

Effects of processed agro-residues on the performance of sodium chloride brine anti-icer

Mehdi Honarvar Nazari,[§] Eden Adele Havens,[§] Anburaj Muthumani,[‡] and Xianming Shi^{§,*}

[§]Laboratory of Corrosion Science & Electrochemical Engineering (CSEE), Department of Civil & Environmental Engineering, P.O. Box 642910, Washington State University, Pullman, WA 99164-2910

[‡]Winter Maintenance & Effects Program, Western Transportation Institute, Montana State University, P.O. Box 174250, Bozeman, MT 59717

*E-mail: xianming.shi@wsu.edu

Abstract

In this laboratory study, the performance and impacts of several new types of anti-icer were examined. A chemico-biological process was employed to prepare liquid extracts from two agro-based feedstocks, specifically, dandelion leaf and sugar beet leaf. The following parameters were examined as a function of the formulation design: ice-melting capacity at -3.9°C (25°F), mass loss and compressive strength of Portland cement mortar (PCM) samples after 10 rapid freeze-thaw cycles with anti-icer exposure, the corrosivity of C1010 carbon steel after 24-hour immersion in anti-icer solutions, and anti-icers impact on asphalt binder. One viable formula (“the best performer”) was tested for freezing point depression phase diagram and friction coefficient of asphalt pavement treated by anti-icing formulation. The agro-based extracts improved the properties of the “green” anti-icer mixtures and the friction coefficient of anti-iced pavement. In addition, they were environmentally friendly in terms of COD and BOD values. The developed anti-icers contain less additive chemicals than traditional agro-based anti-icers, which likely helps to reduce their impacts on the environment.

Keywords: Agro-based anti-icer; sodium chloride brine; ice-melting performance; corrosivity; friction coefficient

INTRODUCTION

Winter maintenance agencies are looking for better ways to ensure safe and reliable roads during wintery weather in terms of cost-effectiveness and environmental stewardship.¹⁻³ The annual cost of corrosion and environmental impacts due to the use of highway deicers in the U.S. is about \$5 billion.¹ Presently, about 27 million tons of NaCl salt is used for winter maintenance of roadways in the U.S. annually.⁴ One of the concerns with chloride-based deicers is their environmental impacts, which can be reduced using best practices. Chloride-based salts are persistent and do not degrade in the environment, therefore, they can accumulate over time and cause a long-term environmental risk.⁵

In order to balance the environmental risks associated with using snow and ice control products with the values they provide, sustainability principles need to be better incorporated into the winter maintenance operations of highways. Relative to sanding and deicing, anti-icing is a more proactive practice that can improve the level of service on pavement and reduce the amount of applied chemicals needed. This can lead to cost savings and benefits in safety and mobility.^{6,7} Similar to deicers, there are some concerns over commercial anti-icers, including their corrosivity toward metals, impacts on asphalt and concrete, and toxicity to aquatic species, etc.

Cumulative research efforts have been devoted to developing alternatives that maximize the benefits of anti-icers while minimizing their impacts. Glycerol, which is a byproduct of biodiesel production, has been widely used in deicing and anti-icing formulations.^{8,9} Talor et al. tested in the laboratory the brines composed of glycerol, MgCl₂, NaCl, and commercial additives and concluded that the mixture of 20% NaCl and 80% glycerol has the best performance and low impacts.¹⁰ This mixture is very viscous, and if diluted can be used for anti-icing; but the dilution will compromise its effectiveness for snow/ice control. In addition, glycerol can negatively affect

water quality, which limits its allowable concentration in the anti-icer. Desugared molasses, an inexpensive byproduct of sugar beet root, has been used as an effective and renewable additive for deicing and anti-icing applications.^{11,12} Yet, at high additive rates, it can reduce the ice melting capacity and pose a significant risk to receiving water with increased oxygen demand.¹³ Koefod proposed the approach of oxidizing the agro-based byproducts to address these issues,¹⁴ but the oxidation could be a costly process.

Up to now, there has been no research on the byproducts of sugar beet leaf and dandelion leaf for potential use in anti-icing or deicing applications. This is because these agro-residues cannot be directly used in the anti-icer or deicer formulation; they must be further processed first. In addition, few studies have comprehensively studied the effect of bio-based materials on the performance and impacts of anti-icers or deicers.

In this work, innovative anti-icing formulations were developed by using renewable bioresources, i.e., sugar beet leaf and dandelion leaf, as agricultural feedstock. A new chemico-biological process was employed for processing these agro-residues. A statistical design of experiments was employed to optimize the formulations while minimizing the number of experiments. The formulations were tested in the laboratory for their ice-melting and corrosion-inhibiting capacities, and their impact on the durability of concrete and asphalt binder. In addition, this study evaluated the effects of these green chemicals on the freezing point of salt brine anti-icer and the friction coefficient of asphalt pavement treated by the anti-icer.

METHODOLOGY

Statistical design of experiments

To minimize the number of required tests for studying a large variety of parameters, a statistical Uniform Design (UD) of experiments was used.¹⁵ The UD scheme used the parameters of X₁, X₂, X₃, and X₄ as the weight percent (wt.%) of dandelion extract, sugar beet leaf extract, sodium metasilicate, and sodium formate, respectively. The wt.% range of 0–3 was chosen for X₁ and X₂, and 0–2 for X₃ and X₄. Sixteen anti-icer mixtures were examined, as shown in Table 1.

Table 1. Experimental design for anti-icer solutions based on uniform design method. Each mixture had 23 wt.% NaCl, the components mentioned in this table, and the rest is deionized (DI) water.

| Sample | Weight percent of each compound (wt.%) | | | | | |
|----------------------|--|-------------------------|---------------------|----------------|-----------------|-------|
| | Dandelion leaf extract | Sugar beet leaf extract | Sodium metasilicate | Sodium formate | Sodium chloride | Water |
| Mix 1 | 0 | 3 | 0 | 0.67 | 23 | 73.33 |
| Mix 2 | 1 | 3 | 2 | 1.34 | 23 | 69.66 |
| Mix 3 | 2 | 1 | 0 | 0 | 23 | 74 |
| Mix 4 | 3 | 3 | 1.34 | 0 | 23 | 69.66 |
| Mix 5 | 0 | 0 | 2 | 0 | 23 | 75 |
| Mix 6 | 1 | 0 | 0 | 2 | 23 | 74 |
| Mix 7 | 3 | 1 | 2 | 2 | 23 | 69 |
| Mix 8 | 3 | 2 | 0 | 2 | 23 | 70 |
| Mix 9 | 2 | 2 | 2 | 0.67 | 23 | 70.33 |
| Mix 10 | 0 | 1 | 0.67 | 1.34 | 23 | 73.99 |
| Mix 11 | 2 | 3 | 0.67 | 2 | 23 | 69.33 |
| Mix 12 | 1 | 2 | 0.67 | 0 | 23 | 73.33 |
| Mix 13 | 3 | 0 | 0.67 | 0.67 | 23 | 72.66 |
| Mix 14 | 0 | 2 | 1.34 | 2 | 23 | 71.66 |
| Mix 15 | 2 | 0 | 1.34 | 1.34 | 23 | 72.32 |
| Mix 16 | 1 | 1 | 1.34 | 0.67 | 23 | 72.99 |
| Control (salt brine) | 0 | 0 | 0 | 0 | 23 | 77 |

Systematic laboratory investigation and formulation optimization

Following the mentioned experimental design, several methods were used for assessing the anti-icer solutions. To make the anti-icer mixtures mentioned in Table 1, rock salt, dandelion leaf

extract, sugar beet leaf extract, reagent-grades sodium formate and metasilicate, and deionized water were used. Each mixture had 23 wt.% rock salt, different amounts of the extracts, and sodium metasilicate and formate determined by using the UD table.

Preparation of the plant extracts

Dried dandelion leaf and sugar beet leaf (dryness ~91%) were obtained from the Western Agricultural Research Center in Montana, USA with the characteristics mentioned in Table 2. The leaf was ground into fine powders with the size $\leq 37 \mu\text{m}$ (Mesh 400) and further processed in two steps: first chemical degradation and then biological degradation. The chemical degradation was designed based on the knowledge that cold NaOH/urea aqueous solutions are capable of dissolving cellulose relatively rapidly.¹⁶ The process began by mixing 120 g urea, 0.5 g Ca(OH)₂ and 200 mL deionized water (DI water). Then 30 g of leaf powder were added to the mixture. The pH was adjusted above 10.5 by adding the appropriate amount of NaOH. This mixture was stirred vigorously for 30 min, and then it was placed in the freezer until a slurry of ice and liquid formed (about -13 °C). Subsequent to the chemical degradation, the biological degradation was designed to further break down the dissolved cellulose, semi-cellulose, lignin, etc. in the solution. The process began by stirring the mixture vigorously while adding 0.5 L DI water to it simultaneously. Then, the pH of the solution was adjusted at about 8.5 by adding HNO₃ and NaOH. In the next step, a mixture of 1.12 g KH₂PO₄, 1.932 g NaH₂PO₄·H₂O, and 0.16 g MgSO₄·7H₂O was added to the solution. Finally, 100 mL of *Bacillus Megaterium* bacteria (NRRL B-14308) was added to the solution, which was subsequently placed in a shaker for 14 days for aerobic biodegradation of the mixture.

The final product was a liquid extract. The concentration of the final product was 224.5 g solid material/1 L liquid extract. This concentration calculated by drying of the extract at room

temperature. In the case of oven drying at 103°C for 24 h, the measured concentration was 114.5 g/L. It is noteworthy that in this work the waste leaf of sugar beet, instead of its root, was used as the feedstock.

It should be mentioned that in this research the waste leaf of sugar beet was used as the feedstock for preparing the extract. This extract thus differs greatly from the beet juice often used by highway agencies to blend with salt brine, where the beet juice was obtained from the root of sugar beet.

Table 2. The characteristics of the leaves.

| Type of leaf | Scientific name | Plant age at harvest (days) | Age of material (year) |
|--------------------|-----------------------------|-----------------------------|------------------------|
| European dandelion | <i>Taraxacum officinale</i> | 30 | 1 |
| Sugar beet | <i>Beta vulgaris L.</i> | 175 | 1 |

Elemental analysis of the extracts

Elemental analysis of the sugar beet leaf extract and dandelion leaf extract was determined by energy dispersive spectroscopy (EDS) method using a Apreo VolumeScope™ SEM instrument equipped with a TEAM™ Pegasus integrated EDS-EBSD (Electron Backscatter Diffraction) system at an accelerating voltage of 20kV. The EDS results are presented in Table 3.

Table 3. Elemental analysis of the extracts obtained by EDS technique.

| Type of extract | Weight percent (wt. %) of element | | | | | | | | | |
|-----------------|-----------------------------------|-------|-------|------|------|------|------|------|------|------|
| | C | N | O | Na | Si | P | S | Cl | K | Ca |
| Dandelion leaf | 17.74 | 20.99 | 29.49 | 5.55 | 0.60 | 6.18 | 3.48 | 3.62 | 8.42 | 3.92 |
| Sugar beet leaf | 26.45 | 40.10 | 23.58 | 0.82 | ---- | 4.73 | ---- | 1.15 | 3.16 | ---- |

Chemical analysis of the extracts

The chemical functional groups of the sugar beet leaf extract and dandelion leaf extract were determined using a Nicolet iS50 FTIR (Fourier transformed infrared) Spectrometer from Thermo

Scientific. The IR spectra was collected over the wave number range of 4000–400 cm^{-1} . Prior the test, the extract samples were uniformly mixed with FTIR grade of potassium bromide KBr. Liquid chromatography–mass spectrometry (LC-MS) method was employed for analysis of extracts out of the sugar beet leaf and dandelion leaf extracts, respectively. LC-MS was carried out by a quadrupole time-of-flight mass spectrometer (Synapt G2-S) in the positive ion mode. The Progenesis QI v. 2.0.5542 software (Nonlinear Dynamics) was used for interpretation of the data. It corrected the accurate masses to the LockMass (LeuEnk, m/z 556.2771 for positive ion mode) and performed the peak alignment and integration using all isotopes belonging to a compound ion. Using Progenesis, the possible elemental compositions were calculated and the external search of the Chemspider database was conducted, considering the following elements: C, H, N, O, P, Na, Ca, Cl, K, and S. All of these elements were derived from EDS results, except hydrogen. The reason that authors added hydrogen to this list was application of the hydrogen-containing compounds in the preparation of the plant extracts, and also considering this fact that hydrogen can be found in natural products.¹⁷ It should be mentioned that since the wt.% of Si in dandelion extract was below 1%, it was not considered in the process of the interpretation of LC-MS results. In this work, based on the elemental analysis, we considered more elements than our previous research¹⁸ for interpretation of LC-MS results. This explains why more compounds or sometimes even different compounds were detected in the sugar beet leaf extract compared to what reported in our previous work.

For calculating the weight percent of each compound, the surface area below the peak associated with that compound was measured using ImageJ software. Then the weight percent of the compound was determined by calculating the percentage area of each compound.

Determination of total phenol content in the extracts

The concentration of phenol in each extract was measured via a spectrophotometric method.¹⁹ For preparation of the samples, 1 mL of methanolic solution of extract with concentration of 1 mg/mL was mixed with 5 mL of 10% Folin-Ciocalteu's reagent dissolved in water and 5 mL of 7.5% NaHCO₃ solution dissolved in water. The blank sample consisted of 1 mL methanol, 5 mL 10% Folin-Ciocalteu's reagent dissolved in water and 5 mL of 7.5% of NaHCO₃ solution. The samples were incubated at 45 °C for 1 hour. Then, the absorbance was measured using a Genesys 20 visible spectrophotometer at λ_{max} of 765 nm. The tests were triplicated to ensure statistical reliability. The same procedure was used for the standard solutions of Gallic acid for making the calibration line and the following equation was obtained: $y = 0.0076x + 0.1823$, $R^2 = 0.9578$; in which y is the absorbance and x is the concentration of Gallic acid. The concentration of phenol was calculated in $\mu\text{g/mL}$ unit based on the measured absorbance values and the calibration line. Finally, the concentration of phenol in the extract was expressed in terms of Gallic acid equivalent ($\mu\text{g of GA/g of extract}$).

Determination of total flavonoids in the extracts

The concentration of flavonoids in each extract was determined using a spectrophotometric method.¹⁹ The test sample was consisted of 5 mL of 1 mg/mL methanolic solution of the extract and 5 mL of 2% AlCl₃ methanolic solution. The incubation of samples was done for two hours at room temperature. The absorbance was determined using a Genesys 20 visible spectrophotometer at λ_{max} of 415 nm. The tests were triplicated to ensure statistical reliability. The same procedure was performed for the standard solutions of Rutin for making the calibration line and the following equation was obtained: $y = 0.0226x + 0.1118$, $R^2 = 0.9821$; in which y is the absorbance and x is the concentration of Rutin. The concentration of flavonoids was calculated in mg/mL unit based

on the measured absorbance values and the calibration line. Then, the concentration of flavonoids in the extract was expressed in terms of Gallic acid equivalent (μg of RU/g of extract).

Ice-melting test

For measuring the ice melted by anti-icer mixtures over time, a modified Strategic Highway Research Program (SHRP) ice-melting test (H-205.1 and H-205.2) was used. In this test, 48 mL DI water was used for making the ice in a 150×20 mm polystyrene petri dish. Then, 1.4 mL anti-icer mixture was applied over the ice at -3.9°C . After 10, 20, 30, 45, and 60 min, the volume of melted ice was measured with a syringe and it was returned to the ice sample evenly. For each measurement, the ice sample was removed from the freezer for about 30 s, and then was returned to the freezer. The tests were triplicated to ensure statistical reliability.

Freeze-thaw test

The impact of anti-icer formulations on the durability of Portland cement mortar (PCM) was evaluated via SHRP H205.8 freeze-thaw (F-T) cyclic test method with minor modifications. This method assesses the combined effects of anti-icer solutions and F-T cycling on the structural integrity of PCM samples. The samples were made in 5.1 cm (diameter) \times 10.2 cm (length) molds. Mortar mixture design was based on the sand-to-cement and water-to-cement ratios of 3:1 and 1:2, respectively, with 1.5 mL water reducer. Portland cement type I-II and Sakrete multipurpose sand were used. They were cured for 24 h in water before being placed in sealed plastic boxes with 100% relative humidity for 28 days. Then the dry weights of the samples were measured before placing them in dishes, equipped with a sponge in their bottom, holding 310 mL of 3% anti-icer liquid. The dishes were sealed with plastic wrap to prevent evaporation. Two mortar samples were placed in each dish and diluted 23% NaCl brine (i.e., a blend of 23% NaCl brine and DI water at 3:97 mass ratio) was used as the control. Using a thermocouple placed in the control PCM sample,

temperature was monitored during freeze-thaw test cycling. Dishes were moved to plastic boxes which were kept at $-20.8 \pm 0.2^\circ\text{C}$ for 16 to 18 h then at $23.2 \pm 0.2^\circ\text{C}$ for 6 to 8 h. In the freeze-thaw cycle, the cooling and heating rates were $0.06^\circ\text{C}/\text{min}$ and $0.07^\circ\text{C}/\text{min}$, respectively. F-T cycles were continued for 10 days. Then the scaled-off materials were removed from samples and they were air-dried overnight before recording the final weight.

Low-temperature behavior of asphalt binder

Low temperature behavior of asphalt binder (PG 64-28 from Western States Asphalt, Inc.) was studied using a bending beam rheometer (BBR) at -18°C . To simulate field conditions of short-term aging (during construction) and long-term aging (during first ten years of service), the binder was aged in the laboratory using a rolling thin-film oven (RTFO) and pressure-aging vessel (PAV), respectively. Then 10 mL of anti-icer solution was added to each 30 g of the aged binder. Finally, the mix was heated in a vacuum oven at 80°C for 1 h, and 150°C for 2 h in atmospheric pressure. The processed binder was then used for the BBR test, from which parameters indicative of the characteristic of asphalt pavement durability in cold climate were derived.

Corrosion behavior

The corrosion rate of the American Society for Testing and Materials (ASTM) C1010 carbon steel samples was measured by linear polarization resistance (LPR) method via a multichannel potentiostat equipped with three-electrode electrochemical cells. The LPR measurement was carried out by polarizing the coupons at ± 20 mV versus the open-circuit potential (OCP) at a scan rate of 0.167 mV/s.²⁰ Prior to test, the surfaces of steel samples were wet polished using 60 to 1500 grade sandpapers, and then the samples were rinsed with ethanol and DI water. Finally, the samples were immersed in anti-icer solutions for 24 h. The concentration of anti-icer solutions were same

as their original concentrations, which have been mentioned in Table 1. The corrosion measurements were performed at least in duplicates.

pH measurements

A Milwaukee MW100 portable pH meter with 0.1 pH resolution was used for measuring the pH of samples.

Snow–pavement bond and friction tests

The best performer formulation was tested for the snow-pavement bond strength and friction coefficient of asphalt pavement treated by the anti-icer at -3.9°C after being applied at 30 gal/lane-mile. This relatively low application rate of 30 gal/lane-mile was considered suitable for relatively high traffic volume roads under light snowfall and for low traffic volume roads under light snowfall with the pavement temperature of 25 °F – 30 °F.²¹ After anti-icer application, snow was applied and compacted to the pavement, then placed in a trafficking machine for 500 tire passes. To investigate the effect of anti-icing on the snow–pavement bond strength, the shear force required to plow the snow from the pavement surface was measured by pulling a hollow metal box equipped with a spring scale. The maximum force required to shear the snow from the pavement divided by the contact area was calculated to be the shear strength. Six snow–pavement bond shear tests were measured on each pavement sample and two pavement samples were examined. After shearing the snow, the coefficient of static friction at six locations on each of the samples mentioned earlier was measured by pulling a rubber-bottomed metal block on the pavement surface and measuring the ratio of the required force to initiate movement divided by the weight of the block.

Eutectic phase diagrams

For plotting the eutectic phase diagrams of anti-icer formulations, ASTM D1177 was adopted. The test set up was a flask containing 100 mL anti-icer, a stainless steel stirrer rotating with the average speed of 70 strokes per minute (35 rpm), and a thermostat coupled with a data logger to measure temperature at 1 sec scans. The test set up was kept in a temperature-controlled chamber. The temperature was decreased with the cooling rate of 0.5°C/min until the anti-icer solution was frozen. The freezing point was considered as the crossing of projections of the cooling and freezing diagrams.

COD measurement

The best-performer sample was used for the COD (chemical oxygen demand) test. Since the run off in roadway contains a diluted concentration of the anti-icer, a 3% solution of the anti-icer (3 wt.% anti-icer with 97 wt.% DI water) was used for COD measurement. Dichromate COD measurement method was used in this work. First, 2 mL of the diluted anti-icer was added to COD standard solution. The mixture was heated at 150°C in a Hach DRB200 reactor for 120 min. Then it cooled down to room temperature (RT), and let it to be at RT for overnight to precipitate suspended particles. Then absorbance was measured at the wavelength of 420 nm using a Hach DR3900 spectrophotometer. The mg/L COD was obtained using the calibration line and the measured absorbance value for the best performer sample. For each test, three replicates were used.

BOD measurement

The biochemical oxygen demand (BOD) of the best performer sample was measured by converting the dichromate COD content to Manganese III COD and then the result was converted to BOD. This process was done by using the tables provided by Hach company.²² In addition, BOD₃ was measured using the following procedure. 45 mL of the diluted anti-icer 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 containing 1mL/L of phosphate buffer solution, magnesium sulfate heptahydrate 2.25%, calcium chloride solution (2.75% w/v), and ferric chloride solution (0.025% w/v). The dilution procedure was repeated three times (three replicates). After measuring DO_0 ($t = 0$) using a calibrated DO meter, the bottles were labeled and placed in the 27°C incubator for 3 days.²³ At day-three, the DO was measured in the incubated bottles using the DO meter (DO_3). The BOD_3 was calculated using following equation.

$$BOD_3 \left(\frac{mg}{L} \right) = \frac{DO_0 - DO_3}{P} \quad (1)$$

Where, DO_0 and DO_3 are dissolved oxygen concentrations (mg/L) at t of 0 and 3 days. P is the dilution fraction which is equal to 0.15.

RESULTS AND DISCUSSION

FTIR results

The FTIR spectra of the dandelion leaf and sugar beet leaf extracts are presented in Figure 1 and Figure 2, respectively. The suggested functional groups are given in Table 4 and Table 5. The results show that the extracts may composed of the following functional groups: 1° and 2° amines, amides, alkanes, carboxylic acids, ketones, alkynes, alkenes, aromatics, and aliphatic amines. These functional groups feature the organic chemicals made of C, H, N, and O.

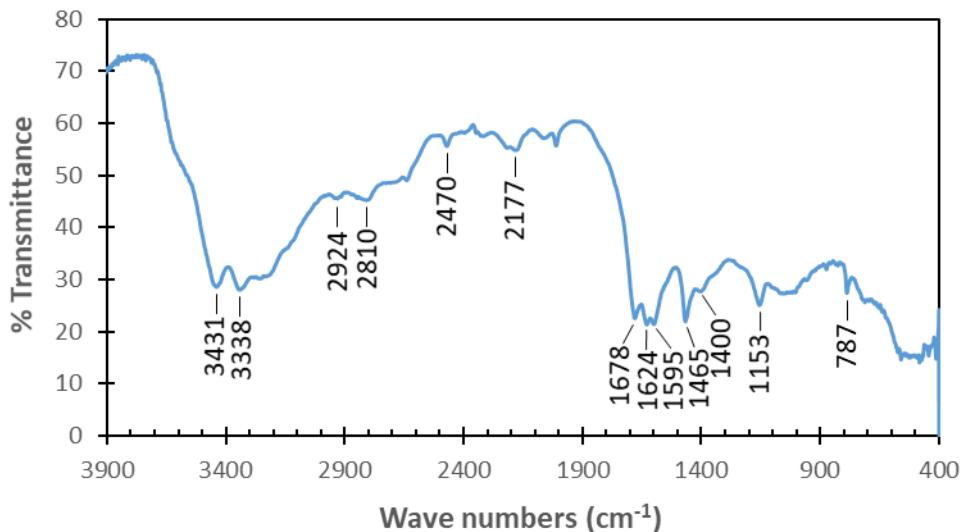


Figure 1. FTIR spectra of dandelion leaf extract.

Table 4. Chemical functional groups of dandelion leaf extract.

| Wave number (cm ⁻¹) | Functional group | Bond | Frequency range (cm ⁻¹) |
|---------------------------------|--------------------------|-----------------------|-------------------------------------|
| 3431 and 3338 | 1°, 2° amines and amides | N–H stretch | 3400–3250 |
| 2924 | alkanes | C–H bend | 3000–2850 |
| 2810 | carboxylic acids | O–H stretch | 3300–2500 |
| 2470 | ketones | O–H stretch | 3400–2400 |
| 2177 | alkynes | –C≡C– stretch | 2260–2100 |
| 1678 | alkenes | –C=C– stretch | 1680–1640 |
| 1624 and 1595 | 1° amines | N–H bend | 1650–1580 |
| 1465 | alkanes | C–H bend | 1470–1450 |
| 1400 | aromatics | C–C stretch (in-ring) | 1500–1400 |
| 1153 | aliphatic amines | C–N stretch | 1250–1020 |
| 787 | alkenes | =C–H bend | 1000–650 |

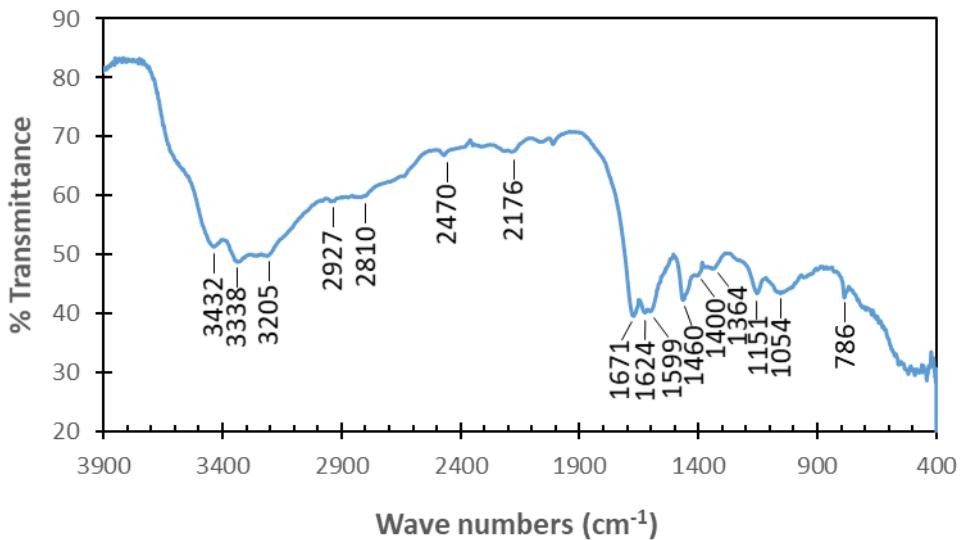


Figure 2. FTIR spectra of sugar beet leaf extract.

Table 5. Chemical functional groups of sugar beet leaf extract.

| Wave number (cm ⁻¹) | Functional group | Bond | Frequency range (cm ⁻¹) |
|---------------------------------|--------------------------|-----------------------|-------------------------------------|
| 3432 and 3338 | 1°, 2° amines and amides | N–H stretch | 3400–3250 |
| 3205 | carboxylic acids | O–H stretch | 3300–2500 |
| 2927 | alkanes | C–H bend | 3000–2850 |
| 2810 | carboxylic acids | O–H stretch | 3300–2500 |
| 2470 | ketones | O–H stretch | 3400–2400 |
| 2176 | alkynes | –C≡C– stretch | 2260–2100 |
| 1671 | alkenes | –C=C– stretch | 1680–1640 |
| 1624 and 1599 | 1° amines | N–H bend | 1650–1580 |
| 1460 | alkanes | C–H bend | 1470–1450 |
| 1400 | aromatics | C–C stretch (in-ring) | 1500–1400 |
| 1364 | alkanes | C–H rock | 1370–1350 |
| 1151 | aliphatic amines | C–N stretch | 1250–1020 |
| 786 | alkenes | =C–H bend | 1000–650 |

LC-MS results

The results for LC-MS analysis of dandelion leaf extract and sugar beet leaf extract are shown in Figure 3 and Figure 4, respectively. The proposed chemical compounds for the extracts are

presented in Table 6 and Table 7. It is seen that based on LC-MS results, extracts are made out of O, C, H, N, P, Na, and S. This is in good agreement with elemental analysis and FTIR results. The organic compounds containing heteroatoms such as oxygen, nitrogen, sulfur, and phosphorous have a polar structure and can be spontaneously adsorbed onto the metallic surfaces.²⁴

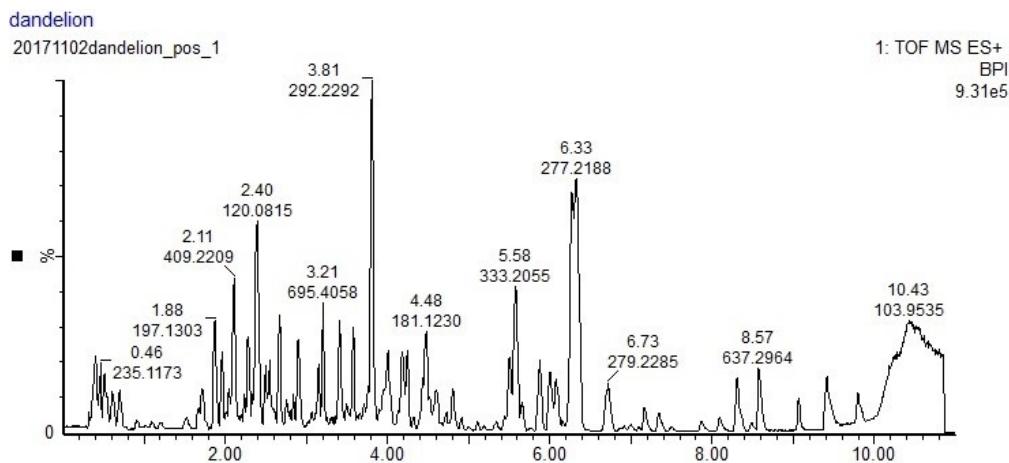


Figure 3. LC-MS spectra of dandelion leaf extract.

Table 6. Chemicals observed in dandelion leaf extract by LC-MS method.

| Formula | Retention time (min) | m/z | Wt.% |
|--|----------------------|----------|------|
| C ₁₁ H ₁₄ N ₄ O ₂ | 0.46 | 235.1173 | 1.2 |
| C ₁₃ H ₁₇ Na | 1.88 | 197.1303 | 4.8 |
| C ₁₈ H ₃₈ N ₂ O ₂ P ₂ S | 2.11 | 409.2209 | 6.9 |
| C ₈ H ₁₀ N | 2.40 | 120.0815 | 12.1 |
| C ₃₄ H ₅₉ N ₂ NaO ₁₁ | 3.21 | 695.4058 | 4.2 |
| C ₁₈ H ₃₀ NO ₂ | 3.81 | 292.2292 | 20.3 |
| C ₁₁ H ₁₇ O ₂ ⁻ | 4.48 | 181.1230 | 6.9 |
| C ₁₆ H ₂₉ KN ₄ O | 5.58 | 333.2055 | 9.2 |
| C ₁₈ H ₂₈ O ₂ | 6.33 | 277.2188 | 28.6 |
| C ₁₈ H ₃₀ O ₂ | 6.73 | 279.2285 | 3.1 |
| C ₂₈ H ₄₅ N ₄ NaO ₁₁ | 8.57 | 637.2964 | 2.7 |

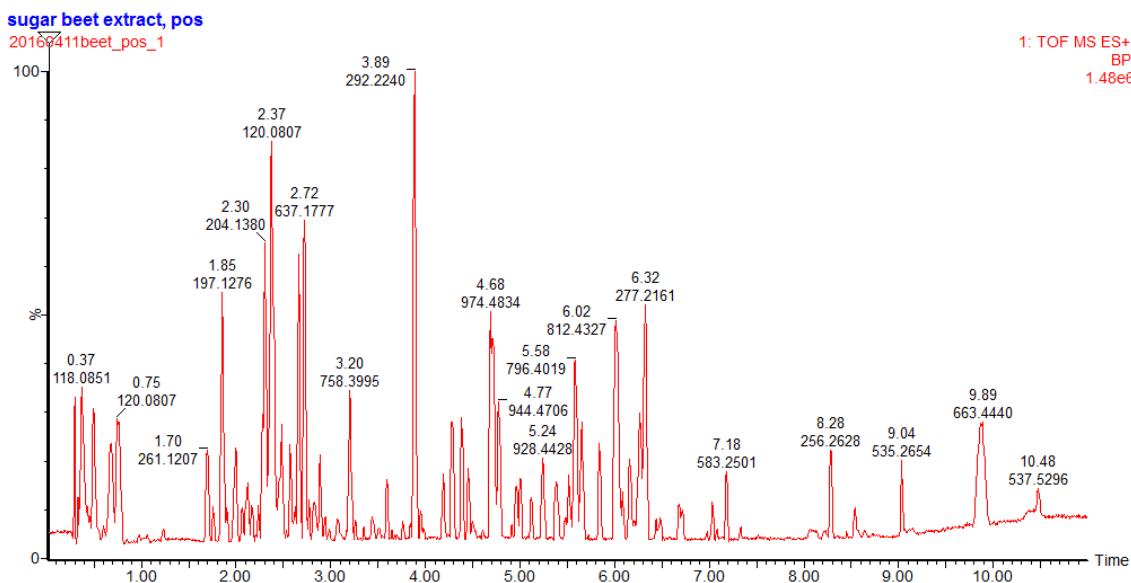


Figure 4. LC-MS spectra of sugar beet leaf extract.¹⁸

Table 7. Chemicals observed in sugar beet leaf extract by LC-MS method.

| Formula | Retention time (min) | m/z | Wt. % |
|--|----------------------|----------|-------|
| C ₆ H ₁₅ NO | 0.37 | 118.0851 | 5.5 |
| C ₁₃ H ₁₇ N ₄ P | 1.70 | 261.1207 | 2.7 |
| C ₁₃ H ₁₇ Na | 1.85 | 197.1276 | 6.6 |
| C ₁₃ H ₁₈ NO | 2.30 | 204.1380 | 7.3 |
| C ₈ H ₁₀ N ⁺ | 2.37 | 120.0807 | 11.3 |
| C ₂₆ H ₃₇ O ₁₆ P | 2.72 | 637.1777 | 8.2 |
| C ₁₈ H ₂₉ NO ₂ | 3.89 | 292.2240 | 12.8 |
| C ₄₁ H ₇₁ N ₁₁ O ₁₄ S | 4.68 | 974.4834 | 8.9 |
| C ₄₅ H ₇₄ N ₃ O ₁₆ P | 4.77 | 944.4706 | 3.9 |
| C ₄₂ H ₇₁ N ₃ NaO ₁₆ P | 5.24 | 928.4428 | 1.9 |
| C ₃₇ H ₆₃ N ₃ NaO ₁₂ P | 5.58 | 796.4019 | 4.2 |
| C ₃₈ H ₆₇ N ₃ NaO ₁₂ P | 6.02 | 812.4327 | 8.7 |
| C ₁₈ H ₂₈ O ₂ | 6.32 | 277.2161 | 6.6 |
| C ₃₃ H ₃₄ N ₄ O ₆ | 7.18 | 583.2501 | 1.4 |
| C ₁₆ H ₃₃ NO | 8.28 | 256.2628 | 2.0 |
| C ₂₈ H ₃₉ N ₄ NaO ₃ S | 9.04 | 535.2654 | 1.6 |
| C ₄₂ H ₆₃ O ₄ P | 9.89 | 663.4440 | 5.9 |
| C ₂₃ H ₅₀ N ₂ NaO ₈ P | 10.48 | 537.5296 | 0.5 |

Total phenol and flavonoids of the extracts

The total phenol and flavonoids contents of the sugar beet leaf extract and dandelion leaf extracts are presented in Table 8. According to this table, both phenol and flavonoids contents of the extracts are in the level of micro grams which shows low level of these components in the extracts. Since these components are usually available in the plants and plant extracts in the level of mg/g,^{19,25} the low concentration of them in the extracts, $\mu\text{g/g}$, may show that most of the phenol and flavonoids of the sugar beet leaf and dandelion leaf are degraded in the degradation process.

Table 8. Total phenol and flavonoids contents of the sugar beet leaf extract and dandelion leaf extract.

| Sample | Total phenol ($\mu\text{g of GA/g of extract}$) | Total flavonoids ($\mu\text{g of RU/g of extract}$) |
|-------------------------|---|---|
| Dandelion leaf extract | 43.21 | 7.53 |
| Sugar beet leaf extract | 42.97 | 10.26 |

Ice-melting capacity (IMC) of anti-icers

The average 60 min ice-melting capacities (IMCs) of anti-icer solutions at -3.9°C are shown in Figure 5. All of the mixtures show an ice melting capacity of 90% or more than the capacity of salt brine, which has been identified by some of the researchers as the lowest acceptable performance for an alternative anti-icer.²⁶ Therefore, all of them have the potential to be used instead of 23% NaCl. There was little difference ($<0.3 \text{ mL/g}$) between the ice-melting capacity of NaCl brine and mixtures 3, 11, and 13-16. On the other hand, Mixes 1, 2, 4, 5, 7-9, and 12 had an ice-melting capacity of at least 0.3 mL/g (12 percent) more than NaCl brine, which make them potential anti-icers for replacing the salt brine.

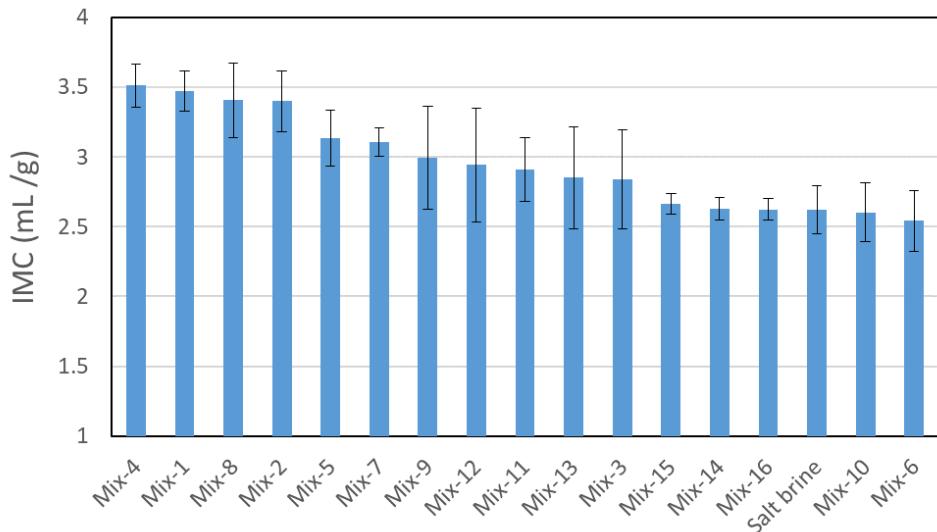


Figure 5. Ranking of anti-icer mixtures according to ice-melting capacity after application of anti-icers at 60 min, -3.9°C (ordered from greatest to least, error bars represent ± 1 SE (standard error)).

In the next step, Fisher's least significant difference (LSD) method was used for statistically comparing the means to make it clear which formula is different from salt brine with statistical significance. The results of LSD analysis including the parameter of "p" and the mean differences of the IMC of control (salt brine) with that of each sample are presented in Table 9. In this table, when p is less than 0.05 then the mean difference of IMC is statistically significant. It is seen that the mean differences for samples 1, 2, 4, and 8 are statistically significant ($p < 0.05$).

Based on the multivariate linear regression analysis on the ice melting data for all 17 samples, it became clear that among the 4 variables of sugar beet leaf extract, dandelion leaf extract, sodium formate, and sodium metasilicate, the sugar beet leaf extract has a statistically significant positive effect (coefficient=0.181 and $p=0.001 < 0.05$). This effect is interesting and noteworthy. On the other hand, the dandelion extract (coefficient=0.082 and $p=0.125 > 0.05$) and formate (coefficient=-

0.102 and $p=0.182>0.05$) had a marginal effect on IMC. Silicate (coefficient=0.041 and $p=0.601>>0.05$) appears to have no significant effect on IMC.

Table 9. Significance of the differences of means (p) for different mixtures.

| Control vs. Mix # | Mean difference ⁺ | p |
|-------------------|------------------------------|-------|
| 1 | -0.85000* | 0.017 |
| 2 | -0.78000* | 0.027 |
| 3 | -0.21933 | 0.521 |
| 4 | -0.89167* | 0.013 |
| 5 | -0.51600 | 0.136 |
| 6 | 0.07667 | 0.822 |
| 7 | -0.48600 | 0.160 |
| 8 | -0.78867* | 0.026 |
| 9 | -0.37233 | 0.278 |
| 10 | 0.01667 | 0.961 |
| 11 | -0.29000 | 0.397 |
| 12 | -0.32267 | 0.347 |
| 13 | -0.23067 | 0.500 |
| 14 | -0.00700 | 0.984 |
| 15 | -0.04567 | 0.893 |
| 16 | -0.00467 | 0.989 |

⁺ Mean difference = $IMC_{control} - IMC_{sample}$

* The mean difference is significant at the 0.05 level.

According to the FTIR results, both sugar beet leaf and dandelion leaf extracts contain amines and amides. It is known that amides and long-chain amines have ice melting properties.²⁷ Therefore, it can be concluded that the ice melting ability of sugar beet leaf and dandelion leaf extracts is may be due to the existence of amides and amines in their compounds. In addition, based on the LC-MS results, sugar beet leaf extract contains C₄₂H₆₃O₄P. The possible structures for this compound are Tris[2,4-bis(2-methylpropyl)phenyl] phosphate or Tris[4-(1,1,3,3-tetramethylbutyl)phenyl] phosphate or Tris(2,4-ditert-butylphenyl)phosphate. As it can be seen, all of these possible structures contain phosphate ion, so, it can be concluded that phosphate is one of the sugar beet leaf extract components. It is known that phosphates are deicing compounds²⁷. Therefore, sugar beet leaf extract contains one more deicing component compared to dandelion leaf extract. This can be the reason of more pronounced effect of sugar beet leaf extract on IMC. The positive effect of sugar beet extract on IMC value observed in this research is in good agreement with the authors' previously published results and the other researchers' results that showed the blend of NaCl, bio-based materials and other proprietaries can outperform NaCl brine.^{28,29}

Freeze-thaw resistance of PCM in the presence of anti-icers

Figure 6 illustrates the mass loss of PCM samples exposed to anti-icer solutions after 10-day freeze-thaw test. Mixes 3, 11, and 13-16 show the highest impact to PCM and are approximately equivalent in terms of impact toward mortar. However, Mixes 1, 2, and 4-10 show lower detrimental impact towards PCM than plain salt brine and the other formulas, which is desirable. The results of LSD analysis shows that the mean differences of mass loss between control and samples 1, 2, 4, 6-9, and 11 are statistically significant. Therefore, in overall it can be concluded that mixtures 1, 2, 4, and 6-9 have statistically lower impacts on control compared to other samples.

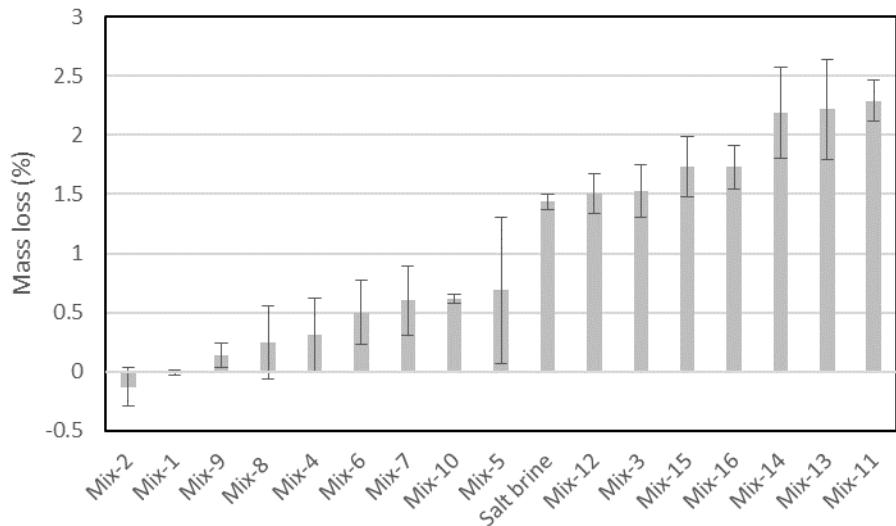


Figure 6. The effect of various anti-icer mixtures on the mass loss of PCM samples after 10-day freeze-thaw test (ordered from least to greatest, error bars represent ± 1 SE).

The impact of deicers on mortar samples can be ascribed to the combination of physical and chemical attacks which undermine the integrity and the strength of mortar.³⁰ The physical attack is mostly caused by freezing/thawing cycles, and can have different symptoms such as scaling, map cracking, and paste disintegration.^{31,32} Salts can cause scaling of the cementitious materials through osmotic pressure, precipitation and growth of salt crystals, thermal shock, and glue spalling.^{33,34} On the other hand, the chemical attack can be in the form of chemical reactions of deicers with cement paste and aggregate phase which can weaken the cementitious materials.³⁵⁻³⁷ For instance, Portlandite $[\text{Ca}(\text{OH})_2]$ may react with deicer ions which can cause formation of expansive oxychloride compounds. The rate of reactions depends on the diffusion coefficient of chloride ions. Usually it takes less than 3 hours for chloride ions to penetrate to the depth of 300 μm in a concrete sample and reach equilibrium.³⁸

Based on the regression analysis on all data, it was revealed that the beet extract has the most obvious effect (coefficient=-0.215 and $p=0.119$). There does appear to be a relationship between

lower PCM mass loss with higher beet extract content, though the effect is not statistically significant at $p<0.05$. In addition, it appears that the effect of dandelion extract is clearly insignificant (coefficient=0.038 and $p=0.782>0.05$). Silicate appears to have a very slight beneficial effect on scaling reduction (coefficient=-0.136 and $p=0.500$), and formate appears to have a very slight effect to make scaling worse (coefficient=0.038 and $p=0.843$), however these effects are not statistically significant at $p<0.05$. The findings of regression analysis were in agreement with the findings by others researchers which showed that agro-based chemicals can decrease mass loss of Portland cement concrete after F-T cycles.²⁹

Yang et al. studied the deicer-scaling resistance of cement-based mortar samples containing ammonium phosphate and the mortar samples made by ordinary Portland cement. Their study showed the beneficial effect of ammonium phosphate in reducing the scaling risk of deicer to mortar samples.³⁹ Based on the FTIR and LC-MS results, the sugar beet leaf extract contains both amines and phosphates, and dandelion extract contains only amines. Therefore, the molecules containing amines and phosphates in the extracts may be active ingredients that increased the resistance of mortar samples against deicer-scaling damage.

Effect of freeze-thaw in the presence of anti-icers on PCM strength

The average compressive strength of the mortar samples exposed to different anti-icer solutions after 10-cycle freeze-thaw (F-T) testing is shown in Figure 7. It can be seen that there is no noticeable relationship between the mass loss results (Figure 6) and the compression test results. For example, the least average mass loss belongs to Mix 2, but the maximum compressive strength is associated with Mix 5. Actually, the compressive strength is more affected by frost damage rather than scaling damage.⁴⁰ Frost damage is mainly due to the osmotic pressure. Since in this research the PCM samples are non-air-entrained, they are more susceptible to this damage.

The results of regression analysis of all 17 samples suggest that silicate has a strong beneficial effect on compressive strength (coefficient=412.992 and $p=0.048$), which is statistically significant at $p<0.05$. It is in good agreement with Phoo-ngernkham et al. observations which show silicate phase reacts with concrete and produces crystalline CSH phase which can improve the mechanical properties of concrete samples.⁴¹ On the other, it appears that dandelion extract does not have any significant beneficial effect on compressive strength (coefficient=80.194 and $p=0.556$). In addition, it looks like formate and beet extract, with coefficients of -38.790 and -38.279, respectively, and p values equal or more than 0.777, do not have any significant negative effect on compressive strength. However, Heikal has claimed that formate compounds can act as an accelerator of strength in cement paste samples.⁴² In addition, LSD analysis on compressive strength results showed no sample has a significant mean difference with control.

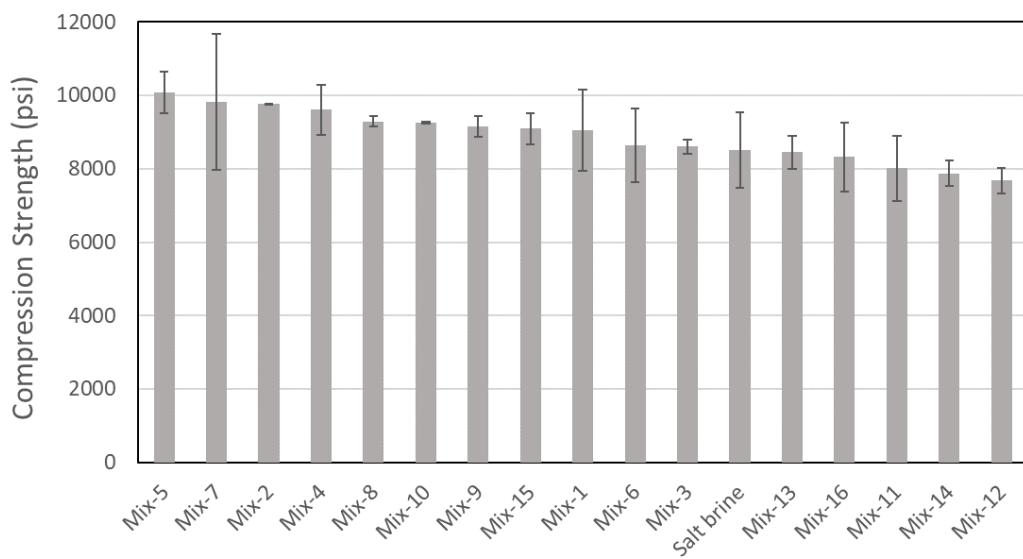


Figure 7. Compressive strength of mortar samples as a function of anti-icer mixture after 10 cycles of freeze-thaw test (ordered from greatest to least, error bars represent ± 1 SE).

So, based on the aforementioned observations and the results of previous section, it can be suggested that sugar beet leaf extract appears to reduce F-T scaling of PCM in the formulas, but similar to dandelion leaf extract, it has no significant effect on compressive strength. This is in good agreement with previous studies which show a little or no impact of agro-based products on the concrete matrix at low temperatures.⁴³

Impacts of anti-icer mixtures on asphalt pavements

The creep stiffness and m-values of the asphalt binder measured at -18°C are shown respectively in Figure 8 and Figure 9. Stiffness value has a direct relationship with thermal stress; therefore, lower values of stiffness are preferred. Instead, m-value has an inverse relationship with the ability to relax; so, higher m-values are favored.

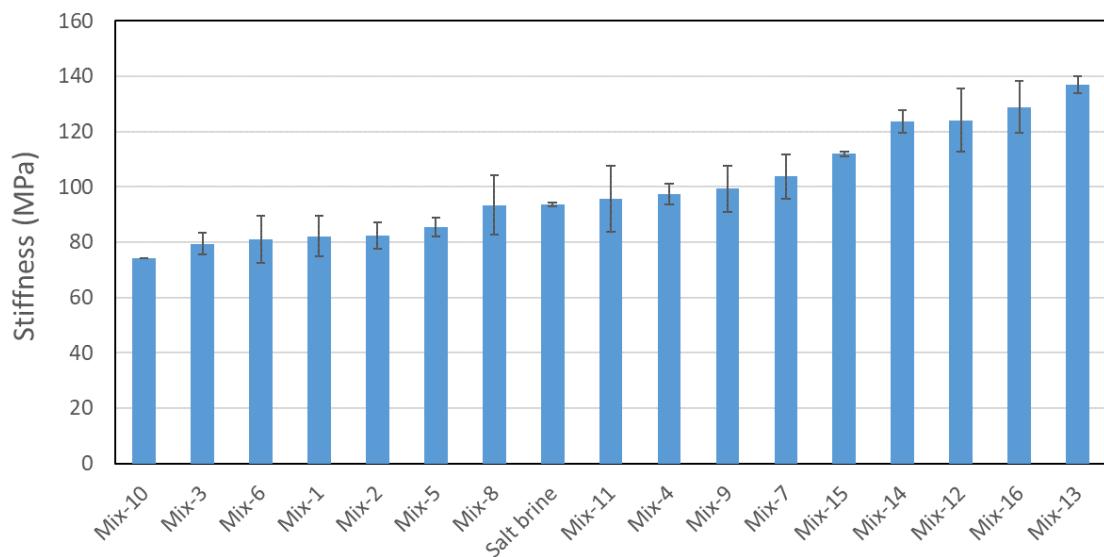


Figure 8. The stiffness of asphalt binder exposed to different anti-icer mixtures (ordered from least to greatest, error bars represent ± 1 SE).

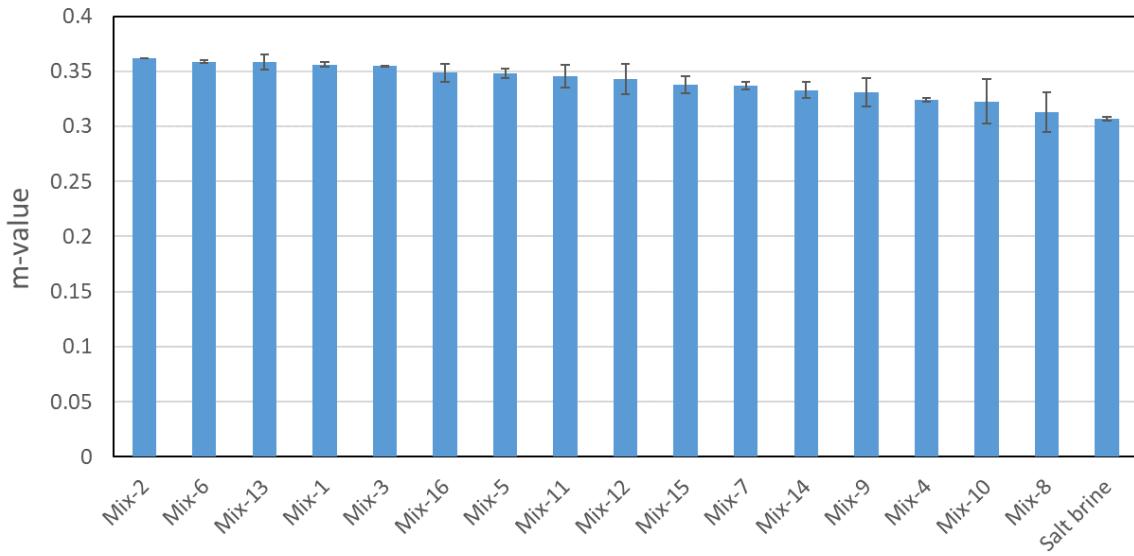


Figure 9. The m-value of asphalt binder exposed to different anti-icer mixtures (ordered from greatest to least, error bars represent ± 1 SE).

The results of LSD analysis showed that samples 12-14 and 16 have statistically higher stiffness compared to control. Considering this fact that higher stiffness is a sign of higher thermal stresses, it can be concluded that no sample showed statistically benefit over control (salt brine) in terms of low temperature asphalt binder stiffness. On the other hand, samples 1-3, 5, 6, 11-13, 15 and 16 had significantly higher m-values than control that shows their more ability to relax. Therefore, the innovative solutions introduced in this research were able to improve the asphalt binder low temperature performance, in terms of the ability of relaxation. Similar results have been reported by Lei et al.⁴⁴ They observed an increase in relaxation rate of asphalt binder due to the use of refined waste oil modifier.⁴⁴ The damaging effect of some anti-icer mixtures on asphalt performance could be due to the binder emulsification, destructive chemical reactions, and generation of additional stress in binder.⁴⁵ However, the regression analysis on stiffness and m-value data showed that none of the additives has a significant effect on the low temperature performance of asphalt binder.

The corrosivity of anti-icer mixtures on mild steel

The corrosion rate of C1010 steel samples exposed to various anti-icer solutions is depicted in Figure 10. It is seen that the solutions containing plant extracts alone (e.g. Mix 3) or with sodium formate (e.g. Mix 1, Mix 6, Mix 8) had higher corrosion rates than solutions that contained metasilicate. Silicate is an effective corrosion inhibitor which has been used in deicers for protecting of galvanized metals.⁴⁶ While mixtures 1, 3, 6, and 8 were more corrosive than the other mixtures, they were still less corrosive than salt brine.

The lower corrosion rate of the steel samples exposed to the mentioned mixtures comparing to those exposed to the salt brine, may imply a weak presence of microbiologically influenced corrosion.⁴⁷ This may suggest that these mixtures do not pose considerable direct risk to the environment in terms of biological activity. However, the BOD test is necessary to confirm this hypothesis.

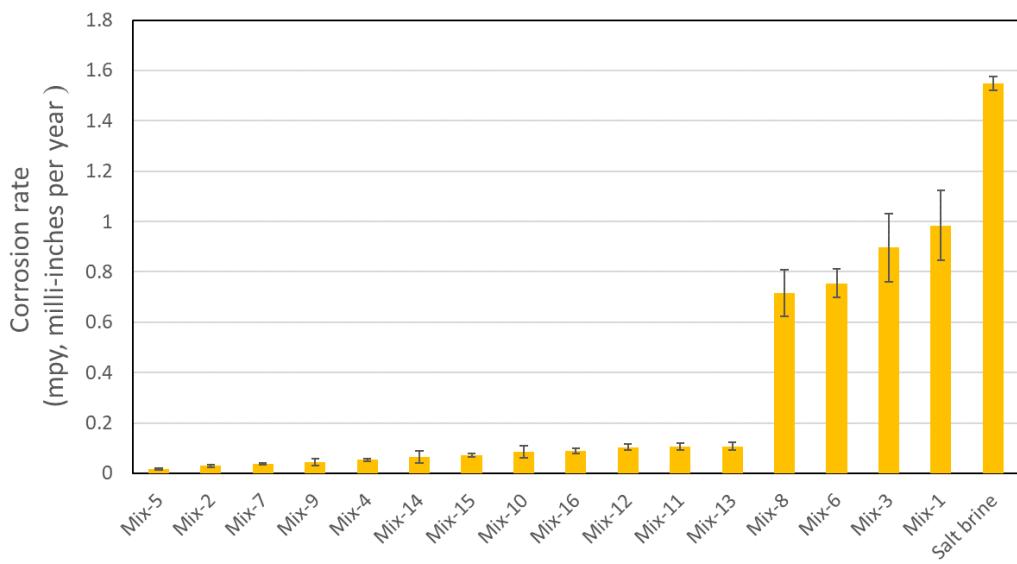


Figure 10. Corrosivity of the anti-icer mixtures on C1010 steel, in milli-inches per year (mpy), after 24 h immersion (ordered from least to greatest, error bars represent ± 1 SE).

The results of regression analysis indicated that sodium metasilicate has a statistically significant beneficial effect on decreasing the corrosion rate (coefficient=-0.439 and $p=4.3\times10^{-9}<0.05$). This effect can be due to high alkalinity of silicates. Measurement of pH showed that all mixtures containing sodium metasilicate have a pH value higher than 11.

Dandelion (coefficient=-0.075 and $p=0.064$) and formate (coefficient=-0.092 and $p=0.104$) have a slight beneficial effect on mitigating the corrosion rate, however these effects are not statistically significant at $p<0.05$. On the other hand, beet extract with coefficient of -0.036 and p value of 0.341 does not have statistically significant effect on decreasing the corrosion rate. The LSD analysis revealed all samples have a statistically lower corrosion rate compared to salt brine.

Decision making process

For choosing the best performer sample, an analytical hierarchy process (AHP) was used. Pairwise comparisons shown in Table 10 are based on the importance of each parameter. Numbers greater than one show that the row parameter is more important than the associated column parameter, and numbers less than one show the vice versa. The magnitude of the numbers shows the degree of importance.

Table 10. 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 | F-T mass loss | Asphalt stiffness | Asphalt m-value |
|--|--|--|----------------|---------------|-------------------|-----------------|
| Ice melting capacity at 20 min, -3.9°C | 1.00 | 1.00 | 5.00 | 5.00 | 9.00 | 9.00 |
| Ice melting capacity at 60 min, -3.9°C | 1.00 | 1.00 | 5.00 | 5.00 | 9.00 | 9.00 |
| Corrosion rate | 0.20 | 0.20 | 1.00 | 1.00 | 2.00 | 2.00 |
| F-T mass loss | 0.20 | 0.20 | 1.00 | 1.00 | 3.00 | 3.00 |

| | | | | | | |
|-------------------|------|------|-------|-------|-------|-------|
| Asphalt stiffness | 0.11 | 0.11 | 0.50 | 0.33 | 1.00 | 1.00 |
| Asphalt m-value | 0.11 | 0.11 | 0.50 | 0.33 | 1.00 | 1.00 |
| Sum | 2.62 | 2.62 | 13.00 | 12.67 | 25.00 | 25.00 |

To determine the importance weight of the decision criteria, a standardized matrix was used (Table 11). It is the result of the given values from Table 10 divided by the sum of the values in the respective columns. For instance, 1.00 from row 2 column 2 in Table 10 divided by the sum of 2.62 in row 8 column 2 gives 0.34 in Table 11. In the next step, the prioritization matrix was determined, in which the columns have been normalized, as shown in Table 12. In this table, the decision weights were determined by averaging the standardized rows in Table 11. For example, from row 2, the average of 0.38, 0.38, 0.38, 0.39, 0.36, and 0.36 is equal to 0.38.

Table 11. A standard matrix based on the comparisons.

| Comparison | Ice melting capacity at 20 min, -3.9°C | Ice melting capacity at 60 min, -3.9°C | Corrosion rate | F-T mass loss | Asphalt stiffness | Asphalt m-value | Weight |
|--|--|--|----------------|---------------|-------------------|-----------------|--------|
| Ice melting capacity at 20 min, -3.9°C | 0.38 | 0.38 | 0.38 | 0.39 | 0.36 | 0.36 | 0.38 |
| Ice melting capacity at 60 min, -3.9°C | 0.38 | 0.38 | 0.38 | 0.39 | 0.36 | 0.36 | 0.38 |
| Corrosion rate | 0.08 | 0.08 | 0.08 | 0.08 | 0.08 | 0.08 | 0.08 |
| F-T mass loss | 0.08 | 0.08 | 0.08 | 0.08 | 0.12 | 0.12 | 0.09 |
| Asphalt stiffness | 0.04 | 0.04 | 0.04 | 0.03 | 0.04 | 0.04 | 0.04 |
| Asphalt m-value | 0.04 | 0.04 | 0.04 | 0.03 | 0.04 | 0.04 | 0.04 |

According to Table 12, the multi-criteria scoring system showed that salt brine (control) received the lowest score of 14. Notably, all of the mixtures' scores were higher than control's score. Mix 1 and Mix 2 exhibited the highest scores of 92 and 88, respectively. These mixtures were

considered to be the best choices. Since Mix 1 had less additive chemicals and higher score, it was chosen as the best performer mixture and was selected for the complementary tests.

For finding the metric amount of the reduction in consumption of anti-icer, the authors examined lower amounts of best performer solution (Mix 1) in ice melting test. They observed that somewhere between 0.9 to 1 mL of Mix 1 could have an ice melting capacity equal to 1.4 mL of control (23% NaCl solution). It means about 29 to 37% decrease in the consumption of NaCl solution.

It should also be mentioned that since the maximum amount of the plant extracts used for each mixture is 6 wt.% or less, it is significantly lower than the commonly used alternative of 23% NaCl brine and sugar beet juice at 80:20 by volume. In addition, the use of such agro-based formulations with increased anti-icing effectiveness have lower application rates than plain 23% NaCl brine (e.g. about 30% for using Mix1 instead of 23% NaCl), further reducing the amount of chemicals needed for providing a reasonable level of service on wintry pavements.

Table 12. Summary of the prioritization.

| Sample | Weight (%) | | | | | | Score |
|--------|------------|--------|--------|--------|--------|--------|-------|
| | 0.38 | 0.38 | 0.08 | 0.09 | 0.04 | 0.04 | |
| Mix 1 | 100.00 | 95.70 | 36.85 | 94.95 | 87.33 | 89.35 | 92 |
| Mix 2 | 80.36 | 88.47 | 99.21 | 100.00 | 87.17 | 100.00 | 88 |
| Mix 3 | 33.43 | 30.57 | 42.56 | 31.54 | 91.70 | 86.78 | 37 |
| Mix 4 | 49.90 | 100.00 | 97.59 | 81.69 | 63.11 | 31.20 | 75 |
| Mix 5 | 24.62 | 61.20 | 100.00 | 66.31 | 81.99 | 74.93 | 52 |
| Mix 6 | 31.51 | 0.00 | 51.88 | 74.06 | 89.31 | 94.04 | 30 |
| Mix 7 | 38.27 | 58.11 | 98.65 | 69.85 | 52.82 | 54.54 | 55 |
| Mix 8 | 4.69 | 89.36 | 54.33 | 84.44 | 69.45 | 10.91 | 50 |
| Mix 9 | 0.00 | 46.37 | 98.14 | 89.04 | 60.00 | 43.25 | 37 |
| Mix 10 | 43.77 | 6.20 | 95.63 | 69.15 | 100.00 | 28.81 | 38 |
| Mix 11 | 22.93 | 37.87 | 94.21 | 0.00 | 65.68 | 69.83 | 35 |

| | | | | | | | |
|---------|-------|-------|-------|-------|-------|-------|----|
| Mix 12 | 6.66 | 41.24 | 94.33 | 32.35 | 20.49 | 65.16 | 32 |
| Mix 13 | 5.56 | 31.74 | 94.09 | 3.09 | 0.00 | 93.46 | 25 |
| Mix 14 | 18.39 | 8.64 | 96.82 | 4.21 | 21.39 | 47.33 | 21 |
| Mix 15 | 18.97 | 12.63 | 96.43 | 23.19 | 39.98 | 56.01 | 25 |
| Mix 16 | 5.51 | 8.40 | 95.31 | 23.17 | 12.87 | 76.11 | 18 |
| Control | 13.75 | 7.92 | 0.00 | 35.38 | 69.09 | 0.00 | 14 |

Complementary tests

Mix 1 was examined for determining the freezing point depression behavior and the friction coefficient of the asphalt pavement treated by anti-icing formulation (vs. no anti-icing and 23 wt.% NaCl) at -3.9°C after being applied at 30 gal/lane-mile.

Friction coefficient and snow–pavement bond strength

Application of Mix 1 resulted in an improvement on the friction coefficient compared to salt brine, as shown in Figure 11. This improvement is statistically significant ($p < 0.05$) based on LSD analysis of the means comparison. The positive effect of bio-based materials on the friction of deiced pavement has also been reported by other researchers.^{48,49} It can be due to the increase in actual contact area caused by agricultural-based constituents.⁵⁰

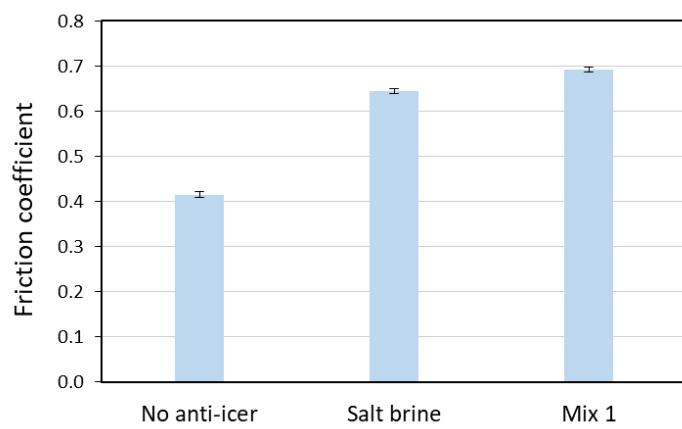


Figure 11. Friction coefficient of the iced asphalt pavement at -3.9°C without anti-icing and after anti-icing by salt brine and Mix 1 (error bars represent ± 1 SE).

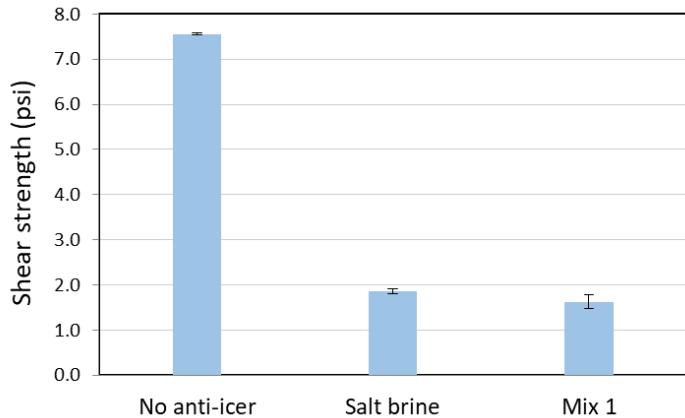


Figure 12. Snow-pavement bond test results at -3.9°C in the absence of anti-icer and after application of salt brine and Mix 1 as anti-icers (error bars represent ± 1 SE).

Figure 12 illustrates the shear strength of snow–pavement bond in the absence of anti-icing and anti-icing by salt brine. It can be seen that anti-icing has decreased the bond shear strength and Mix 1 is more effective anti-icer than salt brine. However, according to LSD analysis, the difference between mean shear stress values of salt brine and Mix 1 is not statistically significant ($p=0.187>0.05$).

Eutectic phase diagram

Figure 13 shows the eutectic phase diagrams for salt brine and Mix 1. The eutectic temperature (lowest freezing point) for salt brine was -22.8°C at 23 wt.% NaCl, while it was -26.5°C for Mix 1 at concentration 25 wt.%. Since Mix 1 has a lower eutectic temperature than salt brine, it may also have a lower effective temperature. This finding is in good agreement with ice melting section results, authors previous research, and the other researches which showed that the agro-based additives can depress the freezing point of deicer and act as an ice melting agent.^{51,52}

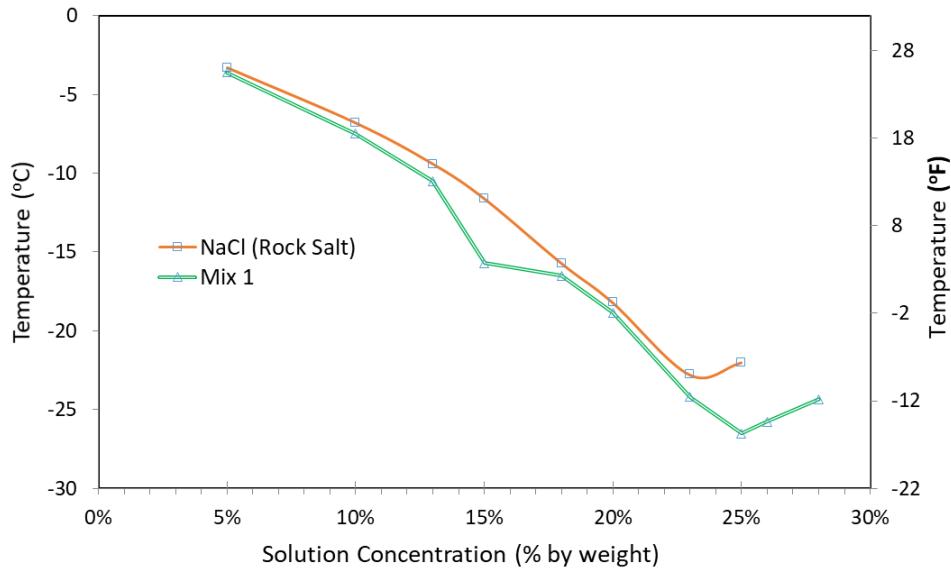


Figure 13. Eutectic phase diagrams of salt brine and Mix 1.

COD and BOD measurements

The COD and BOD contents of the Mix 1 are presented in Table 13. It is seen that the obtained COD and BOD values are lower than the maximum levels of COD (300 mg/L) and BOD (100 mg/L) allowed by word health organization (WHO) for an effluent to irrigation channel.⁵³ The values measured in this research are much less than the obtained COD (215.6 mg/L) and BOD (78.0 mg/L) from the modified coffee processing wastewater.⁵⁴

Table 13. COD and BOD values for Mix1.

| Sample | Dichromate COD (mg/L) \pm 1 SE | Manganese III COD (mg/L) \pm 1 SE | Estimated BOD (mg/L) \pm 1 SE | Actual BOD ₃ results \pm 1 SE |
|------------------------|----------------------------------|-------------------------------------|---------------------------------|--|
| Mix-1 (3wt.% in water) | 114.37 \pm 3.71 | 101.04 \pm 3.51 | 27.07 \pm 0.94 | 40.78 \pm 0.70 |

CONCLUSIONS

This work demonstrates a viable solution to diverting agricultural wastes to green anti-icing formulations with balanced properties and reduced impact on natural environment. In this regard, agricultural-based solutions derived from locally sourced feedstock mixed with 23 wt.% sodium chloride brine, and commercial additives with no heavy metal ions were tested for their ice-melting capacity, ability to protect asphalt binder and mortar, corrosion inhibition properties, snow-pavement bond strength, and effect on the friction coefficient of the anti-iced asphalt pavement. A decision making process based on an analytical hierarchy process (AHP) was used to determine the best performing anti-icer, i.e., Mix 1 (a water-based solution made of 3 wt.% sugar beet leaf extract, 0.67 wt.% sodium metasilicate, and 23 wt.% NaCl). This decision came mainly from its high ice-melting capacity at -3.9°C. The enhanced snow/ice control performance of Mix 1 may translate to a reduced application rate required on pavement. In addition, Mix 1 features relatively low risks to the engineering properties of Portland cement mortar and asphalt concrete, while being effective in improving the friction coefficient with low impact on environment in terms of BOD and COD.

The experimental results and the subsequently regression analysis shows that sugar beet leaf extract has a clear beneficial effect on IMC, with a marginal effect on IMC by dandelion leaf extract ($p>0.05$). Beet leaf extract may have some marginal benefit on PCM F-T scale reduction, but this also failed to be demonstrable at $p<0.05$, and the dandelion extract clearly did not have a statistically significant effect on PCM F-T scaling. Neither had a statistically significant effect on F-T compressive strength, asphalt stiffness or m-value. Dandelion extract had a marginal effect on corrosion rate ($p>0.05$), and the beet leaf extract had essentially no significant effect on corrosion ($p=0.34>>0.05$). In addition, the plant extracts lowered the freezing point of the deicers, and

significantly improved the friction coefficient of anti-iced pavement surface. The molecules containing amines and phosphates in the sugar beet leaf and dandelion leaf extracts were suggested as possible active ingredients that improve the anti-icing properties of the “green” mixtures.

Future work should focus on the further enhancements of the process used to extract the green chemicals from agro-based feedstock, in order to obtain compositions that are optimized in light of the specific user priorities in performance and impacts of anti-icing formulations.

AUTHOR INFORMATION

Corresponding Author

*E-mail: xianming.shi@wsu.edu. Tel.: +1 (509) 335-7088. Fax: +1 (509) 335-7632.

ORCID

Mehdi Honarvar Nazari: 0000-0002-6348-8862

Xianming Shi: 0000-0003-3576-8952

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors acknowledge the financial support of the CESTiCC and the NSF CRISP Program (Award 1638384). They also thank Laura Fay at Western Transportation Institute – Montana State University for providing access to her lab to run complementary tests, Natalia Kaiser for providing laboratory access to run COD and BOD test, Jillian Morrison at Center for Interdisciplinary Statistical Education and Research (CISER), and Washington State Department of Transportation

for the rock salt. The authors would also like to thank Dr. Gang Xu and Sen Du for their assistance in the laboratory work.

REFERENCES

1. Fay, L., Shi, X. & Huang, J. *Strategies to Mitigate the Impacts of Chloride Roadway Deicers on the Natural Environment*. (Transportation Research Board, 2013).
2. Li, Y. *et al.* Corrosion by Chloride Deicers on Highway Maintenance Equipment: Renewed Perspective and Laboratory Investigation. *Transp. Res. Rec. J. Transp. Res. Board* **2361**, 106–113 (2013).
3. Nazari, M. H., Bergner, D., Shi, X. & Fay, L. *Best Practices for the Prevention of Corrosion of Department of Transportation Equipment: A User's Manual*. (Minnesota Department of Transportation and the Clear Roads Program, 2015).
4. Lilek, J. Roadway deicing in the United States. *American Geosciences Institute* (2017). Available at: <https://www.americangeosciences.org/critical-issues/factsheet/roadway-deicing-united-states>. (Accessed: 9th June 2018)
5. Honarvar Nazari, M., Laura, F., Jungwirth, S. & Shi, X. Water Quality Implications and the Toxicological Effects of Chloride-Based Deicers. *Environ. Sustain. Transp. Infrastruct.* (2015). doi:10.1061/9780784479285.022
6. Staples, J. M., Gamradt, L., Stein, O. & Shi, X. *Recommendation for Winter Traction Materials Management on Roadways Adjacent to Bodies of Water*. (Montana Department of Transportation, 2004).
7. Conger, S. M. *Winter Highway Operations*. (Transportation Research Board, 2005).

8. Johnson, A. R. Methods fluids by producing and employing oil and gas well drilling and completion fluids as well as hydraulic fracturing fluids employing triglyceride processing by products and propylene glycol recovered from aircraft deicing operations. U.S. Patent US9725641B2, August 8 (2017).
9. Samuels, W. D. *et al.* Deicing/anti-icing fluids. U.S. Patent US7105105B2, September 12 (2006).
10. Talor, P., Gopalakrishnan, K., Verkade, J., Wadhwa, K. & Kim, S. Development of an Improved Agricultural-Based Deicing Product. *InTrans Proj. Rep.* 32 (2010).
http://lib.dr.iastate.edu/intrans_reports/32
11. Bloomer, T. A. Anti-freezing and deicing composition and method. U.S. Patent US6416684B1, July 9 (2002).
12. Ossian, K. C. & Behrens, K. Processed raffinate material for enhancing melt value of de-icers. U.S. Patent US20080128651A1, June 5 (2008).
13. Shi, X. & Jungwirth, S. The Search for “Greener” Materials for Winter Road Maintenance Operations. in *Sustainable Winter Road Operations* 378–401 (Wiley-Blackwell, 2018).
doi:10.1002/9781119185161.ch17
14. Koefod, R. S. Corrosion-inhibiting deicer composition. U.S. Patent US7658861B2, February 9 (2010).
15. Fang, K.-T., Lin, D. K. J., Winker, P. & Zhang, Y. Uniform Design: Theory and Application. *Technometrics* **42**, 237–248 (2000).
16. Zhou, J. & Zhang, L. Solubility of Cellulose in NaOH/Urea Aqueous Solution. *Polym. J.* **32**, 866–870 (2000).

17. Cortright, R. D., Davda, R. R. & Dumesic, J. A. Hydrogen from catalytic reforming of biomass-derived hydrocarbons in liquid water. in *Materials for Sustainable Energy* 289–292 (Co-Published with Macmillan Publishers Ltd, UK, 2010).
doi:10.1142/9789814317665_0043

18. Honarvar Nazari, M., Shi, X., Jackson, E., Yan, Z. & Li, Y. Laboratory Investigation of Washing Practices and Bio-Based Additive for Mitigating Metallic Corrosion by Magnesium Chloride Deicer. *J. Mater. Civ. Eng.* **29**, 04016187 (2017).

19. Stankoic, M. S. Total phenolic content, flavonoid concentration and antioxidant activity of *Marrubium peregrinum* L. extracts. *Kragujev. J. Sci.* **33**, 63–72 (2011).

20. Nazari, M. H., Shihab, M. S., Cao, L., Havens, E. A. & Shi, X. A peony-leaves-derived liquid corrosion inhibitor: protecting carbon steel from NaCl. *Green Chem. Lett. Rev.* **10**, 359–379 (2017).

21. Shi, X. *et al. Evaluation and Analysis of Liquid Deicers for Winter Highway Maintenance Operations.* (Western Transportation Institute (WTI) - Montana State University, 2013).

22. Boyles, W. *The science of chemical oxygen demand.* LIT7053-Technical Information Series Booklet No. 9. (Hach USA, 1997).

23. Bureau of Indian Standards (BIS). *IS 3025 (Part 44): Method of Sampling and Test (Physical and Chemical) for Water and Wastewater, Part 44: Biochemical Oxygen Demand (BOD) (First Revision).* (1993).

24. Shihab, M. S., Nazari, M. H. & Fay, L. Study of inhibition effect of pyridinium salt derivative on corrosion of C1010 carbon steel in saline solution. *Prot. Met. Phys. Chem. Surf.* **52**, 714–720 (2016).

25. Sulaiman, C. T. & Balachandran, I. Total Phenolics and Total Flavonoids in Selected Indian Medicinal Plants. *Indian J. Pharm. Sci.* **74**, 258–260 (2012).

26. Wang, Z. *et al.* Snow Melting Agent (GB/T 23851-2017). (2017).

27. Wiesenfeld, A., Meyers, A. & Leicht, R. Deicing and anti-icing concentrated composition for aircraft. U.S. Patent US5935488A, August 10 (1999).

28. Hossain, S. M. K., Fu, L. & Lake, R. Field evaluation of the performance of alternative deicers for winter maintenance of transportation facilities. *Can. J. Civ. Eng.* **42**, 437–448 (2015).

29. Jungwirth, S. & Shi, X. Laboratory Investigation of Naturally Sourced Liquid Deicers and Subsequent Decision Support. *J. Cold Reg. Eng.* **31**, 06017002 (2017).

30. Farnam, Y. *et al.* The Influence of Calcium Chloride Deicing Salt on Phase Changes and Damage Development in Cementitious Materials. *Cem. Concr. Compos.* **64**, 1–15 (2015).

31. Jain, J., Olek, J., Janusz, A. & Jozwiak-Niedzwiedzka, D. Effects of Deicing Salt Solutions on Physical Properties of Pavement Concretes. *Transp. Res. Rec. J. Transp. Res. Board* **2290**, 69–75 (2012).

32. Sutter, L., Dam, T., Peterson, K. & Johnston, D. Long-Term Effects of Magnesium Chloride and Other Concentrated Salt Solutions on Pavement and Structural Portland Cement Concrete: Phase I Results. *Transp. Res. Rec. J. Transp. Res. Board* **1979**, 60–68 (2006).

33. Sumsion, E. S. & Guthrie, W. S. *PHYSICAL AND CHEMICAL EFFECTS OF DEICERS ON CONCRETE PAVEMENT: LITERATURE REVIEW*. (Utah Department of Transportation, 2013).

34. Valenza, J. J. & Scherer, G. W. A review of salt scaling: II. Mechanisms. *Cem. Concr. Res.* **37**, 1022–1034 (2007).

35. Shi, X., Fay, L., Peterson, M. M., Berry, M. & Mooney, M. A FESEM/EDX investigation into how continuous deicer exposure affects the chemistry of Portland cement concrete. *Constr. Build. Mater.* **25**, 957–966 (2011).

36. Sutter, L., Peterson, K., Touton, S., Van Dam, T. & Johnston, D. Petrographic evidence of calcium oxychloride formation in mortars exposed to magnesium chloride solution. *Cem. Concr. Res.* **36**, 1533–1541 (2006).

37. Dang, Y., Shi, X., Xie, N., McVey, E. & Kessel, A. Accelerated Laboratory Test Suggests the Importance of Film Integrity of Sealers on the Protection of Concrete from Deicer Scaling. *J. Mater. Civ. Eng.* **28**, 04016065 (2016).

38. Xu, G. & Shi, X. Impact of Chemical Deicers on Roadway Infrastructure. in *Sustainable Winter Road Operations* 211–240 (Wiley-Blackwell, 2018).
doi:10.1002/9781119185161.ch11

39. Yang, Q., Zhang, S. & Wu, X. Deicer-scaling resistance of phosphate cement-based binder for rapid repair of concrete. *Cem. Concr. Res.* **32**, 165–168 (2002).

40. Cao, J. A study of effects of a new agricultural-based deicer on the properties of pavement concrete. *Graduate Theses and Dissertations* (2014). <https://lib.dr.iastate.edu/etd/13770>.

41. Phoo-ngernkham, T., Maegawa, A., Mishima, N., Hatanaka, S. & Chindaprasirt, P. Effects of sodium hydroxide and sodium silicate solutions on compressive and shear bond strengths of FA–GBFS geopolymer. *Constr. Build. Mater.* **91**, 1–8 (2015).

42. Heikal, M. Effect of calcium formate as an accelerator on the physicochemical and mechanical properties of pozzolanic cement pastes. *Cem. Concr. Res.* **34**, 1051–1056 (2004).

43. Omer, R., Fu, L., Hossain, K., Muresan, M. & Hosseini, F. *Evaluation and Optimization of Winter Snow and Ice Control Operations for Railway Platforms*. (Transportation Planning & Development, GO Transit, 2013).

44. Lei, Z., Bahia, H. & Yi-qiu, T. Effect of bio-based and refined waste oil modifiers on low temperature performance of asphalt binders. *Constr. Build. Mater.* **86**, 95–100 (2015).

45. Shi, X. *et al.* Deicer Impacts on Pavement Materials: Introduction and Recent Developments. *Open Civ. Eng. J.* **3**, 16–27 (2009).

46. Koefod, R. S. Deicer compositions including corrosion inhibitors for galvanized metal. U.S. Patent US7655153B2, February 2 (2010).

47. Nazari, M. H. & Shi, X. Vehicle Risks of Winter Road Operations and Best Management Practices. in *Sustainable Winter Road Operations* 241–272 (Wiley-Blackwell, 2018). doi:10.1002/9781119185161.ch12

48. Hosseini, F., Hossain, S. M. K. & Fu, L. Bio-based materials for improving winter pavement friction. *Can. J. Civ. Eng.* **44**, 99–105 (2016).

49. Pylkkanen, V. & Nelson, K. Corrosion-inhibiting deicers derived from biomass. U.S. Patent US8845923B2, September 30 (2014).

50. Waluś, K. J. & Olszewski, Z. Analysis Of Tire-road Contact Under Winter Conditions. in *the World Congress on Engineering 2011 Vol III* (2011).

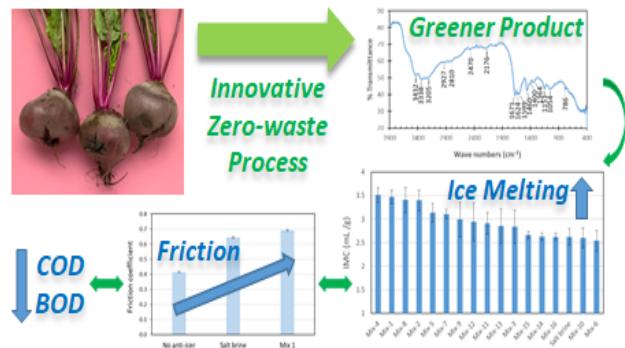
51. Bottura, F., Ferhout, H. & Theotiste, F. M. A. Biodegradable organic product designed for producing a road snow melting agent. (2016).

52. Muthumani, A. & Shi, X. Effectiveness of Liquid Agricultural By-Products and Solid Complex Chlorides for Snow and Ice Control. *J. Cold Reg. Eng.* **31**, 04016006 (2017).

53. WHO. Guideline for discharge of industrial Effluent characteristics. **3**, 231–236 (1995).

54. Devi, R., Singh, V. & Kumar, A. COD and BOD reduction from coffee processing wastewater using Avacado peel carbon. *Bioresour. Technol.* **99**, 1853–1860 (2008).

For Table of Contents Use Only.



A brief (~ 20 word) synopsis

This work introduces a greener anti-icer for increasing the sustainability of winter roadways, automobiles, infrastructure, and the environment.