et al. 2015).

### *3.2. Effect of Freeze-Thaw in the Presence of Anti-Icers on PCM Strength*

Figure 3 illustrates the average splitting strength of PCM (Portland cement mortar) samples after 10-cycle freeze-thaw testing in various anti-icers, along with two control samples in 23%NaCl brine and beet juice/salt brine blend. These results show that the splitting strength of the PCM samples exposed to all mixtures but mixtures 2 and 21 was higher than that of the samples exposed to 23% NaCl. Note that all mortar samples exhibited lower splitting strength values than the samples exposed to the beet juice/salt brine blend, suggesting more compromised mortar materials.

In a freeze-thaw process, water penetrates into the surface and internal pores of the cementitious material in the thawing cycle and it then freezes in the freezing cycle. The main mechanisms by which freeze/thaw cycles deteriorate mortar and concrete include the buildup of tensile stresses by volume expansion (due to phase transition from water to ice) and by hydraulic or osmotic pressures (Chen et al. 2016; Pigeon and Pleau 2010; Xu and Shi 2018). Common symptoms of freeze/thaw damage include cracking, surface scaling, and internal damage of the mortar or concrete’s microstructure. The main impacts of surface scaling include weight loss and reduction of its surface cover, while internal damage leads to a decrease in splitting tensile strength, compressive strength, and elastic modulus of the material (Zandi Hanjari et al. 2011; Zhang et al. 2017). The presence of deicer (or anti-icer) can further complicate the mechanisms of freeze/thaw damage of mortar and concrete, by a host of pathways. For instance, deicer can lower the saturation or vapor pressure and lower the ice formation temperature, which may help reduce the damage. Deicer can also increase the number of freeze/thaw cycles, increase the degree of saturation, aggravate the temperature variations across the concrete matrix, and amplify the osmotic pressures during freezing, all of which contribute to more damage (Pigeon and Pleau 2010; Xu and Shi 2018). More importantly, deicers can chemically react with cement paste and cause calcium leaching, degradation of C-S-H gel and formation of deleterious crystalline phases inside the concrete (Qiao et al. 2018; Shi et al. 2010; Xie et al. 2017).

As mentioned earlier, most of the mortar samples exposed to bio-based anti-icers had higher splitting tensile strength than the samples exposed to 23% NaCl. This shows lower internal damage, which may be due to reduced activity of bio-based anti-icers with cement paste, or to formation of new phases with higher strength as the result of chemical reactions between the additives and mortar constituents (Heikal 2004; Shi et al. 2010).

### *3.3. Impacts of Anti-Icer Mixtures on Low Temperature Behavior of Asphalt Binder*

The effect of anti-icers on asphalt was assessed with a bending beam rheometer (BBR) by exposing the asphalt binder to anti-icers and thermal and pressure aging, and subsequent testing of the binder beams with the BBR. The BBR test provides values for creep stiffness and *m*-value (Figure 4 and Figure 5). Higher stiffness values correspond to higher thermal stresses and higher risk of thermal cracking (at cold temperatures experienced during the use phase instead of construction phase of asphalt pavement), so a maximum limit of 185.13 MPa was specified. On the other hand, lower *m*-values indicate less ability to relax and thus higher risk of thermal cracking, so a minimum limit of about 0.271 was specified. The *m*-value and stiffness values varied in the range of 0.271–0.406 and 112.13–185.13 MPa, respectively. In terms of both parameters, Mix-20 features values close to the beet juice/salt brine blend and salt brine. The experimental results indicated the higher impact of anti-icer design on the stiffness values than on the *m*-value. The impact of examined anti-icer mixtures on the creep stiffness of the asphalt binder could be attributed to the binder emulsification phenomenon (Pan et al. 2008; Yang et al. 2018) and possibly other physicochemical interactions between the anti-icer and asphalt molecules.

### ***3.4. The Corrosivity of Anti-Icer Mixtures on Mild Steel***

As shown in Figure 6, the corrosion rates of most of C1010 carbon steel samples exposed to anti-icer mixtures were lower than the corrosion rates of the samples exposed to 23% NaCl brine and beet juice/salt brine blend. The steel samples exposed to mixtures 2, 3, 5, 6, 8–10, 12–15, 17, and 20 showed average corrosion rates lower than 2 $\mu A/cm^2$. Among them, Mix-15, which had the highest amount of glycerin (4.8%), caused the lowest corrosion rate of the steel samples (0.32 $\mu A/cm^2$); Mix-16 showed the corrosivity of 3.36 $\mu A/cm^2$. Samples exposed to mixtures 1, 4, 7, 11, and 21 had corrosion rates below 8 $\mu A/cm^2$. Note that Mix-18, with zero-percent sodium formate, caused the most severe corrosion on the coupons. This result shows the critical role of sodium formate in mitigating general corrosion.

The product of steel corrosion is rust, which is made of iron oxide and hydroxide compounds (Wang et al. 2019). Some researchers have shown that formate compounds can react with the rust and form Fe(II–III) hydroxy-formate which is able to interfere in the steel corrosion and thus serve as a corrosion inhibitor (Refait et al. 2006). This is in good agreement with the results obtained in this research, which showed anti-corrosion property of sodium formate.

An interesting point is that mixtures 10 and 20, which had the best ice-melting capacity, provided inhibition efficiency (IE) of 92.3% and 86.1%, respectively (calculated using the following equation).

$$IE\% = \left(\frac{CR_{uninhibited} - CR_{inhibited}}{CR_{uninhibited}}\right) \times 100 \quad (2)$$

where $CR_{uninhibited}$ and $CR_{inhibited}$ are the corrosion rates of the steel samples exposed to salt brine and to anti-icer mixtures, respectively.

### *3.5. Decision-Making Process*

The analytical hierarchy process (AHP) was employed for making a decision matrix to prioritize the anti-icer solutions. This process, which assisted us in the multi-criteria decision-making process, allows agencies to evaluate various alternatives in terms of a set of given criteria. Pairwise comparisons, shown in Table 2, are made based on the fact that, if the row parameter is considered more important than the parameter in the column, a number greater than one is assigned to the matrix based on the intensity of importance. A higher number indicates greater importance. Conversely, if the parameter in the column is considered more important, the reciprocal of the nonzero value is assigned in the matrix (Triantaphyllou and Mann 1995).

The comparisons are used in a standardized matrix to determine the weights of importance of the decision criteria, as shown in Table 3. The standardized matrix is the result of the assigned value from Table 2 divided by the sum of the assigned values in the respective columns. For example, the 1.00 from row 2 column 2 in Table 2 divided by the sum of 3.42 in row 8 column 2 of Table 2 gives us 0.29 in row 2 column 2 of Table 3. A summary of the prioritization matrix is shown in Table 4, in which each column has been normalized, with 0 and 100 being the worst and best performer, respectively. Each decision weight in Table 4 was determined by calculating the average of the standardized rows in Table 3. For example, from row 1, the average of 0.29, 0.29, 0.38, 0.20, 0.38, and 0.38 is equal to 0.32.

Based on the priorities set in Table 4, the multi-criteria scoring matrix resulted in Mix-21 having the lowest score (20). Note that six mixtures featured a higher score than 23% NaCl brine control (61) under the investigated conditions and given priorities. Specifically, Mix-10 exhibited the highest score: 81, which is too close to the score of beet juice/salt brine blend (82). In the next step, the obtained scores for each anti-icer listed in Table 4 and the weight percent of each additive listed in Table 1 were used as inputs in Design-Expert® software to obtain the "best performer" sample based on the central composite design method. According to this analysis, the "best performer" sample consisted of 0.89% Concord grape extract, 4.57% glycerin, 4.54% sodium formate, 0.19% sodium metasilicate, and 18.4% NaCl.

### *3.6. Characteristic Temperature*

The warming cycle DSC thermogram was used for studying the anti-icers (Figure 7), because the warming cycle is less affected by super-cooling effect and is thus more reliable than the cooling cycle thermogram. Six samples plus BP-4 aged were examined; their composition is shown in Table 5.

For 23% NaCl solution, at around -18.5°C, a drop in heat flow between the sample and air occurred, which corresponds to the phase transition from ice to water. The temperature associated with the lowest (peak) heat flow (-18.4°C) is defined as the characteristic temperature ($T_C$) of the salt brine sample. The $T_C$ peak relates to the initiation and growth of ice crystals in the test solution. Different chemical solutions would feature thermograms with peaks of unique shape with different values of $T_C$, which is the basis for using a DSC thermogram as the "fingerprint" of the chemical solutions being tested. Tc coincides with the "effective temperature" of the test solution as a deicer, below which temperature ice crystals start to form and the pavement becomes icy.

By adding 0.19 wt.% sodium metasilicate ($Na_2SiO_3$) in sample BP-1, the $T_C$ shifted to -19.2°C. Sample BP-2 had a $T_C$ of around -22°C, which showed an almost 2.8°C decrease in the characteristic temperature due to the addition of 4.54 wt.% sodium formate (HCOONa) to the deicer. Adding 4.57 wt.% glycerin moved the $T_C$ to -23.5°C. Since nearly the same amount of sodium formate and glycerin were used, it can be concluded that sodium formate is a more effective freezing point depressant than glycerin in the examined deicer. Sample BP-4 had a $T_C$ of -23.9°C, which was close to that of Sample BP-3. Therefore, adding 0.89 wt.% Concord grape extract made a minor improvement in the $T_C$. The $T_C$ of the best-performer sample (BP-4) was less than that of the beet juice/salt brine blend, with a $T_C$ of -22.8°C. In addition, the characteristic temperature of BP-4 aged sample was about -23.1°C which is very close to that of BP-4. This shows that aging has not affected the behavior of the BP-4 sample. It should be mentioned that the aging process for anti-icers is performed at 59°C for 3 days (72h) which simulates one-year storage at 24°C (the temperature inside our lab cabinet).

### *3.7. Complementary Tests*

In the complementary tests, the effect of different constituents of the "best performer" solution was studied by measuring the following properties for BP-1, BP-2, BP-3, BP-4, and BP-4 aged anti-icers.

- Ice melting capacity at -3.9°C after 20 and 60 min
- Splitting strength of PCM after a 10-cycle freeze-thaw test
- Low temperature behavior of asphalt binder
- Corrosion rate of mild steel

The results of ice melting test at 20 min and 60 min, presented in Figure 8, show that there is an increasing trend on ice melting capacity by adding new additives and as a result, mixture BP-4, which contains all of four additives (sodium metasilicate, sodium formate, glycerin, and Concord grape extract), has the highest ice melting capacity. In addition, it can be seen that the aging process decreased the ice melting capacity of BP-4. However, the aged solution still has higher ice melting capacity than the beet juice/salt brine blend.

Figure 9 presents the splitting strength of mortar samples after ten rapid freeze-thaw (and wet-dry) cycles along with exposure to different anti-icers. In contradiction with the trend seen in ice melting capacity, adding the additives to anti-icer formulation decreased the splitting strength of mortar samples. However, all samples still had more splitting strength than the samples exposed to 23% NaCl (with the mean splitting strength of 2.27 MPa). In addition, aging process did not have any considerable impact on the splitting strength. It is also noteworthy that the splitting strength of the sample exposed to beet juice/salt brine blend was more than BP-4.

The low temperature BBR test results for different anti-icers are presented in Figure 10. It is seen by adding sodium metasilicate, sodium formate, and glycerin (BP-1 to BP-3), the *m*-value increased which is good since higher *m*-value indicates higher ability to relax and thus lower risk of thermal cracking. On the other hand, by adding the grape extract *m*-value decreased and the aged sample showed even lower *m*-value. It is also seen that all of the samples have lower *m*-value compared to the samples exposed to beet juice/salt brine blend.

As mentioned earlier, higher stiffness values correspond to higher thermal stresses and higher risk of thermal cracking. BP-4 showed the highest stiffness that indicates it has the most impact on asphalt binder in terms of increasing the thermal stresses. The aging process on this sample had a positive effect on stiffness of sample. However, the least stiffness belonged to the sample exposed to beet juice/salt brine blend.

Figure 11 shows that by adding different additives, the corrosion rate has decreased and BP-4 has the best anti-corrosion performance. However, the aging process had a negative effect on its performance, and as a result, the aged BP-4 caused a higher corrosion rate compared to BP-4. It is noteworthy that even the aged BP-4 caused a lower corrosion rate than the beet juice/salt brine blend.

### *3.8. Friction performance of anti-icers under the simulated "black ice" scenario*

Figure 12 shows the friction coefficient of the asphalt concrete pavement after different anti-icing treatment under the simulated "black ice" scenario. It is worth mentioning that anti-icing using 23% NaCl solution increased the friction coefficient of the icy asphalt pavement by 67.3%. After adding sodium metasilicate (BP-1), sodium formate (BP-2), and glycerin (BP-3) to the salt brine, the friction coefficient of anti-iced asphalt pavement decreased. However, by adding the Concord grape extract, the friction coefficient increased and became slightly better than the case anti-iced by the beet juice/salt brine blend. The increase of friction coefficient after adding the grape extract may be due to more contact area induced by the agro-based materials (Waluś and Olszewski 2011), or the weaker microstructure of the ice remaining on the pavement. Similar observations on the benefit of bio-based deicers to the friction of asphalt pavement has been described by Hosseini et al. (2016).

In the next step, the same process shown in Table 4 for prioritizing the solutions was used again for the samples of BP-4, 23% NaCl, and beet juice/salt brine blend, by considering the friction coefficient as a new parameter which is as important as ice melting capacity (Tables 8 and 9 in Appendix). As a result, the following scores were obtained for the mentioned solutions respectively: 59, 31, and 34 (Table 10 in Appendix). This shows that BP-4 with score of 59 performs better than 23% NaCl with score of 31 and beet juice/salt brine blend with score of 34.

### *3.9. Chemical Oxygen Demand*

The mg/L COD (chemical oxygen demand) data reflect measures of milligrams of oxygen consumed per liter of sample via the standard procedure mentioned earlier. In measuring the mg/L COD, both solutions were diluted to a ratio of 1000:1 by adding DI (deionized) water. For measuring the pH, original solutions were used. The associated data are presented in Table 6, which shows that the best-performer sample has almost half the COD of the beet juice/salt brine blend. However, the pH of the best-performer sample is twice that of the beet juice/salt brine blend. By increasing the pH value, the COD removal efficiency increases in wastewater systems (Sivrioğlu and Yonar 2015). In fact, in the alkaline condition, a high concentration of $OH^-$ ions can provide oxygen necessary for oxidation of chemicals and can decrease the need for external oxygen.

### *3.10. Biological Oxygen Demand*

Biochemical oxygen demand (BOD), which is also known as biological oxygen demand, refers to the amount of DO used by aerobic microorganisms to decompose the biodegradable organic matter in a water sample over a specific time (Real Tech Inc. 2017). BOD is a measure of the degree of water pollution in receiving water bodies such as streams and lakes. It takes a long time for microorganisms to degrade the organic matter. Therefore, the most common time periods for BOD are the 5-day oxygen demand ($BOD_5$) and the 20-day oxygen demand ($BOD_{20}$).

The $BOD_5$ data for the “best performer” sample, beet juice/salt brine blend, and the control are presented in Table 7, which shows that the best-performer sample has much less $BOD_5$ (0.77 mg/L), substantially lower than the beet juice/salt brine blend ($BOD_5$ of 25.82 mg/L). This shows the significant advantage of the produced anti-icer over the traditional beet juice/salt brine blend in terms of lower risk to water bodies receiving the deicer-laden runoff.

## 4. CONCLUSIONS

This work describes the performance and impacts of 21 anti-icer mixtures that were designed using the central composite design method based on the preliminary experiments of the authors. Selected constituent materials pose minimal toxicity to the environment (e.g., no heavy metal content) and were derived from eco-friendly, cost-effective processes. Agro-based solutions derived from locally sourced agro-based materials mixed with salt brine, and commercial additives (with little toxicity) were tested for their ice-melting capacity, ability to protect asphalt binder and mortar, effect on the friction coefficient of anti-iced asphalt pavement, and anti-corrosion performance. The main criteria for choosing the best-performing anti-icer was ice-melting capacity and friction coefficient of anti-iced asphalt pavement in a simulated "black ice" scenario. A decision-making process based on an analytical hierarchy process (AHP) was used to determine the best-performing anti-icer, which is the mixture containing 0.89% Concord grape extract, 4.57% glycerin, 4.54% sodium formate, 0.19% sodium metasilicate, 18.4% NaCl, and water. Based on the overall evaluation of the laboratory testing results, this mixture outperforms 23% NaCl brine and the beet juice/salt brine blend (the two controls). It also exhibited lower COD and $BOD_5$ values than the traditional beet juice/salt brine blend, thus posing less risk of oxygen depletion in the receiving water bodies. Differential scanning calorimetry thermograms revealed the critical role of glycerin and sodium formate in the relatively low critical temperature of this mixture (-23.9°C). The importance of this role remained the same even after aging of the anti-icer.

## APPENDIX: Complementary Tables

Tables 8-10 show the AHP process used for scoring BP-4 mixture, 23% NaCl solution, and a beet juice/salt brine blend. The process used for prioritization of these solutions is very similar to the process used earlier in Tables 2–4. The only difference is that in the current process, friction coefficient is added as a new parameter with an importance equal to the ice melting capacity.

## ACKNOWLEDGMENTS

The authors acknowledge the financial support provided by the Center for Environmentally Sustainable Transportation in Cold Climates (CESTiCC) and the National Science Foundation (Award No. 1638384). The authors would also like to thank Sen Du, Taekil Oh and Deborah Ave Okon for their assistance in running some of the laboratory experiments.

## References

Bahia, H. U., and Anderson, D. A. (1993). "The Pressure Aging Vessel (PAV): A Test to Simulate Rheological Changes Due To Field Aging." *Physical Properties of Asphalt Cement Binders*, Dallas/Fort Worth Airport, TX.

Chappelow, C. C., McElroy, A. D., Blackburn, R. R., Darwin, D., de Noyelles, F. G., and Locke, C. E. (1992). *Handbook of test methods for evaluating chemical deicers*. Strategic Highway Research Program, Washington, DC.

Chen, J., Bharata, R., Yin, T., Wang, Q., Wang, H., and Zhang, T. (2016). "Assessment of sulfate attack and freeze–thaw cycle damage of cement-based materials by a nonlinear acoustic technique." *Materials and Structures*, 50(2), 105.

Corsi, S. R., De Cicco, L. A., Lutz, M. A., and Hirsch, R. M. (2015). "River chloride trends in snow-affected urban watersheds: increasing concentrations outpace urban growth rate and are common among all seasons." *Science of The Total Environment*, 508, 488–497.

Corsi, S. R., Mericas, D., and Bowman, G. T. (2012). "Oxygen Demand of Aircraft and Airfield Pavement Deicers and Alternative Freezing Point Depressants." *Water, Air, & Soil Pollution*, 223(5), 2447–2461.

Dang, Y., Shi, X., Xie, N., McVey, E., and Kessel, A. (2016). "Accelerated Laboratory Test Suggests the Importance of Film Integrity of Sealers on the Protection of Concrete from Deicer Scaling." *Journal of Materials in Civil Engineering*, 28(9), 04016065.

Farnam, Y., Dick, S., Wiese, A., Davis, J., Bentz, D., and Weiss, J. (2015). "The Influence of Calcium Chloride Deicing Salt on Phase Changes and Damage Development in Cementitious Materials." *Cement & concrete composites*, 64, 1–15.

Fay, L., and Shi, X. (2012). “Environmental Impacts of Chemicals for Snow and Ice Control: State of the Knowledge.” *Water, Air, & Soil Pollution*, 223(5), 2751–2770.

Fay, L., Shi, X., and Huang, J. (2013). *Strategies to Mitigate the Impacts of Chloride Roadway Deicers on the Natural Environment*. NCHRP Synthesis 449, Transportation Research Board, Washington, DC.

Heikal, M. (2004). “Effect of calcium formate as an accelerator on the physicochemical and mechanical properties of pozzolanic cement pastes.” *Cement and Concrete Research*, 34(6), 1051–1056.

Honarvar Nazari, M., Laura, F., Jungwirth, S., and Shi, X. (2015). “Water Quality Implications and the Toxicological Effects of Chloride-Based Deicers.” *Environmental Sustainability in Transportation Infrastructure*, 272-292.

Honarvar Nazari, M., Shi, X., Jackson, E., Yan, Z., and Li, Y. (2017). “Laboratory Investigation of Washing Practices and Bio-Based Additive for Mitigating Metallic Corrosion by Magnesium Chloride Deicer.” *Journal of Materials in Civil Engineering*, 29(1), 04016187.

Hossain, S. M. K., Fu, L., and Lake, R. (2015). “Field evaluation of the performance of alternative deicers for winter maintenance of transportation facilities.” *Canadian Journal of Civil Engineering*, 42(7), 437–448.

Hosseini, F., Hossain, S. M. K., and Fu, L. (2016). “Bio-based materials for improving winter pavement friction.” *Canadian Journal of Civil Engineering*, 44(2), 99–105.

Li, Y., Fang, Y., Seeley, N., Jungwirth, S., Jackson, E., and Shi, X. (2013). “Corrosion by Chloride Deicers on Highway Maintenance Equipment.” *Transportation Research Record: Journal of the Transportation Research Board*, 2361, 106–113.

Metal Samples. (2018). “Introduction to Linear Polarization Resistance (LPR) Monitoring.” <http://www.alspi.com/lprintro.htm> (May 10, 2018).

Nazari, M. H., and Shi, X. (2018). “Vehicle Risks of Winter Road Operations and Best Management Practices.” *Sustainable Winter Road Operations*, Wiley-Blackwell, 241–272.

Pan, T., He, X., and Shi, X. (2008). “Laboratory Investigation of Acetate-Based Deicing/Anti-Icing Agents Deteriorating Airfield Asphalt (With Discussion).” *Journal of the Association of Asphalt Paving Technologists*, 77, 773–794.

Pieper, K. J., Tang, M., Jones, C. N., Weiss, S., Greene, A., Mohsin, H., Parks, J., and Edwards, M. A. (2018). “Impact of Road Salt on Drinking Water Quality and Infrastructure Corrosion in Private Wells.” *Environmental Science & Technology*, 52(24), 14078–14087.

Pigeon, M., and Pleau, R. (2010). *Durability of Concrete in Cold Climates*. CRC Press.

Qiao, C., Suraneni, P., and Weiss, J. (2018). “Damage in cement pastes exposed to NaCl solutions.” *Construction and Building Materials*, 171, 120–127.

Real Tech Inc. (2017). “Biochemical Oxygen Demand (BOD).” <https://realtechwater.com/parameters/biochemical-oxygen-demand/> (Feb. 2, 2019).

Refait, P., Abdelmoula, M., Génin, J.-M., and Jeannin, M. (2006). “Synthesis and characterisation of the Fe(II-III) hydroxy-formate green rust.” *Hyperfine Interactions*, 167, 717–722.

Shi, X., Fay, L., Peterson, M. M., and Yang, Z. (2010). “Freeze–thaw damage and chemical change of a portland cement concrete in the presence of diluted deicers.” *Materials and Structures*, 43(7), 933–946.

Shi, X., Fortune, K., Smithlin, R., Akin, M., and Fay, L. (2013). “Exploring the performance and corrosivity of chloride deicer solutions: Laboratory investigation and quantitative modeling.” *Cold Regions Science and Technology*, 86, 36–44.

Shi, X., Quilty, S. M., Long, T., Jayakaran, A., Fay, L., and Xu, G. (2017). “Managing airport stormwater containing deicers: challenges and opportunities.” *Frontiers of Structural and Civil Engineering*, 11(1), 35–46.

Sivrioğlu, Ö., and Yonar, T. (2015). “Determination of the acute toxicities of physicochemical pretreatment and advanced oxidation processes applied to dairy effluents on activated sludge.” *Journal of Dairy Science*, 98(4), 2337–2344.

Triantaphyllou, E., and Mann, S. H. (1995). “Using the analytic hierarchy process for decision making in engineering applications: Some challenges.” *International Journal of Industrial Engineering*, 2(1), 35–44.

Waluś, K. J., and Olszewski, Z. (2011). “Analysis of Tire-road Contact under Winter Conditions.” *WCE (World Congress on Engineering) 2011*, London, U.K.

Wang, L., Dai, L., Bian, H., Ma, Y., and Zhang, J. (2019). “Concrete cracking prediction under combined prestress and strand corrosion.” *Structure and Infrastructure Engineering*, 15(3), 1–11.

Xie, N., Shi, X., and Zhang, Z. (2017). “Impacts of Potassium Acetate and Sodium-Chloride Deicers on Concrete.” *Journal of Materials in Civil Engineering*, 29(3), 04016229.

Xu, G., and Shi, X. (2018). “Impact of Chemical Deicers on Roadway Infrastructure.” *Sustainable Winter Road Operations*, Wiley-Blackwell, 211–240.

Yang, Z., Zhang, Y., and Shi, X. (2018). “Impact of nanoclay and carbon microfiber in combating the deterioration of asphalt concrete by non-chloride deicers.” *Construction and Building Materials*, 160, 514–525.

Zandi Hanjari, K., Utgenannt, P., and Lundgren, K. (2011). “Experimental study of the material and bond properties of frost-damaged concrete.” *Cement and Concrete Research*, 41(3), 244–254.

Zhang, X., Wang, L., and Zhang, J. (2017). “Mechanical behavior and chloride penetration of high strength concrete under freeze-thaw attack.” *Cold Regions Science and Technology*, 142, 17–24.

**Tables**

**Table 1.** Anti-icer mixtures designed based on central composite design method using Design-Expert® software

| Mix # | Weight percent of additives (%) | | | |
|---|---|---|---|---|
| | **Concord grape extract** | **Glycerol** | **Sodium formate** | **Sodium metasilicate** |
| Mix 1 | 2.40 | 2.40 | 2.40 | 1.80 |
| Mix 2 | 4.80 | 2.40 | 2.40 | 1.80 |
| Mix 3 | 2.40 | 2.40 | 2.40 | 1.80 |
| Mix 4 | 1.94 | 2.86 | 1.94 | 2.14 |
| Mix 5 | 1.94 | 2.86 | 2.86 | 2.14 |
| Mix 6 | 2.40 | 2.40 | 2.40 | 1.80 |
| Mix 7 | 2.40 | 2.40 | 2.40 | 1.80 |
| Mix 8 | 2.40 | 2.40 | 4.80 | 1.80 |
| Mix 9 | 1.94 | 1.94 | 1.94 | 1.46 |
| Mix 10 | 1.94 | 1.94 | 2.86 | 1.46 |
| Mix 11 | 2.86 | 1.94 | 1.94 | 2.14 |
| Mix 12 | 2.86 | 2.86 | 2.86 | 1.46 |
| Mix 13 | 2.40 | 2.40 | 2.40 | 3.60 |
| Mix 14 | 2.86 | 2.86 | 1.94 | 1.46 |
| Mix 15 | 2.40 | 4.80 | 2.40 | 1.80 |
| Mix 16 | 2.40 | 2.40 | 2.40 | 0.00 |
| Mix 17 | 2.40 | 0.00 | 2.40 | 1.80 |
| Mix 18 | 2.40 | 2.40 | 0.00 | 1.80 |
| Mix 19 | 2.86 | 1.94 | 2.86 | 2.14 |
| Mix 20 | 0.00 | 2.40 | 2.40 | 1.80 |
| Mix 21 | 2.40 | 2.40 | 2.40 | 1.80 |

**Table 2.** Pairwise comparisons based on multiple criteria

| **Comparison** | **Ice-melting capacity at 20 min, -3.9°C** | **Ice-melting capacity at 60 min, -3.9°C** | **Corrosion rate** | **PCM splitting strength** | **Asphalt binder stiffness** | **Asphalt binder *m*-value** |
|---|---|---|---|---|---|---|
| **Ice-melting capacity at 20 min, -3.9°C** | 1.00 | 1.00 | 5.00 | 1.00 | 9.00 | 9.00 |
| **Ice-melting capacity at 60 min, -3.9°C** | 1.00 | 1.00 | 5.00 | 1.00 | 9.00 | 9.00 |
| **Corrosion rate** | 0.20 | 0.20 | 1.00 | 1.00 | 2.00 | 2.00 |
| **PCM splitting strength** | 1.00 | 1.00 | 1.00 | 1.00 | 2.00 | 2.00 |
| **Asphalt binder stiffness** | 0.11 | 0.11 | 0.50 | 0.50 | 1.00 | 1.00 |
| **Asphalt binder *m*-value** | 0.11 | 0.11 | 0.50 | 0.50 | 1.00 | 1.00 |
| **Sum** | 3.42 | 3.42 | 13.00 | 5.00 | 24.00 | 24.00 |

**Table 3.** A standard matrix based on comparisons

| Comparison | Ice-melting capacity at 20 min, -3.9°C | Ice-melting capacity at 60 min, -3.9°C | Corrosion rate | PCM splitting strength | Asphalt binder stiffness | Asphalt binder m-value | Weight |
|---|---|---|---|---|---|---|---|
| **Ice-melting capacity at 20 min, -3.9°C** | 0.29 | 0.29 | 0.38 | 0.20 | 0.38 | 0.38 | 0.32 |
| **Ice-melting capacity at 60 min, -3.9°C** | 0.29 | 0.29 | 0.38 | 0.20 | 0.38 | 0.38 | 0.32 |
| **Corrosion rate** | 0.06 | 0.06 | 0.08 | 0.20 | 0.08 | 0.08 | 0.09 |
| **PCM splitting strength** | 0.29 | 0.29 | 0.08 | 0.20 | 0.08 | 0.08 | 0.17 |
| **Asphalt binder stiffness** | 0.03 | 0.03 | 0.04 | 0.10 | 0.04 | 0.04 | 0.05 |
| **Asphalt binder m-value** | 0.03 | 0.03 | 0.04 | 0.10 | 0.04 | 0.04 | 0.05 |
| **Sum** | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |

**Table 4.** Summary of the prioritization (all values associated with different properties are normalized and dimensionless)

| Sample | Weight | | | | | | Score |
|---|---|---|---|---|---|---|---|
| | 0.32 | 0.32 | 0.09 | 0.17 | 0.05 | 0.05 | |
| | **Ice-melting capacity at 20 min, -3.9°C** | **Ice-melting capacity at 60 min, -3.9°C** | **Corrosion rate** | **PCM splitting strength** | **Asphalt binder stiffness** | **Asphalt binder *m*-value** | |
| Mix 1 | 64.97 | 78.64 | 26.13 | 57.61 | 34.13 | 26.63 | 61 |
| Mix 2 | 70.06 | 46.12 | 94.23 | 25.52 | 0.00 | 18.69 | 51 |
| Mix 3 | 76.84 | 64.56 | 95.95 | 45.23 | 29.41 | 22.33 | 64 |
| Mix 4 | 51.41 | 45.63 | 13.32 | 36.89 | 69.67 | 29.25 | 43 |
| Mix 5 | 70.62 | 64.56 | 89.02 | 43.89 | 62.80 | 33.78 | 64 |
| Mix 6 | 53.11 | 49.03 | 89.10 | 45.06 | 57.71 | 36.90 | 53 |
| Mix 7 | 41.81 | 69.42 | 23.66 | 37.15 | 76.53 | 31.98 | 49 |
| Mix 8 | 25.42 | 18.93 | 96.89 | 34.34 | 56.62 | 25.62 | 33 |
| Mix 9 | 20.34 | 39.81 | 87.03 | 71.31 | 39.43 | 26.99 | 43 |
| Mix 10 | 92.66 | 100.00 | 86.14 | 48.04 | 33.38 | 21.48 | 81 |
| Mix 11 | 45.76 | 44.17 | 28.47 | 56.31 | 31.56 | 32.93 | 44 |
| Mix 12 | 27.12 | 46.12 | 88.59 | 64.00 | 33.16 | 27.74 | 46 |
| Mix 13 | 22.03 | 32.52 | 96.24 | 55.33 | 30.91 | 24.96 | 39 |
| Mix 14 | 58.76 | 36.41 | 90.88 | 36.81 | 65.74 | 30.29 | 50 |
| Mix 15 | 66.10 | 41.75 | 100.00 | 73.63 | 7.98 | 28.24 | 58 |
| Mix 16 | 67.23 | 74.27 | 61.97 | 54.41 | 25.83 | 32.64 | 63 |
| Mix 17 | 16.95 | 0.00 | 79.41 | 60.99 | 15.77 | 0.00 | 24 |
| Mix 18 | 19.21 | 22.82 | 0.00 | 30.20 | 17.67 | 34.07 | 21 |
| Mix 19 | 50.85 | 76.21 | 93.09 | 37.42 | 2.13 | 33.33 | 57 |
| Mix 20 | 100.00 | 65.53 | 82.63 | 50.31 | 100.00 | 94.44 | 79 |
| Mix 21 | 0.00 | 41.26 | 25.49 | 0.00 | 40.23 | 48.89 | 20 |
| 23% NaCl | 73.45 | 69.42 | 16.38 | 29.29 | 94.42 | 98.15 | 61 |
| Beet juice/salt brine blend | 78.53 | 87.86 | 19.72 | 100.00 | 96.95 | 100.00 | 82 |

**Table 5.** Composition of different deicers used to obtain DSC thermograms

| Sample | Weight% of additive in DI water-based solution | | | | |
|---|---|---|---|---|---|
| | **Concord grape extract** | **Glycerin** | **HCOONa** | **$Na_2SiO_3$** | **NaCl** |
| Salt brine | | | | | 23 |
| BP-1 | | | | 0.19 | 18.4 |
| BP-2 | | | 4.54 | 0.19 | 18.4 |
| BP-3 | | 4.57 | 4.54 | 0.19 | 18.4 |
| BP-4 | 0.89 | 4.57 | 4.54 | 0.19 | 18.4 |

Note: Beet juice/salt brine blend used as control with the composition of 80% (v/v) 23% NaCl solution and 20% (v/v) beet juice.

**Table 6.** Chemical oxygen demand and pH of best-performer sample and beet juice/salt brine blend

| Sample | mg/L COD | pH |
|---|---|---|
| Beet juice/salt brine blend | 277.94 | 5.3 |
| Best performer (BP-4) | 135.17 | 11.7 |

**Table 7.** Biochemical oxygen demand of "best performer" sample, beet juice/salt brine blend, and control

| Sample | mg/L $BOD_5$ |
|---|---|
| Beet juice/salt brine blend | 25.82 |
| Best performer (BP-4) | 0.77 |
| Control | 0.15 |

**Table 8.** Pairwise comparisons based on multiple criteria by considering friction coefficient as a parameter

| Comparison | Ice-melting capacity at 20 min, -3.9°C | Ice-melting capacity at 60 min, -3.9°C | Corrosion rate | PCM splitting strength | Asphalt binder stiffness | Asphalt binder *m*-value | Friction coefficient |
|---|---|---|---|---|---|---|---|
| **Ice-melting capacity at 20 min, -3.9°C** | 1.00 | 1.00 | 5.00 | 1.00 | 9.00 | 9.00 | 1.00 |
| **Ice-melting capacity at 60 min, -3.9°C** | 1.00 | 1.00 | 5.00 | 1.00 | 9.00 | 9.00 | 1.00 |
| **Corrosion rate** | 0.20 | 0.20 | 1.00 | 1.00 | 2.00 | 2.00 | 0.20 |
| **PCM splitting strength** | 1.00 | 1.00 | 1.00 | 1.00 | 2.00 | 2.00 | 1.00 |
| **Asphalt binder stiffness** | 0.11 | 0.11 | 0.50 | 0.50 | 1.00 | 1.00 | 0.11 |
| **Asphalt binder *m*-value** | 0.11 | 0.11 | 0.50 | 0.50 | 1.00 | 1.00 | 0.11 |
| **Friction coefficient** | 1.00 | 1.00 | 5.00 | 1.00 | 9.00 | 9.00 | 1.00 |
| **Sum** | 4.42 | 4.42 | 18.00 | 6.00 | 33.00 | 33.00 | 4.42 |

**Table 9.** A standard matrix based on comparisons by considering friction coefficient as a parameter

| Comparison | Ice-melting capacity at 20 min, -3.9°C | Ice-melting capacity at 60 min, -3.9°C | Corrosion rate | PCM splitting strength | Asphalt binder stiffness | Asphalt binder m-value | Friction coefficient | Weight |
|---|---|---|---|---|---|---|---|---|
| **Ice-melting capacity at 20 min, -3.9°C** | 0.23 | 0.23 | 0.28 | 0.17 | 0.27 | 0.27 | 0.23 | 0.24 |
| **Ice-melting capacity at 60 min, -3.9°C** | 0.23 | 0.23 | 0.28 | 0.17 | 0.27 | 0.27 | 0.23 | 0.24 |
| **Corrosion rate** | 0.05 | 0.05 | 0.06 | 0.17 | 0.06 | 0.06 | 0.05 | 0.07 |
| **PCM splitting strength** | 0.23 | 0.23 | 0.06 | 0.17 | 0.06 | 0.06 | 0.23 | 0.15 |
| **Asphalt binder stiffness** | 0.03 | 0.03 | 0.03 | 0.08 | 0.03 | 0.03 | 0.03 | 0.04 |
| **Asphalt binder m-value** | 0.03 | 0.03 | 0.03 | 0.08 | 0.03 | 0.03 | 0.03 | 0.04 |
| **Friction coefficient** | 0.23 | 0.23 | 0.28 | 0.17 | 0.27 | 0.27 | 0.23 | 0.24 |
| **Sum** | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |

**Table 10.** Summary of the prioritization by considering friction coefficient as a parameter (all values associated with different properties are normalized and dimensionless)

| **Sample** | **Weight** | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 0.24 | 0.24 | 0.07 | 0.15 | 0.04 | 0.04 | 0.24 | **Score** |
| | **Ice-melting capacity at 20 min, -3.9°C** | **Ice-melting capacity at 60 min, -3.9°C** | **Corrosion rate** | **PCM splitting strength** | **Asphalt binder stiffness** | **Asphalt binder *m*-value** | **Friction coefficient** | |
| BP-4 | 100.00 | 100.00 | 100.00 | 27.64 | 0.00 | 0.00 | 2.27 | 59 |
| 23% NaCl | 0.00 | 0.00 | 0.00 | 0.00 | 97.86 | 97.41 | 100.00 | 31 |
| Beet juice/salt brine blend | 11.62 | 39.53 | 4.82 | 100.00 | 100.00 | 100.00 | 0.00 | 34 |

**Figure captions**

Figure 1. Ranking of mixtures based on ice-melting capacity after application of anti-icers at 20 min, -3.9°C obtained using a SHRP test method (error bars represent standard error)

Figure 2. Ranking of mixtures based on ice-melting capacity after application of anti-icers at 60 min, -3.9°C obtained using a SHRP test method (error bars represent standard error)

Figure 3. Splitting strength of mortar as a function of anti-icer type after 10-cycle freeze-thaw test (error bars represent standard error)

Figure 4. The stiffness of asphalt binder exposed to various anti-icer mixtures obtained by a BBR (error bars represent standard error)

Figure 5. The m-value of asphalt binder exposed to various anti-icer mixtures obtained by a BBR (error bars represent standard error)

Figure 6. Corrosion rates of C1010 carbon steel coupons measured by LPR technique after 24 h immersion in different anti-icer mixtures (error bars represent standard error)

Figure 7. DSC thermogram of different deicers; warming cycle

Figure 8. Ice-melting capacity of different anti-icers at -3.9°C after (a) 20 min and (b) 60 min, obtained using a SHRP test method (error bars represent standard error)

Figure 9. Splitting strength of mortar as a function of anti-icer type after 10-cycle freeze-thaw test (error bars represent standard error)

Figure 10. The (a) m-value and (b) stiffness of asphalt binder exposed to various anti-icer mixtures obtained by a BBR (error bars represent standard error)

Figure 11. Corrosion rates of C1010 carbon steel coupons measured by LPR technique after 24 h immersion in different anti-icer mixtures (error bars represent standard error)

Figure 12. Friction coefficient of the iced asphalt pavement, measured at -9.4°C after different anti-icing scenarios (error bars represent standard errors)