



## Exploring the performance and corrosivity of chloride deicer solutions: Laboratory investigation and quantitative modeling

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### ABSTRACT

Maintenance agencies are continually challenged to provide a high level of service and improve safety and mobility of winter roads in a cost-effective manner while minimizing corrosion and other adverse effects to the environment. This study investigated the baseline performance data of typical chloride deicers used on highways, by conducting the Modified SHRP (Strategic Highway Research Program) Ice Melting Test of select solid chemicals and liquid deicers at  $-1\text{ }^{\circ}\text{C}$  ( $30\text{ }^{\circ}\text{F}$ ),  $-9\text{ }^{\circ}\text{C}$  ( $15\text{ }^{\circ}\text{F}$ ), and  $-18\text{ }^{\circ}\text{C}$  ( $0\text{ }^{\circ}\text{F}$ ), respectively. The thermal properties and ice melting performance of solid chemicals and liquid deicers were also tested in the laboratory, and the effect of blending two chloride deicer solutions with or without an agro-based product was explored. Furthermore, this work aims to demonstrate the feasibility of using an electrochemical corrosion test as a supplement to the gravimetric corrosion test. It also aims to shed light on the correlations between the composition and the corrosivity and performance of deicers respectively. To this end, artificial neural networks (ANNs) were used to establish predictive models and to quantify such cause-and-effect relationships. One ANN model was established to correlate the electrochemical corrosion data (along with solution conductivity) with those from the gravimetric test method. Two additional ANN models were established to achieve better understanding of the correlation between the deicer composition (type, chloride and inhibitor concentrations, pH, and electrical conductivity) and their corrosivity and performance respectively. According to the modeling, there are strong correlations inherent in the deicer samples, whereas the trends differ as a function of the deicer type and the solution conductivity. The established ANN models were then used for numerical investigations on the parameters affecting the deicer properties and for quality assurance of deicers or enhancing deicer design.

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### 1. Introduction

Chloride-based salts are the most common chemicals used to serve as freezing-point depressants for winter road maintenance applications. Despite the previous studies on the performance of such salts as deicers (Fay and Shi, 2011; Nixon et al., 2005, 2007), they often tested commercial products (with salts mixed with proprietary additives) and reported performance at given temperatures or given time of application (e.g., 60 min). As such, there still is the need for more reliable baseline data in the published domain to illustrate how the ice melting performance of pure chloride salts evolves over time once applied on an ice layer. While such laboratory data cannot be directly used to guide field operations, they can unravel the interactions between the applied salt and the ice and shed light on the complex dynamics on field pavement where salt, snow/ice,

pavement, traffic and possibly solar radiation and wind all come into play. Yehia and Tuan (1998) suggested that the lowest effective application temperature for calcium chloride ( $\text{CaCl}_2$ ), magnesium chloride ( $\text{MgCl}_2$ ) and sodium chloride ( $\text{NaCl}$ ) was  $-25\text{ }^{\circ}\text{C}$  ( $-13\text{ }^{\circ}\text{F}$ ),  $-15\text{ }^{\circ}\text{C}$  ( $5\text{ }^{\circ}\text{F}$ ), and  $-10\text{ }^{\circ}\text{C}$  ( $14\text{ }^{\circ}\text{F}$ ), respectively.  $\text{CaCl}_2$  and  $\text{MgCl}_2$  are more costly than  $\text{NaCl}$ , and they can be difficult to handle. At low relative humidity, their residue on roads can attract more moisture than  $\text{NaCl}$ , resulting in dangerous, slippery conditions under certain circumstances (Center for Watershed Protection, 2003). One laboratory study demonstrated that at  $23\text{ }^{\circ}\text{F}$  ( $-5\text{ }^{\circ}\text{C}$ ) the relative area deiced by chemicals followed the descending order:  $\text{NaCl}$ ,  $\text{CaCl}_2$ , calcium magnesium acetate (CMA), and urea, whereas their relative rate at which the chemicals debonded ice and pavement followed the descending order:  $\text{CaCl}_2$ ,  $\text{NaCl}$ , urea, and CMA (Trost et al., 1987).

The growing use of deicers has raised concerns about their effects on motor vehicles (Johnson, 2002; Menzies, 1991), transportation infrastructure (Shi et al., 2009a, 2009b, 2010), and the environment (Fay and Shi, 2012). For instance, a 1985–1990 field study in Sweden revealed that compared with those exposed to ( $\text{NaCl}$ ) salted roads, the cars driven on unsalted roads had 50% less incidence of cosmetic

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corrosion and the carbon steel test panels had a more than 90% reduction in corrosion rate (Rendahl and Hedlund, 1992). The corrosion of motor vehicles due to road salts was estimated to cost \$2.8 billion to \$5.6 billion per year, including the added manufacturing expense for vehicle protection and preventive maintenance and the cost of owner preventive maintenance and cosmetic-corrosion-related vehicle depreciation (Menzies, 1992). Arguably the cost of vehicular corrosion should have decreased since then, as vehicles today feature improved corrosion resistance via better design and materials selection. There are a variety of thermodynamic and kinetic factors (e.g., humidity, chloride and inhibitor concentrations, dissolved oxygen, pH, and temperature) that determine the tendency and rate of vehicular corrosion respectively. Deicers can pose significant corrosion risk to bare or coated metals in transportation infrastructure, such as steel bridges, guard rails, dowel bars, and rebars (Shi et al., 2009b, 2010). One study published in 1992 estimated that road salt imposed infrastructure corrosion costs of at least \$615/t, vehicular corrosion costs of at least \$113/t, aesthetic costs of \$75/t if applied near environmentally sensitive areas, plus uncertain human health costs (Vitaliano, 1992).

Often, commercially available, corrosion-inhibited versions of chloride salts are used to reduce their deleterious impacts on vehicles and infrastructure. Fay and Shi (2011) developed a systematic approach to assist maintenance agencies in selecting or formulating their deicers, which integrates the information available pertinent to various aspects of deicers and incorporates agency priorities. The Pacific Northwest Snowfighters (PNS), an Association of transportation professionals for British Columbia, Colorado, Idaho, Montana, Oregon, and Washington, has implemented testing protocols and guidelines for new product qualification for deicers. A central feature of these requirements is the presence of corrosion inhibitor in all deicers, and the qualification and evaluation of all deicers by a modified National Association of Corrosion Engineers (NACE) corrosion test. The PNS/NACE test is based on a gravimetric method that entails cyclic immersion of multiple parallel coupons for 72 h on a custom design machine (PNS, 2010). For quality assurance and litigation purposes, a faster, more reliable technique is desirable to evaluate the corrosivity of chemical deicers. In this context, this work aims to evaluate the feasibility of using a rapid (electrochemical) test to predict the corrosivity of deicers without running the gravimetric test.

Prior to this study, there is a lack of studies in the published domain that illustrate how the concentrations of various chlorides and corrosion inhibitors contribute to the corrosivity and deicing performance of the formulated product. As such, this work also aims to establish predictive models that shed light on the quantitative correlations between the composition and the corrosivity and performance of deicers respectively. Such models can be used to improve the design of more powerful and less corrosive deicers.

## 2. Experimental

### 2.1. Deicers of interest and laboratory testing

As detailed elsewhere (Akin and Shi, 2012), Modified SHRP Ice Melting Tests were conducted in a Plexiglas chamber in a 12 ft. × 14 ft. state-of-the-art temperature-regulated environmental chamber using de-ionized water. The tests were conducted at  $-1\text{ }^{\circ}\text{C}$  ( $30\text{ }^{\circ}\text{F}$ ),  $-9\text{ }^{\circ}\text{C}$  ( $15\text{ }^{\circ}\text{F}$ ), and  $-18\text{ }^{\circ}\text{C}$  ( $0\text{ }^{\circ}\text{F}$ ),  $\pm 0.3\text{ }^{\circ}\text{C}$  ( $0.5\text{ }^{\circ}\text{F}$ ), with triplicate samples tested for each combination of deicer type and temperature. For testing solid deicers,  $4.170 \pm 0.005\text{ g}$  of deicer are broadcast over the ice sample. For testing liquid deicers, 3.8 ml of deicer is applied evenly over the ice surface with a syringe. After 10, 20, 30, 45, and 60 min respectively, the liquid volume is removed and volumetrically measured with a calibrated syringe (after measuring the liquid is returned to the ice sample). All liquid deicers tested were commercial products, whereas all solid deicers were reagent-grade chemicals featuring high purity and little contaminants or additives. Reagent-grade solid NaCl (from

Fisher Scientific),  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  (from Sigma-Aldrich), and  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  (from Acros Organics) with minimum purity of 99.0% were used. In addition, commercial deicers and their blends were tested. The Illinois Department of Transportation (DOT) provided the 23% NaCl deicer, the 32%  $\text{CaCl}_2$  deicer, and AGBP (an anti-icing liquid product/additive derived from the sugar beet industry). The Minnesota DOT provided the 30%  $\text{MgCl}_2$  deicer.

The rest of this work involved an inhibited NaCl liquid deicer, an inhibited  $\text{CaCl}_2$  liquid deicer (Calcium Chloride with Boost, or CCB™), and an inhibited  $\text{MgCl}_2$  liquid deicer (FreezGard CI Plus™). They represent deicer products under select PNS categories. The inhibited NaCl liquid deicer was prepared by adding a given amount of Shield GLT™ inhibitor (by Paradigm Chemical LLC, Lakewood, CO) into the mixture of well water and solid “rock salt” from Compass Minerals (Overland Park, KS) with salt/water weight ratio of 20/80 and stirring to blend (as specified by the GLT vendor), whereas the CCB and FreezGard were purchased from America West (Pasco, WA) and Compass Minerals (Overland Park, KS) respectively. As a diverse representation of these three types of deicers was essential to enable modeling, samples were made both by sampling the liquid deicer tanks over 14 months of field storage (Shi et al., 2012) and by mixing each non-inhibited brine with its associated inhibitor provided by vendors, at 0%, 1%, 2%, 3%, 4%, and 5%, respectively. The details of measuring chloride and inhibitor concentrations, pH, electrical conductivity, and thermal properties of deicer samples are provided elsewhere (Shi et al., 2011). The corrosion of deicer samples to carbon steel was also tested using two different methods, one of which was a gravimetric method and the other was an electrochemical method. The gravimetric method followed the NACE Standard TM0169-95 as modified by the PNS Association (PNS, 2010), but used de-ionized water in place of distilled water. Three replicate  $1.38'' \times 0.56'' \times 0.11''$  ASTM F436, Type 1 TSI® steel washers with a Rockwell Hardness of C 38–45 were used in each deicer solution and in the control solutions (de-ionized water and a 3% NaCl aqueous solution) for testing. The average cross-section loss result in MPY (milli-inch per year) was translated into a percentage, or percent corrosion rate (PCR, with no unit), in terms of the 72-h average corrosivity of the deicer solution relative to solid salt (NaCl). The electrochemical method was established to allow rapid determination of corrosion rate of metals and to reveal information pertinent to the corrosion and inhibition mechanisms. Corrosion of the deicers (diluted to 3% aqueous solution of the as-received sample) to ASTM A36 mild steel coupons was measured using a Gamry Instruments® Potentiostat and a conventional three-electrode system. At 24 h of continuous immersion, the potentiodynamic polarization curve of four replicate steel specimens in each diluted deicer was taken respectively. The current-potential plot of the steel in deicer solution was measured when an external potential signal (DC perturbation) was applied within  $\pm 30\text{ mV}$  range of its open circuit potential at a sweeping rate of 1 mV/s. The resulted weak polarization curve, potential ( $E$ , in mV) as a function of logarithm of current density ( $i$ , in  $\mu\text{A}/\text{cm}^2$ ), was then used to derive the corrosion potential ( $E_{\text{corr}}$ ) of the steel in the specific solution and its instantaneous corrosion rate in terms of corrosion current density ( $i_{\text{corr}}$ ). These parameters were taken from the point where the anodic current density ( $i_a$ ) equals the cathodic current density ( $i_c$ ) on the working electrode (i.e., mild steel).

### 2.2. Modeling technique

In this work, one quantitative model was established to predict the 72-h average corrosivity of chloride-based deicers (PCR) as a function of deicer type,  $E_{\text{corr}}$ ,  $i_{\text{corr}}$ , and solution conductivity, so as to demonstrate the feasibility of using a rapid (electrochemical) test to predict the corrosivity of deicers without running the gravimetric test. Two other quantitative models were established to predict the deicer corrosivity (PCR) and performance (in characteristic temperature,  $T_c$ ), respectively,

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