A Multi-Criteria Decision Making Approach to the Formulation and Selection of Anti-icing Liquids

Xianming Shi, Ph.D., P.E.*
Western Transportation Institute
Associate Research Professor, Civil Engineering
Montana State University
PO Box 174250
Bozeman, MT 59717-4250
Phone: (406) 994-6486
Fax: (406) 994-1697
Email: xianming_s@coe.montana.edu

Michelle Akin, M.Sc.
Research Associate
Western Transportation Institute
Montana State University
PO Box 174250
Bozeman, MT 59717-4250
Phone: (406) 994-6356
Fax: (406) 994-1697
Email: michelle.akin@coe.montana.edu

*Corresponding author

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ABSTRACT

To effectively fight snow storms in the challenging funding environment, many maintenance agencies in North America have started to produce their own anti-icing liquids, instead of procuring commercial anti-icers. This work demonstrates a systematic approach to data-driven, multi-criteria decision-making, by conducting a set of laboratory tests to assess twenty blended chloride-based anti-icing formulations. The laboratory data were then used to establish predictive models correlating the multiple design parameters with the anti-icer performance and impacts or with an *anti-icer composite index*. We used artificial neural networks for modeling and examined anti-icer performance (characteristic temperature and ice-melting capacity at 30°F and 15°F respectively) and impacts (splitting tensile strength of concrete after ten freeze-thaw cycles and corrosivity to mild steel) as a function of the formulation design. The *anti-icer composite index* was calculated for four different user priority scenarios (*cost-first*, *performance-first*, *impacts-first*, or a *balanced approach*), each of which placed a different set of decision weights on various target attributes. Three-dimensional response surfaces were then constructed to illustrate such predicted correlations and to guide the direction for formulation improvements.

BACKGROUND

In the last decades, maintenance agencies in North America have increasingly relied on the use of chemicals to provide reasonably safe driving conditions on the winter road surface. Currently, the United States applies approximately 20 million tons of salts each year for winter road maintenance. This is partially owing to the negative impact of abrasives on water quality and aquatic species, air quality, vegetation, and soil and the hidden cost of sanding [1,2]. It has been recognized that the detrimental environmental impacts of abrasives are generally greater than those of chemicals [3]. The increased use of chemical deicers and anti-icers has also raised concerns about their effects on motor vehicles, the transportation infrastructure, and the environment [4, 5, 6].

More recent years have seen the transition from mostly deicing to anti-icing wherever possible [7], in light of the multiple benefits of the latter (e.g., improved level of service, reduced need for chemicals, and associated cost savings and safety/mobility benefits) [8,9]. In current practice, liquid chemicals are used either for anti-icing or in conjunction with applications of solid chemicals and abrasives (i.e., pre-wetting). It is desirable to further expand the use of liquid chemicals such that the overall use of abrasives and solid chemicals can be significantly reduced while maintaining or enhancing the level of service on winter roads.

Chloride-based salts are the most common chemicals used to serve as freezing-point depressants for winter road maintenance applications. Sodium chloride (NaCl) is the most widely used chemical due to its abundance and low cost. Magnesium chloride ($MgCl_2$) brines are often used instead of NaCl, and laboratory tests have demonstrated that they exhibit better ice-melting performance at lower temperatures [10]. Field studies have shown calcium chloride ($CaCl_2$) to be more effective than NaCl, owing to its ability to attract moisture and stay on the roads [11]. However, some agencies choose not to use $CaCl_2$ as it does not dry and can cause roads to become slippery [12]. Chlorides are generally considered the most corrosive winter maintenance chemicals [13]; commercially available, corrosion-inhibited versions of these chemicals are often used to reduce their corrosive effects on metals. In addition, acetates and formates are available for anti-icing applications but are much more costly and thus rarely used by highway agencies. Also available are a variety of chemicals derived from agricultural byproducts, used either alone or as additives for deicers or anti-icers.

To effectively fight snow storms in the challenging funding environment, many maintenance agencies in North America have started to produce their own anti-icing liquids, instead of procuring commercial anti-icers. Such “brine-making” operations not only can result in cost savings and enhance the agency preparedness during winter storms, but also allow agencies to blend different liquid chemicals for improved performance at lower temperatures. While a variety of laboratory tests exist for assessing deicers or anti-icers, research is still needed to improve the knowledge of performance characteristics of blended liquid products and their deleterious impacts on motor vehicles and transportation infrastructure. Research is also needed to establish a framework that would enable data-driven decision-making when it comes to selecting or formulating anti-icing liquids for snow and ice control. This can be accomplished by integrating agency priorities with laboratory testing data wherever possible. As such, each agency can take a holistic approach to anti-icer procurement or design, and strike the right balance in meeting its multiple goals of winter maintenance, including safety, mobility, environmental stewardship, infrastructure preservation, and economics.

This work demonstrates a systematic approach to data-driven, multi-criteria decision-making, by conducting a set of laboratory tests to assess twenty blended chloride-based anti-icing formulations. The laboratory data were then used to establish predictive models correlating the multiple design parameters with the anti-icer performance and impacts or with an anti-icer composite index and to construct response surfaces illustrating such correlations.

METHODOLOGY

Design of Experiments

When blending various amounts of corrosion inhibitor, $MgCl_2$ and $CaCl_2$ into the NaCl brine, the resultant anti-icer is expected to change its performance and impacts. In this study, we used a unique tool for the statistical design of experiments, known as *uniform design* [14], to reduce the number of experiments needed to explore a large unknown domain of anti-icer design parameters and to capture their complex interactions. We chose to investigate only twenty anti-icer formulations by adopting the design parameters and associated target attributes as shown in Table 1. Note that there would be a total of $4 \times 4 \times 5 = 80$ formulations to be investigated in the absence of a statistical design, as the dosage of $MgCl_2$, $CaCl_2$, and corrosion inhibitor (GLT) varied at 4, 4, and 5 levels respectively.

TABLE 1 Experimental data used for ANNs training and testing (with asterisk) respectively

Anti-icer Mix No.	$MgCl_2.6H_2O$ (g/g NaCl)	$CaCl_2.2H_2O$ (g/g NaCl)	GLT (mL/g NaCl)	**T_c (°F)**	**IMC, 15°F, 60 min (%, mL/mL)**	**IMC, 30°F, 60 min (%, mL/mL)**	**Predicted PCR**	Freeze-Thaw Mass Loss (%)	**STS after Freeze-Thaw (psi)**	Freeze Thaw Mass Loss Index	Freeze Thaw STS Index	Estimated Cost (dollars / gallon)	**Composite Index 1**	**Composite Index 2**	**Composite Index 3**	**Composite Index 4**
1	0.968	0.326	0.129	24.52	133.2	388.9	14.5	2.69	1014.51	46.2	31.4	0.27	73.6	84.9	38.3	65.0
2	0.646	1.305	0.194	22.11	129.5	414.9	15.9	5.97	569.71	110.8	133.2	0.39	28.0	46.8	58.1	46.5
3	0.968	1.304	0.258	19.47	128.4	441.2	16.2	3.83	577.76	68.8	131.3	0.42	21.8	58.9	87.2	61.4
4	0.323	0.978	0.129	24.15	135.6	390.6	17.8	5.06	647.84	93.0	115.3	0.31	53.4	52.7	38.3	46.9
5	0.646	0.652	0.258	24.35	91.8	421.2	13.1	4.01	741.86	72.3	93.8	0.32	53.1	65.6	36.4	51.6
6	0.646	0.652	0.065	24.52	123.2	396.2	12.5	1.96	883.30	31.8	61.5	0.28	70.4	83.2	37.8	63.4
7	0.646	0.652	0	24.25	143.6	383.7	61.9	4.83	684.38	88.5	107.0	0.26	65.4	20.6	35.0	35.5
8	0.323	0.326	0.129	25.44	72.1	425.2	10.3	2.76	829.62	47.7	73.7	0.22	86.0	78.8	27.4	60.6
9	0.646	0.978	0.065	23.08	137.8	399.3	18.9	6.37	649.04	118.7	115.0	0.32	51.4	46.8	49.1	48.0
10	1.291	0.652	0.194	22.37	131.9	410.5	11.6	2.19	826.66	36.5	74.4	0.34	48.7	81.0	59.6	66.2
11	0.323	0.652	0.194	24.85	134.0	385.0	13.2	1.66	956.51	26.0	44.7	0.28	68.3	87.1	34.6	63.5
12	0.968	0.978	0.129	22.14	131.0	413.4	11.1	2.36	877.14	39.7	62.9	0.35	46.5	83.2	62.1	67.6
13	0.646	0.652	0	23.94	129.9	396.9	57.2	2.23	835.65	37.2	72.4	0.26	69.8	44.1	40.5	48.6
14	0.646	0.326	0.258	25.08	126.9	388.2	13.2	2.64	871.30	45.3	64.2	0.27	69.4	78.3	31.3	58.7
15	1.291	0.326	0	23.78	133.5	395.7	63.5	3.66	758.44	65.4	90.0	0.26	67.8	28.8	40.8	41.8
16	1.291	1.304	0.065	19.81	144.5	425.9	16.4	4.50	747.12	81.9	92.6	0.40	29.2	64.0	84.7	64.2
17	0.646	0.978	0.194	23.12	131.9	403.3	13.1	1.72	875.86	27.0	63.2	0.34	47.7	83.6	51.7	64.2
18*	0.323	1.304	0	23.06	137.4	399.8	13.1	3.37	702.91	59.7	102.7	0.33	52.0	68.0	51.3	58.0
19	0.968	0.652	0.065	23.32	130.1	402.6	12.4	2.69	740.20	46.2	94.2	0.30	63.3	73.9	49.5	62.2
20	1.291	0.652	0.258	22.23	142.1	404.3	12.6	2.82	800.68	48.9	80.4	0.36	43.3	75.9	60.5	63.2

Note: 1. Only the target attributes highlighted with bold fonts were quantitatively modeled using neural networks. 2. T_c = characteristic temperature derived from Differential Scanning Calirometry (DSC) thermograms; *IMC* = ice-melting capacity; *PCR* = Percent Corrosion Rate; *STS* = Splitting Tensile Strength. 3. The composite indices were calculated for four different user priority scenarios respectively, i.e., *cost-first*, *performance-first*, *impacts-first*, or a *balanced approach.*

Anti-icing Formulations and Laboratory Tests

Understanding the performance characteristics and negative impacts of anti-icers is critical to effective and responsible winter maintenance operations. As such, laboratory tests were conducted to assess the performance of blended chloride brines and their impacts on metal, concrete and asphalt. To prepare the anti-icer formulations shown in Table 1, we used reagent-grade chloride chemicals and de-ionized water, whereas in practice maintenance agencies would have used less pure chemicals and tap water. A commercial corrosion inhibitor, GLT from Paradigm Chemical (Acworth, Georgia) was used in some blends. Each formulation had the same amount of NaCl (116 grams per Liter) and various amounts of $CaCl_2$, $MgCl_2$, and GLT (which were determined using the uniform design table).

The performance characteristics of anti-icers were assessed by measuring their Differential Scanning Calorimetry (DSC) thermogram with a TA Instruments Q200 apparatus. The use of DSC to quantify deicer or anti-icer performance is relatively new [15], even though it has been widely employed to rapidly and consistently characterize and quantify the thermal properties of materials. The thermograms were measured in the temperature range of 25 to -60°C (77 to -76°F) with a cooling/heating rate of 2°C (3.6°F) per minute. The anti-icers were first diluted using the anti-icer/water volume ratio of 1.5:1 and then allowed to reach ambient temperature. Subsequently, ten μL samples were pipetted into an aluminum sample pan and hermetically sealed for DSC measurements. At least three samples were run for each anti-icer to minimize data variability. The first peak at the warmer end of the heating cycle thermogram was used to derive the characteristic temperature of the anti-icer tested (T_c), which along with the heat flow (*H*, integrated surface area of the peak) are used to estimate the ice melting capacity (*IMC*) of the anti-icer at 60 minutes of application. Specifically, the *IMC* of anti-icers at 60 minutes were estimated for 15°F and 30°F respectively, using the following equations [15]:

$$IMC_{30^\circ F}(\%, \frac{\text{mL melt}}{\text{mL applied}}) = \left[-0.02265T_c + 1.965\log(\Delta H) + 0.03285t - 2.1761\right]/0.9 \cdot 100 \quad (R^2 = 0.94) \tag{1}$$

$$IMC_{15^\circ F}(\%, \frac{\text{mL melt}}{\text{mL applied}}) = \left[-0.08667T_c - 2.651\log(\Delta H) - 0.000716t + 9.114\right]/0.9 \cdot 100 \quad (R^2 = 0.80) \tag{2}$$

Where:

IMC = Amount of ice melted per unit of brine applied (%)

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

T_c = characteristic temperature from DSC (°F)

t = time between 10 and 60 (minutes)

The corrosion of anti-icers to mild steel (ASTM A36) was assessed using a three-electrode electrochemical cell and a Gamry Instruments® Potentiostat with an 8-channel Electrochemical Multiplexer. Each anti-icer formulation prepared was further diluted by water at 3:100. Prior to testing, the steel coupons were cleaned with acetone and de-ionized water. For each anti-icer, four steel coupons were subjected to wet-dry cycling in the diluted anti-icer as follows: 1-hour wet, 4-hour dry, 1-hour wet, 16-hour dry, 2-hour wet. For each steel coupon, a weak polarization curve was measured at the end of the 24-hour cycle, from which its corrosion potential (E_{corr}) was derived. As such, the electrochemical technique provides an alternative to the gravimetric method in rapidly assessing corrosivity of solutions. The corrosivity of each anti-icer was reported as Percent Corrosion Rate (*PCR*), as defined in the PNS/NACE corrosion test method, where it is normalized from actual mass loss of metallic coupons by setting the PCR of water at 0 and the PCR of a 3% dilution of a 23% NaCl brine solution at 100. In this study, the *PCR* values of the anti-icers were estimated from the E_{corr} data, using the following equation [16]:

$$PCR(\%) = 667.24E_{corr}^{\ 2} + 448.93E_{corr} + 83.184 \qquad (3)$$

Where E_{corr} = Corrosion potential (mV, vs. Ag/AgCl)

The impacts of anti-icers on concrete were assessed by conducting freeze-thaw tests of Portland cement concrete (PCC) samples in the presence of anti-icers, following the SHRP H205.8 test method 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 concrete. Concrete samples were made in 1½′′ diameter × $1^7/_8$′′ length (3.8 cm × 4.8 cm) poly(vinyl chloride) piping with a volume of 54 cm^3. The concrete mix design had a water-to-cement ratio of 0.55, a slump of 5.5′′ (14 cm) and air content of 1.6 percent. Samples were cured in water in the first 24 hours before being placed in a container with 100 percent relative humidity. The average 28-day compressive strength of three test cylinders was 7474 psi (51.5 MPa). The dry weight of each sample was recorded before placing it 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 concrete samples into the sponge and then placed in a Ziploc bag. Three concrete specimens were tested in each anti-icer solution. There were two controls: 1) a 3% NaCl solution and 2) de-ionized water. A thermocouple was embedded in one of the control concrete samples to monitor temperatures during freeze-thaw cycling. The sealed dishes were placed in the freezer for 16 to 18 hours at -17.8 ± 2.7°C (0 ± 4.9°F), then placed in the laboratory environment at 23.0 ± 1.7°C (73.4 ± 3°F) for 6 to 8 hours. This cycle was repeated for 10 days. The test specimens were then removed from the dish and rinsed under running water to remove any scaled-off material. The specimens were air-dried overnight before the final weight of each was recorded.

The mass loss due to freeze-thaw exposure was relatively minor for most concrete specimens. Therefore, the concrete specimens were also tested for splitting tensile strength. The specimens were laid on their side with a thin wooden stick above and below where the specimen contacted the compressive testing machine. Compressive stress caused the specimens to split in half; the maximum load was used to calculate the splitting tensile strength (STS) as follows:

$$STS\ (\text{psi}) = \frac{P \cdot C}{\pi \cdot L \cdot D} \qquad (4)$$

Where:

P = Load at failure (lb)

C = Estimated length of contact on the top and bottom (for undamaged specimens, C = 2; but scaled specimens had lower contact areas, from 0.7 to 1.9)

L = Length of specimen (1.875 in.)
D = Diameter of specimen (1.5 in.)

The impacts of anti-icers on asphalt were assessed with a bending beam rheometer (BBR). A PG 64-28 asphalt binder was first aged in a rolling thin film oven to simulate the effects of hot-mixing asphalt concrete. Asphalt binder (in contact with anti-icer solution) was then placed in a pressure aging vessel to simulate 7-10 years of in-service aging. After degassing, beams were molded and tested in the BBR.

The anti-icer mix design and laboratory test results are shown in Table 1. The costs of anti-icer formulations were estimated by assuming the raw material of NaCl, $MgCl_2 \bullet 6H_2O$, $CaCl_2 \bullet 2H_2O$, corrosion inhibitor GLT, and water delivered at \$60, \$150, \$300, \$400 and \$2 per tonne respectively and a mixing cost of \$0.10 per gallon, based on individual communications with winter maintenance practitioners in the United States. These numbers are for demonstration purpose only and may not reflect actual costs.

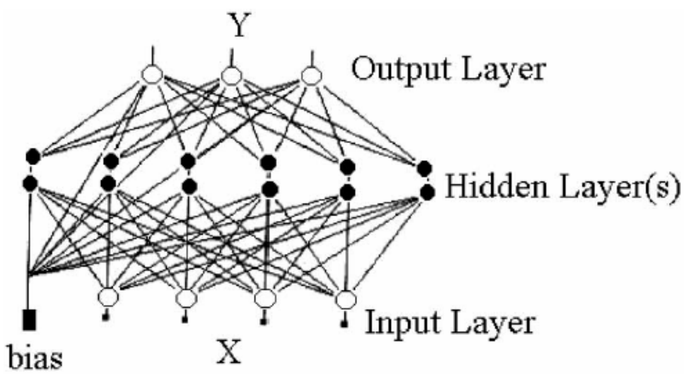


FIGURE 1 A typical multi-layer feed-forward ANN architecture.

Modeling Technique

To explore the complex relations between anti-icer design parameters and the resultant performance and impact attributes, artificial neural networks (ANNs) were chosen to be the modeling tool. ANNs provide a non-parametric, self-adaptive approach to information processing and are powerful in tackling complex, non-linear problems [17, 18, 19] where conventional modeling techniques (e.g., multiple regression) fail. We adopted multi-layer feed-forward ANNs for modeling, of which a typical architecture is shown in Figure 1. The nodes in the input and output layers consist of independent variables and response variable(s), respectively, whereas the topological structure of the hidden layer(s) depends on the complexity of the relationships. In this study, a modified back propagation algorithm was employed for the ANN training. The detailed description of data normalization, transfer function, and error propagation algorithm is provided elsewhere [17].

RESULTS AND DISCUSSION

Modeling Technique

The parameters and performance of the ANN models in this study are provided in Table 2. The relatively small training and testing errors show that the established ANN models have good "memory" and the trained matrices of interconnected weights and bias ("fabric" of the neural networks) reflect the hidden functional relationships well.

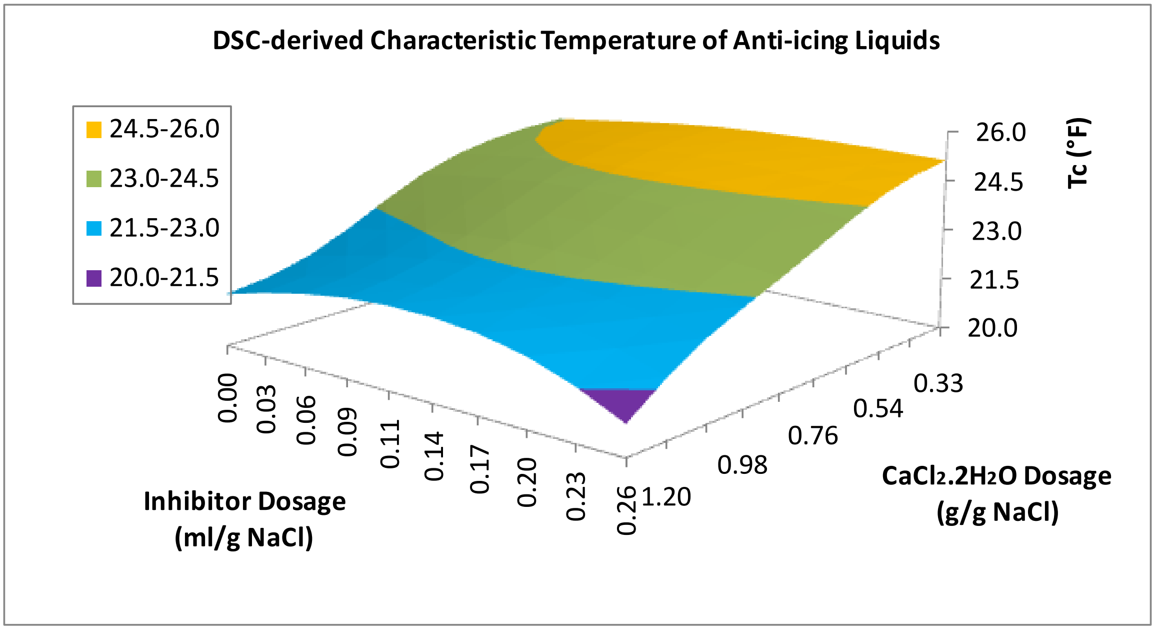
On a different note, the effort of using ANN to establish a predictive model for the mass loss of concrete after freeze-thaw exposure led to unreasonable and extremely irregular predictions. As such, the ANN model was discarded. This failed effort was consistent with the observation that the mass loss data featured high coefficients of variance, indicative of noise in the experimental data. This confirms the rule that *the predictive quality of any model would not exceed the quality of the data used to construct it*.

TABLE 2 Parameters and performance of the ANN models in this study

Response Variable	***Sum of the Mean Squared Error (SMSE)***		***Topological Structure of the ANN model***
	Training	Testing	
T_c (°F)	0.011	0.012	*3-6-1*
IMC at 60 min, 15°F (%, mL/mL)	0.038	0.042	*3-5-1*
IMC at 60 min, 30°F (%, mL/mL)	0.047	0.048	*3-5-1*
Predicted corrosivity (*PCR*)	0.021	0.030	*3-4-1*
STS of concrete after freeze-thaw cycling (psi)	0.049	0.055	*3-6-1*
Anti-icer composite index 1 (*cost-first*)	0.012	0.015	*3-5-1*
Anti-icer composite index 2 (*effects-first*)	0.057	0.055	*3-6-1*
Anti-icer composite index 3 (*performance-first*)	0.015	0.017	*3-6-1*
Anti-icer composite index 4 (*balanced approach*)	0.064	0.054	*3-6-1*

Anti-icer Performance and Impacts

For each anti-icer performance or impact attribute (also termed as "target attribute" or "response variable"), once the empirical ANN model was trained and tested it was used to predict the anti-icer property as a function of various design variables. This serves to identify meaningful trends and to guide the direction for formulation improvements. Such predictions were made with each design variable varying in the range of training data, since ANNs are not suitable for extrapolation.



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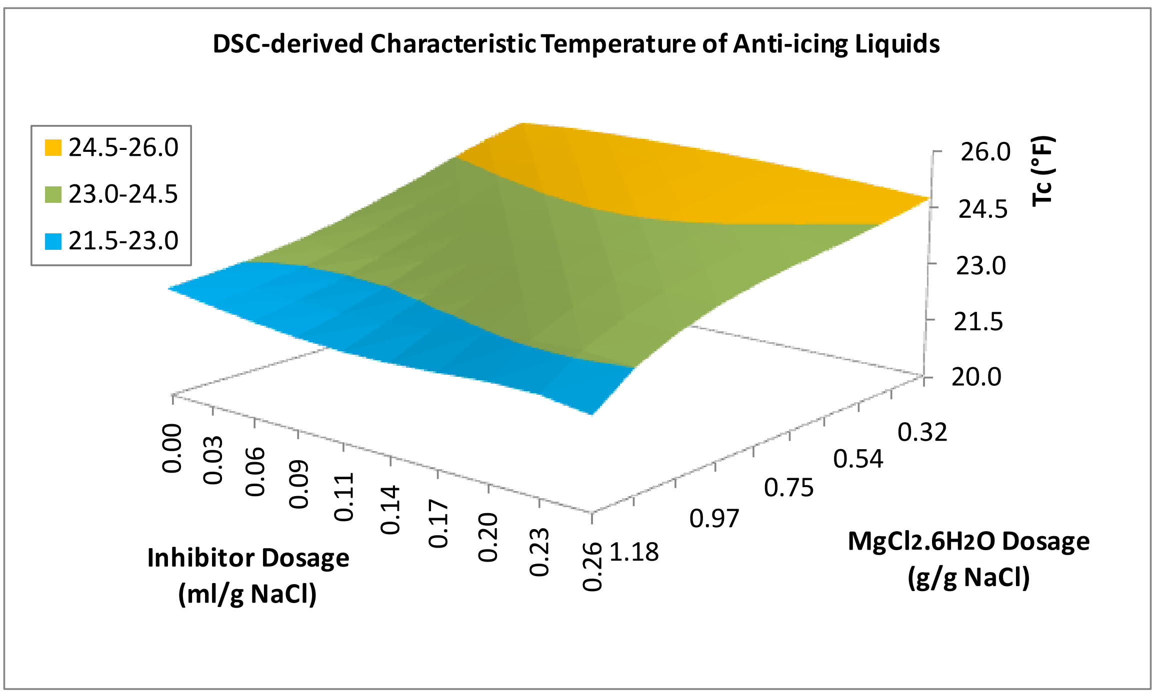
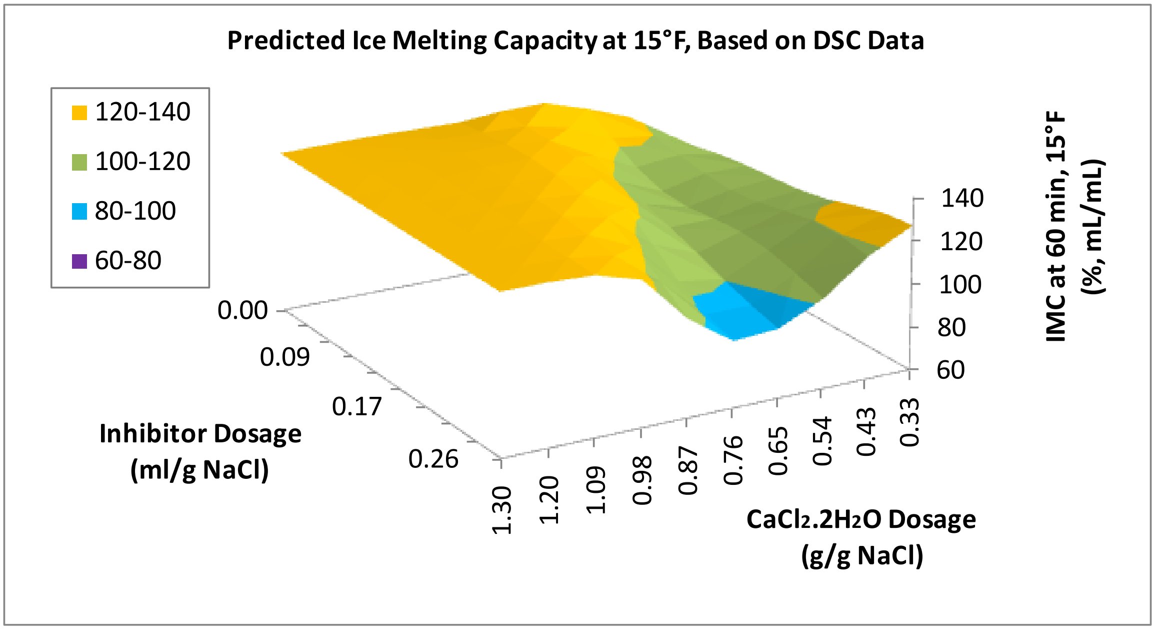


(b)

FIGURE 2 Predicted characteristic temperature as a function of (a) inhibitor and calcium chloride dosages, with $MgCl_2$•$6H_2O$/NaCl set at 0.65 g/g; (b) inhibitor and magnesium chloride dosages, with $CaCl_2$•$2H_2O$/NaCl set at 0.65 g/g.



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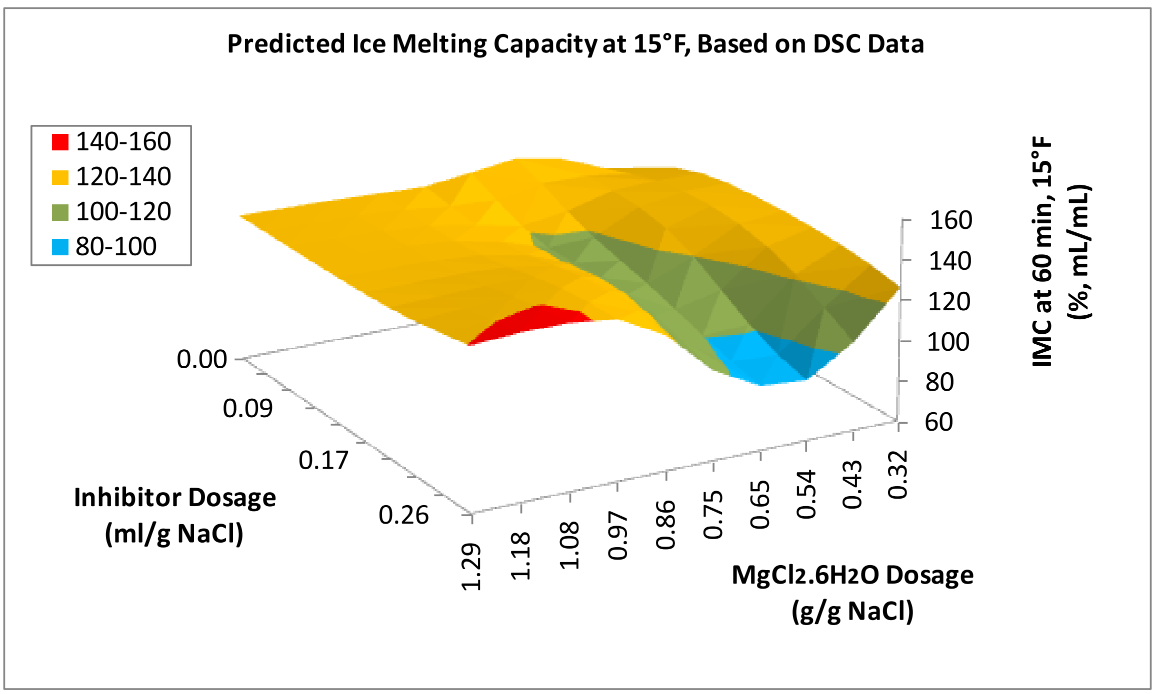
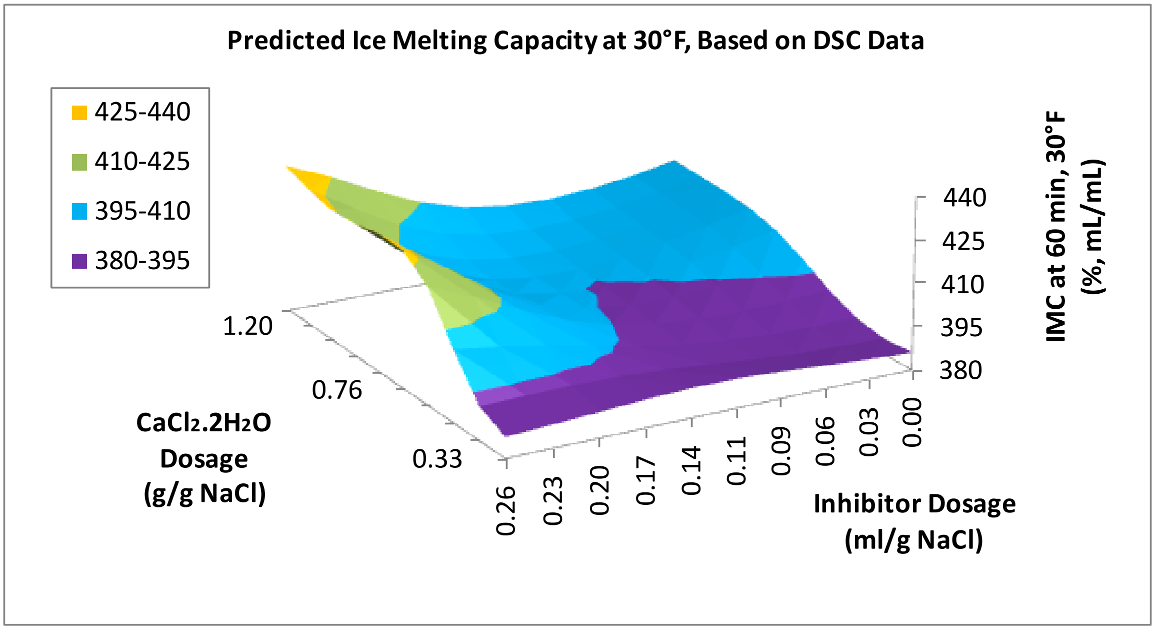


(b)

FIGURE 3 Predicted ice melting capacity at 60 min, 15°F, as a function of (a) inhibitor and calcium chloride dosages, with $MgCl_2 \cdot 6H_2O/NaCl$ set at 0.65 g/g; (b) inhibitor and magnesium chloride dosages, with $CaCl_2 \cdot 2H_2O/NaCl$ set at 0.65 g/g.



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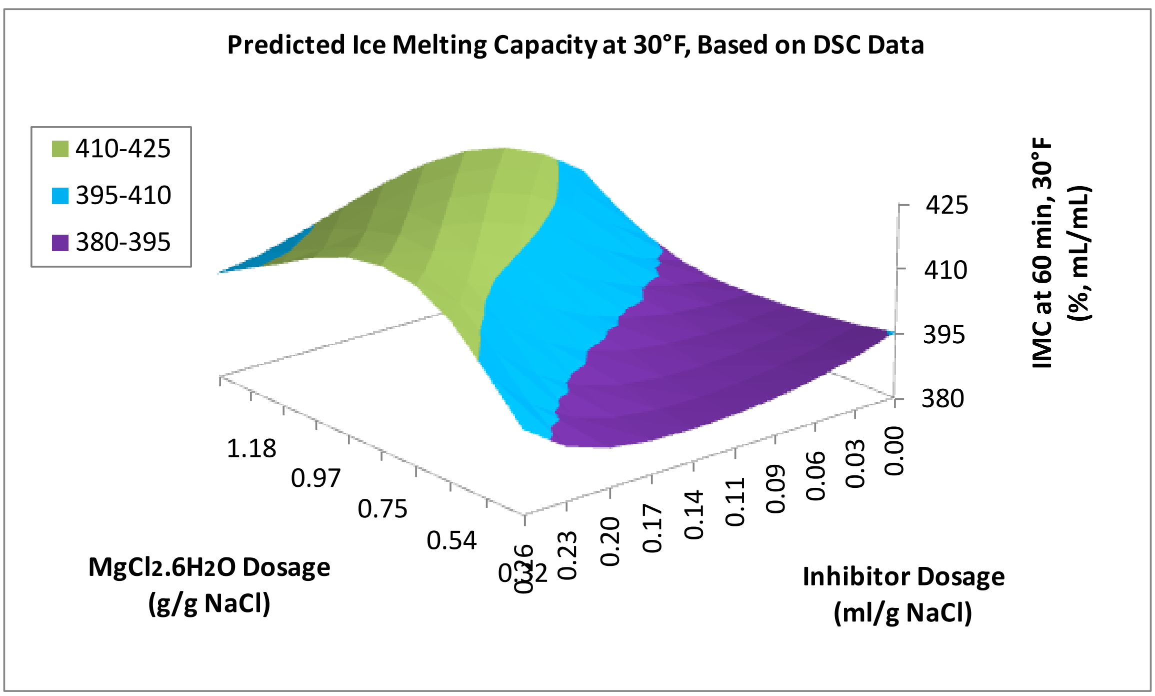


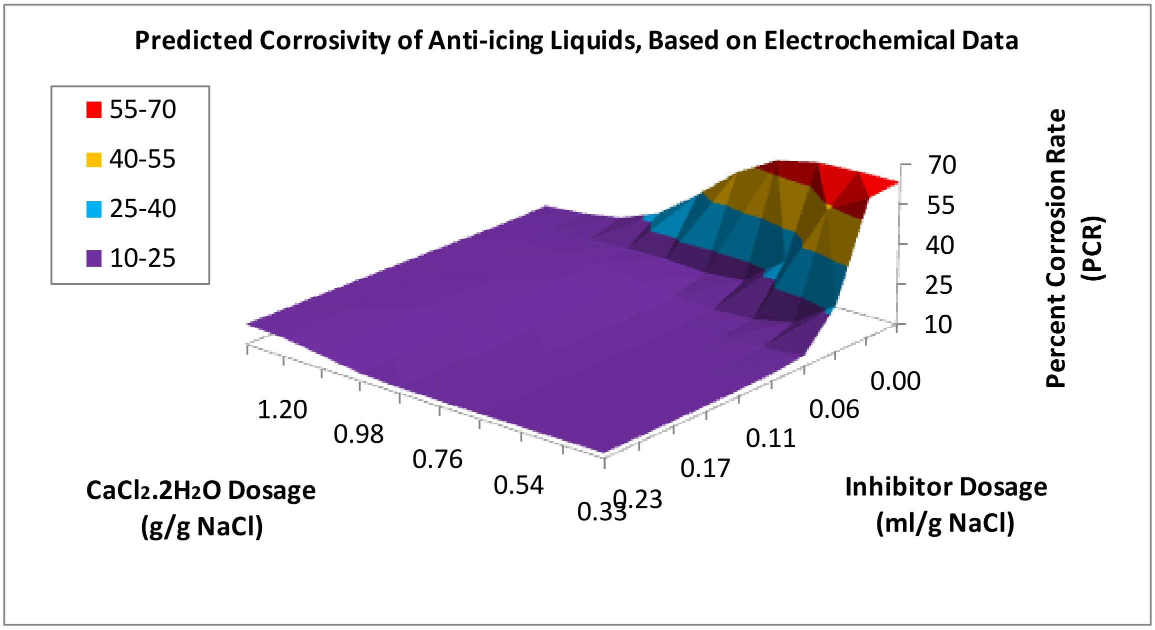
(b)

FIGURE 4 Predicted ice melting capacity at 60 min, 30°F, as a function of (a) inhibitor and calcium chloride dosages, with $MgCl_2$•$6H_2O$/NaCl set at 0.65 g/g; (b) inhibitor and magnesium chloride dosages, with $CaCl_2$•$2H_2O$/NaCl set at 0.65 g/g.

The performance characteristics of the anti-icers were assessed using DSC thermograms, which can detect phase transitions and shed light on the thermal behavior of each chloride-water-inhibitor mixture. As shown in Table 1, we used three parameters to characterize the performance of anti-icers: T_c, *IMC* (60-min) at 15°F (-9.4°C) and at 30°F (-1°C), the experimental data of which were used to establish ANN models and to construct response surfaces as shown in Figure 2, Figure 3, and Figure 4 respectively. Figure 2 indicates that T_c tends to decrease as the dosage of calcium chloride or magnesium chloride increases, which suggests the beneficial role of such addition in suppressing the freezing-point temperature of the mixture. It should be noted that the addition of more chlorides into the anti-icer is ultimately limited by the solubility of these chlorides in water. Figure 2 also shows that the effect of inhibitor concentration on T_c is much less obvious.

Figure 3 and Figure 4 present surface plots that illustrate the highly non-linear nature of the dependency of *IMC* on the anti-icer mix design, even though the maximum *IMC* values tend to correspond to high concentrations of calcium chloride or magnesium chloride. Figure 3 shows that the minimum *IMC* values at 15°F (-9.4°C) correspond to high inhibitor concentrations, when calcium or magnesium chloride by weight of sodium chloride falls in the range of 0.65-0.76. *IMC* values lower than 100 (%, mL/mL) suggest a negative melting amount, or freezing of the applied anti-icer. Figure 4 shows that the maximum *IMC* values at 30°F (-1°C) correspond to high inhibitor concentrations, with chloride concentrations in the high range as well.

The corrosion impact of the anti-icers on metals was assessed using the electrochemical testing of mild steel exposed to diluted anti-icers and wet-dry cycling. The electrochemical data were ultimately translated to corrosion rate information, in terms of PCR for each diluted anti-icer. The higher the PCR value, the more corrosive the solution is to mild steel. The PCR data were used to establish ANN models, the predictions of which were then used to construct response surfaces. Figure 5 indicates that *PCR* tends to decrease as the concentration of corrosion inhibitor increases, which confirms the designed role of the inhibitor. The corrosivity of anti-icer to mild steel becomes low (with PCR generally lower than 25) when the inhibitor concentration exceeds 0.06 mL per gram of sodium chloride. Beyond this critical concentration, further increase in the inhibitor concentration shows little benefit in reducing anti-icer corrosivity. It should be cautioned that these findings may change if a different corrosion inhibitor is chosen for anti-icer formulations or if a different metal is considered in the evaluation. Figure 5 also shows that the effect of chloride concentration on *PCR* is much less obvious.



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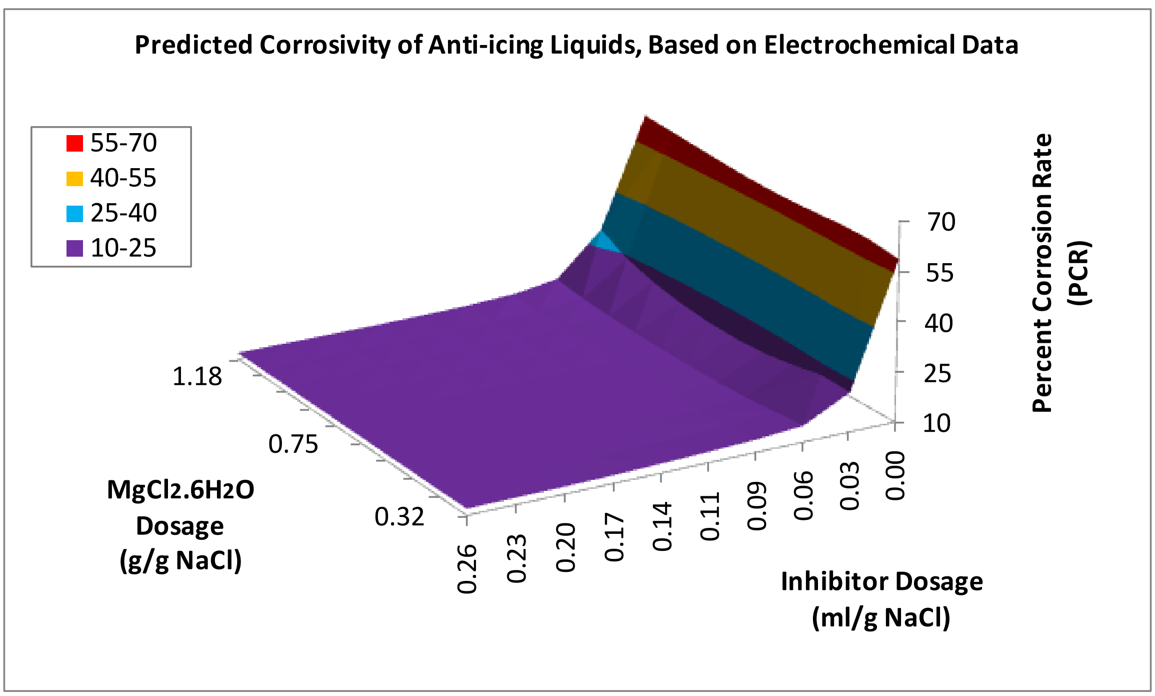
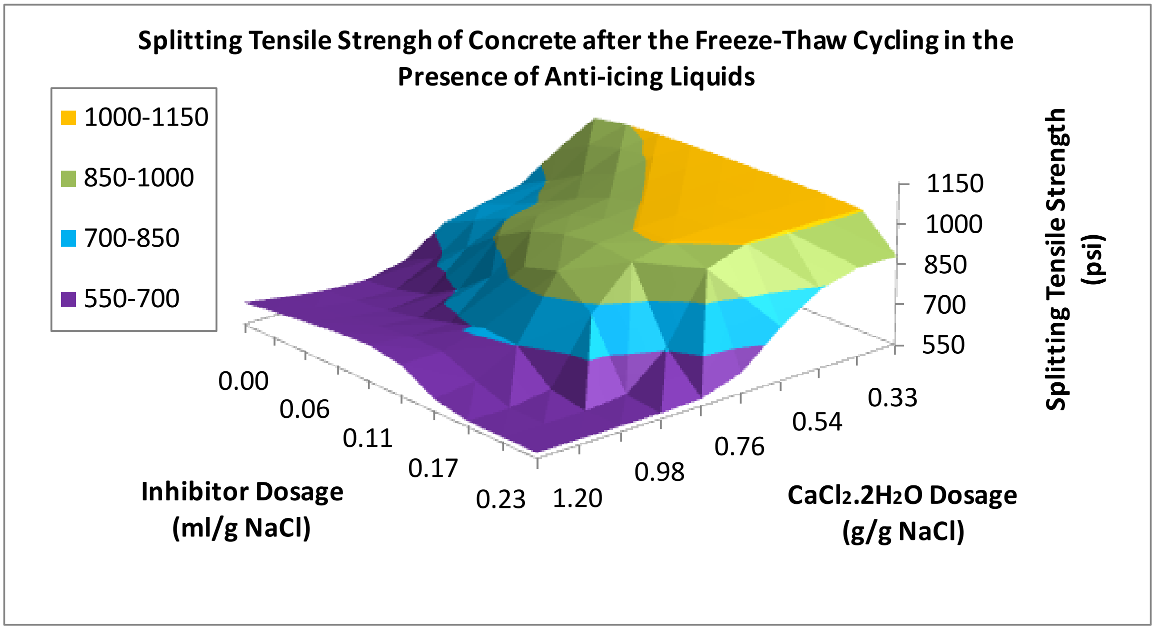


(b)

FIGURE 5 Predicted anti-icer corrosivity as a function of (a) inhibitor and calcium chloride dosages, with $MgCl_2 \cdot 6H_2O/NaCl$ set at 0.65 g/g; (b) inhibitor and magnesium chloride dosages, with $CaCl_2 \cdot 2H_2O/NaCl$ set at 0.65 g/g.



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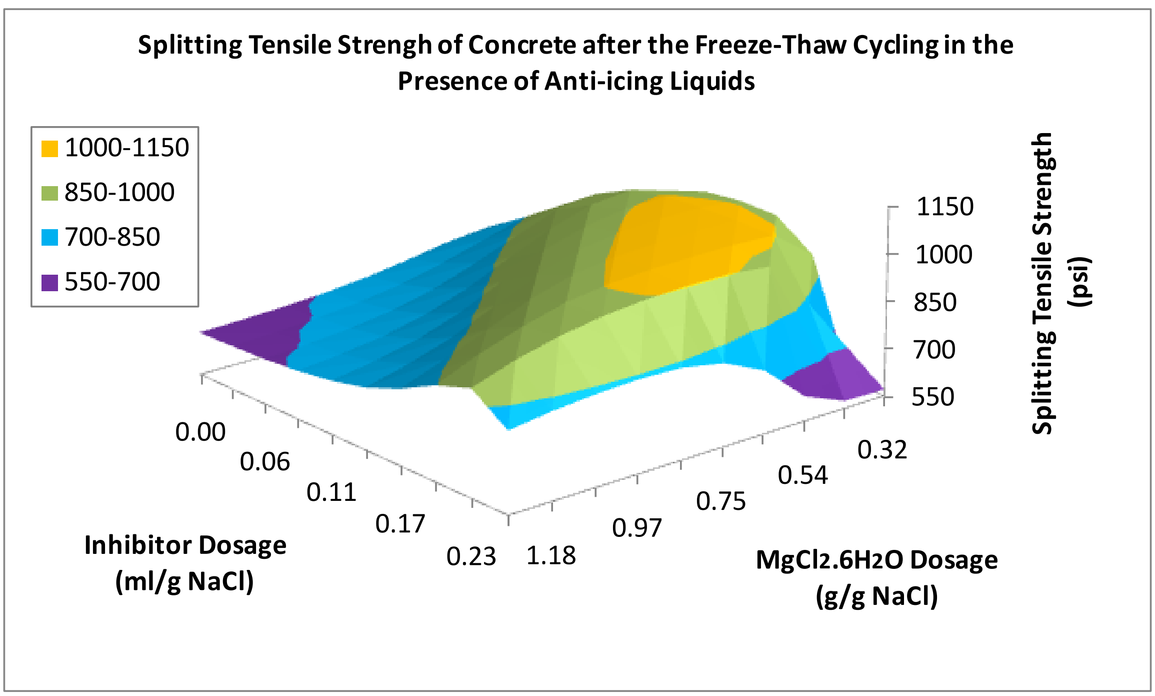


(b)

FIGURE 6 Predicted splitting tensile strength of concrete after the freeze-thaw cycling in the presence of anti-icer, as a function of (a) inhibitor and calcium chloride dosages, with $MgCl_2{\bullet}6H_2O$/NaCl set at 0.65 g/g; (b) inhibitor and magnesium chloride dosages, with $CaCl_2{\bullet}2H_2O$/NaCl set at 0.65 g/g.

The impact of the anti-icers on concrete was assessed by exposing PCC specimens to diluted anti-icers and freeze-thaw cycling and subsequently measuring the mass loss of the specimens and testing their *STS*. As shown in Table 1, greater freeze-thaw damage (higher mass loss) is generally associated with reduced *STS*. Note that the indices of freeze-thaw mass loss and *STS* were normalized from actual mass loss (%) and *STS* (psi) by setting the mass loss and *STS* of concrete exposed to water and 3% NaCl as 0 and 100 respectively. The freeze-thaw mass loss of concrete exposed to water and 3% NaCl averaged 0.34% and 5.42% respectively, whereas the *STS* of concrete exposed to water and 3% NaCl averaged 1152 psi (7.9 MPa) and 715 psi (4.9 MPa) respectively.

The *STS* data were used to establish ANN models, the predictions of which were then used to construct response surfaces. Figure 6 shows that the high *STS* values of concrete, i.e., those greater than 1000 psi (6.9 MPa) correspond to anti-icer formulations with inhibitor and calcium or magnesium chloride by weight of sodium chloride in the range of 0.11-0.23 and 0.43-0.65 respectively. Figure 6(a) indicates that the low *STS* values of concrete (indicative of severe freeze-thaw damage) correspond to high calcium chloride concentrations. Figure 6(b) indicates that the low *STS* values of concrete correspond to either high magnesium chloride concentrations coupled with low inhibitor concentrations, or low magnesium chloride concentrations coupled with high inhibitor concentrations. It should be cautioned that these findings may change if a different corrosion inhibitor is chosen for anti-icer formulations or if a different concrete mix (e.g., with air entrainment) is considered in the evaluation.

The impact of the anti-icers on asphalt was assessed by exposing asphalt binder to anti-icers and thermal and pressure aging and subsequently testing the binder beams with BBR. The BBR test provides values for creep stiffness (higher *S* values correspond to higher thermal stresses so a maximum limit of 300 MPa was specified) and *m*-value (lower *m* values indicate a lesser ability to relax so a minimum limit of 0.30 was specified). We tested a few anti-icer formulations shown in Table 1 (Mix Nos. 5, 7, 8, and 16) that feature the highest and lowest chloride or corrosion inhibitor concentrations in addition to two controls (1: standard practice and 2: exposure to water). The experimental results indicated little effect of anti-icer design on the performance of asphalt binder. In all exposures tested, the *m*-value and stiffness met specifications (fell in 0.315-0.333 and 185-207 MPa respectively). As such, the anti-icer impact on asphalt was excluded from further analysis, such as the calculations of composite indices or the modeling process. Acetate-based anti-icers have demonstrated negative effects on asphalt performance, primarily through binder emulsification [5]. If the techniques described in this paper are used to evaluate non-chloride anti-icers, their impacts to asphalt should be investigated for possible inclusion in the comprehensive assessment.

Finally, in this study, we assumed the differences in the environmental impacts of the anti-icers and their persistence on the road surface statistically insignificant and thus excluded these target attributes from further analysis. It is desirable to include the environmental impacts of anti-icers into the comprehensive evaluation, especially when chlorides are compared against acetates, formates, or other alternatives and when quantitative or semi-quantitative data of different anti-icers on water quality, air quality, soil, vegetation, wildlife, etc. become available.

Multi-criteria Decision-making Framework for Anti-icer Formulation

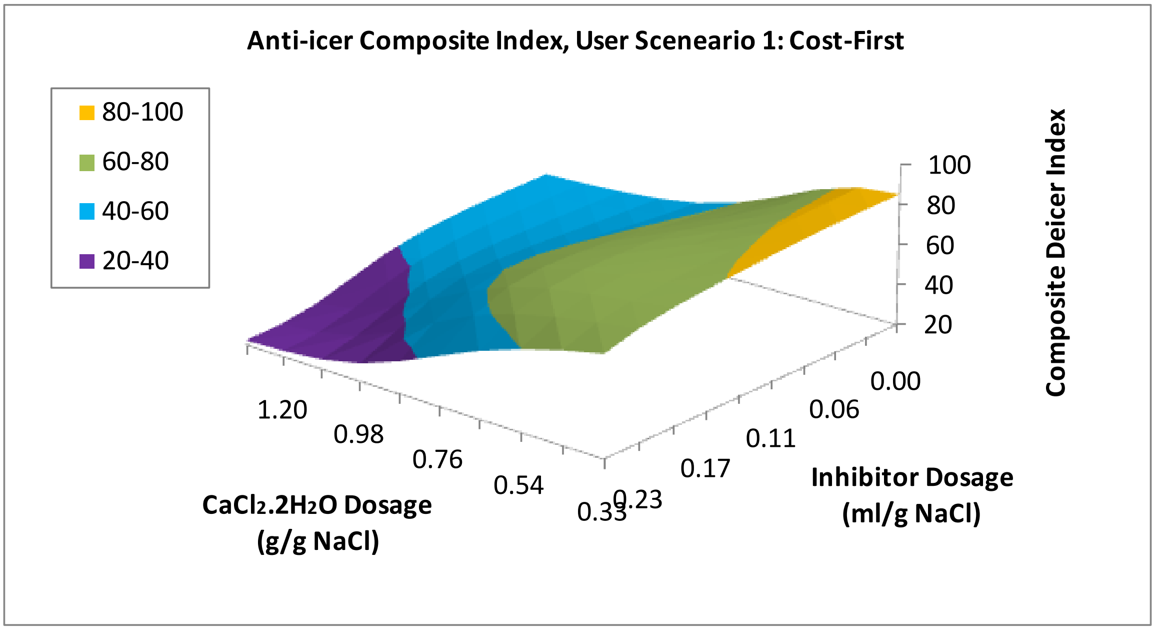
This section will demonstrate a holistic perspective in the design and selection of anti-icer liquids, by integrating user priorities with the laboratory testing data and cost data. A recent practitioner survey identified some key desirable attributes of anti-icers, e.g., low cost per lane mile, low effective temperature, high ice-melting capacity, ease of application, and overall safety benefits for winter roads. Major concerns regarding anti-icers included: corrosion to metals, damage to concrete and asphalt pavements, and reduced water quality [20]. To enable data-driven, multi-criteria decision making, we present herein four user priority scenarios and describe how in each scenario the anti-icer formulation could be optimized with the use of a composite index. This type of "*what-if*" analysis demonstrates how agencies may make more informed, defensible decisions in selecting, purchasing, or formulating liquids for snow and ice control.

TABLE 3 Decision weights for four possible scenarios

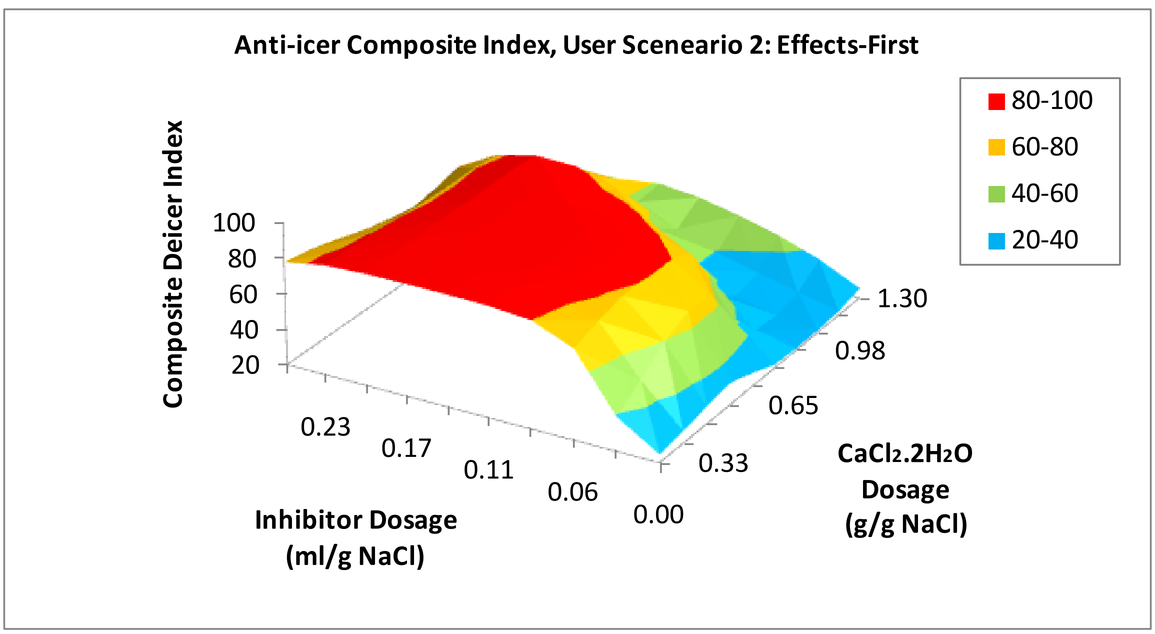
Scenario	***Cost***	***Characteristic Temperature***	***Ice Melting Capacity***	***Corrosion to Metals***	***Effect on Concrete***
1: Cost-first	10	1	1	1	1
2: Effects-first	1	1	1	10	10
3: Performance-first	1	10	10	1	1
4: Balanced-approach	7.0	7.5	7.8	7.9	8.6

As shown in Table 3, the four different scenarios to consider are: *cost-first*, *effects-first*, *performance-first* and a *balanced approach*, each of which places a different set of decision weights on various target attributes, with 1 being least important and 10 being most important. The decision weights were then normalized so that their sum across all target attributes becomes 100%. For each anti-icer in Table 1, the values of each target attribute were first normalized between 0 and 100, with 0 being the worst performance or most severe impact and 100 being the best performance or least impact. For the given scenario, the composite index for each anti-icer was calculated by multiplying the normalized decision weight with the corresponding value of the specific target attribute before addition across attributes. The *composite index* data were used to establish ANN models, the predictions of which were then used to construct response surfaces as shown in Figure 7, which highlights the change of optimal anti-icer formulation (indicated by high index values) with the user priorities. For instance, the optimal anti-icer in the *cost-first* scenario would feature low inhibitor concentration, whereas that in the *effects-first* scenario would feature relatively high inhibitor concentration, as illustrated by Figures 7(a) and 7(b). In the other two scenarios illustrated by Figures 7(c) and 7(d), the optimal inhibitor and chloride concentrations fall in different ranges, relative to the former two scenarios.

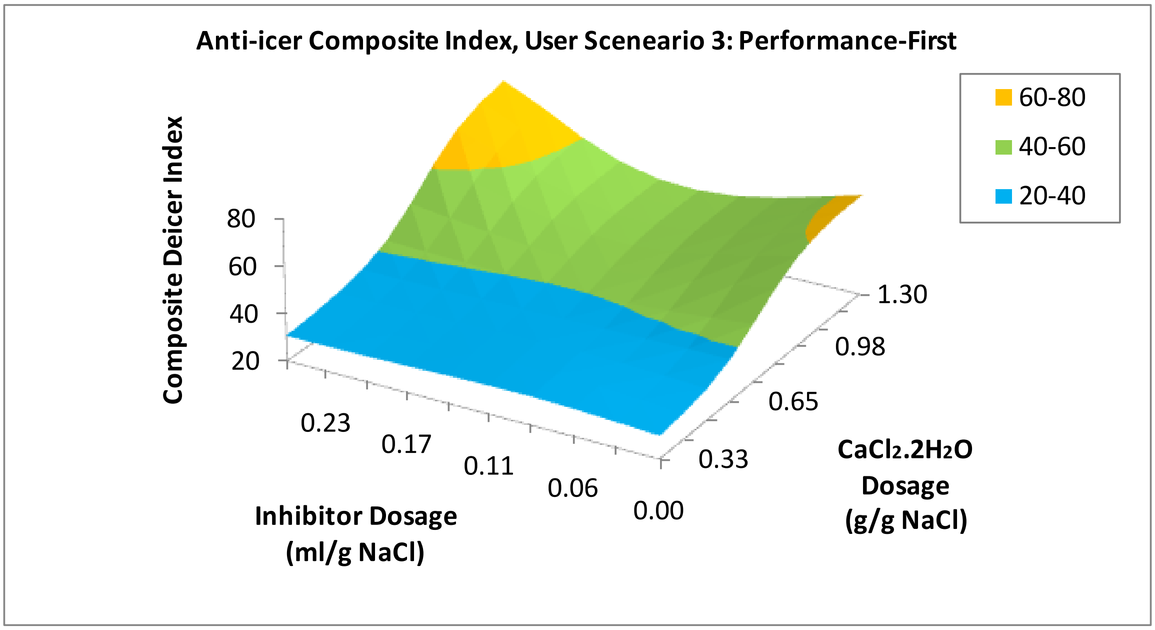
Note that the multi-criteria decision-making approach demonstrated herein has its own caveats and the conclusions derived from the laboratory testing should be used with caution. For instance, the laboratory testing data may not be good predictors of field performance or impacts, which tend to be site-specific and change as a function of many variables beyond those simulated in the laboratory setting. Existing laboratory tests may not be comprehensive enough to examine all aspects of anti-icers. For instance, the persistence of the chemicals on the road surface is an important aspect to consider when transportation agencies purchase or formulate their anti-icing liquids. Currently there are significant data gaps when it comes to the quantification of environmental impacts of anti-icers (e.g., toxicity to aquatic species) and their longevity on the road surface. These present challenges and knowledge gaps to be addressed by future research.



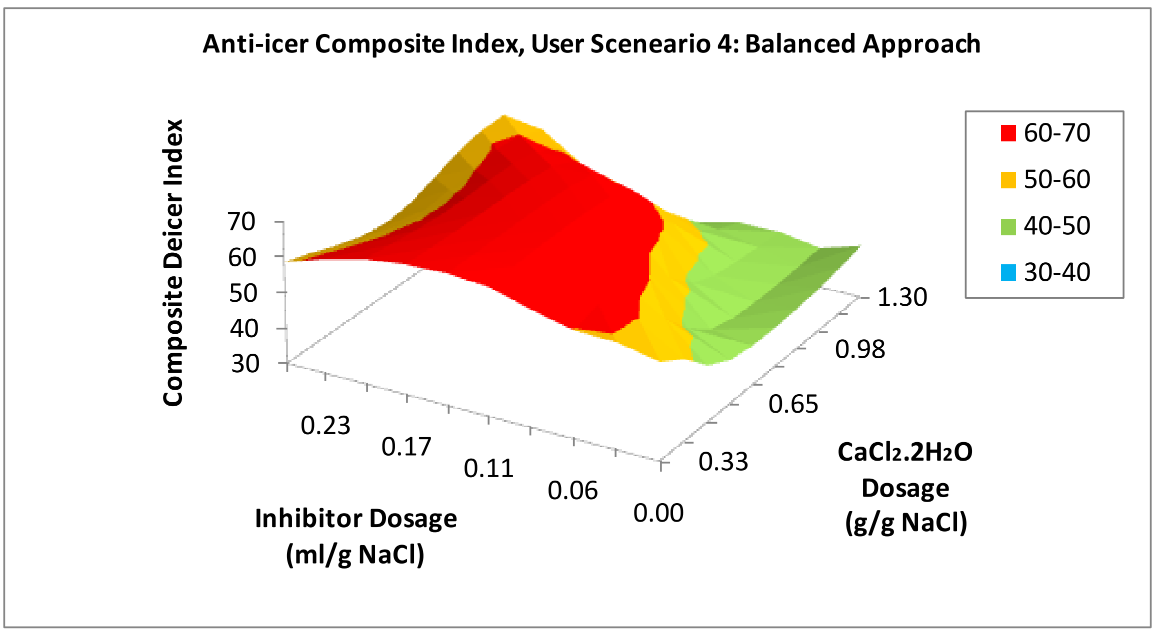
(a)



(b)



(c)



(d)

FIGURE 7 Predicted anti-icer composite index for different user priority scenarios: (a) *cost-first*, (b) *effects-first*, (c) *performance-first*, and (d) *balanced-approach*, as a function of inhibitor and calcium chloride dosages, with $MgCl_2 \cdot 6H_2O/NaCl$ set at 0.65 g/g.

CONCLUSIONS

This work demonstrates a systematic approach to data-driven, multi-criteria decision-making, by conducting a set of laboratory tests to assess twenty blended chloride-based anti-icing formulations. The laboratory data were then used to establish predictive models correlating the multiple design parameters with the anti-icer performance and impacts or with an *anti-icer composite index*. We used artificial neural networks for modeling and examined anti-icer performance (characteristic temperature and ice-melting capacity at 30°F and 15°F respectively) and impacts (splitting tensile strength of concrete after ten freeze-thaw cycles and corrosivity to mild steel) as a function of the formulation design. The *anti-icer composite index* was calculated for four different user priority scenarios, each of which placed a different set of decision weights on various target attributes. Response surfaces were then constructed to illustrate such predicted correlations and to guide the direction for formulation improvements. This work also adds to the knowledge base relevant to the performance and impacts of chloride blends.

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