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Addition of amines to molasses and lees as corrosion inhibitors in sustainable de-icing materials

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ABSTRACT

The waste formed during sugar- and wine-making activities has attracted our attention given its ability to inhibit corrosion in the presence of brine in a de-icing formulation. Herein the addition of amines to de-sugared beet molasses and winery lees is found to improve their anti-corrosive properties. Thus, weight-loss experiments clearly show that the addition of a small amount of amines to molasses or lees results in marked corrosion inhibition on carbon and galvanized steel. Subsequent electrochemical experiments and microscopy studies supported this finding. In addition, microscopy images indicated that triethanolamine was the best candidate amongst the amines tested for use in the final de-icing formulation. Ice-melting experiments demonstrated that the presence of molasses/lees together with triethanolamine does not alter the properties of the de-icing agent. When corrosion on galvanized and carbon steel probes was measured under environmental conditions, a decrease of 88% for galvanized steel and 65% for carbon steel was achieved due to the inhibiting action of the molasses/triethanolamine mixture. These results suggest that the addition of molasses/lees and triethanolamine to brine-based de-icing agents is recommended.

1. Introduction

Winter road maintenance is essential for public transportation while ensuring population safety and minimizing risks. The use of chemicals (mainly chloride salts) plays a critical role in de-icing formulations. However, these salts are also claimed to be responsible for detrimental effects, such as the corrosion of road elements and environmental contamination. As such, there is a need to minimize the adverse effects of these de-icing formulations while maintaining their de-icing properties. De-sugared beet molasses (Garcia Serrada and Vara Pazos, 2017; Ossian and Behrens, 2008; Bloomer, 2000; Higgin-Botham et al., 2014; Petkuviene and Paliulis, 2009; Augsburger and Darlington, 1985; Maslow et al., 2013; Mertz and Gall, 2000; Chandler et al., 2002) and winery lees (Janke George and Johnson, 1998), when combined with brine, are considered to be good materials for road maintenance as the main components of anti-freezing and de-icing formulations. Brine solutions mainly comprise chlorides as counteranions in salts that are used worldwide in winter to improve road safety. Anti-freezers mitigate the possibility of snow and ice formation on the pavement surface, while de-icers increase the grip between vehicle tires and the pavement in snowy and icy conditions (Terry et al., 2020; Shi and Jungwirth, 2018).

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Nevertheless, the use of chloride salts has some negative effects on the environment, such as roadside vegetation, soils and ground water on the surrounding land (Baltrenas et al., 2006; Ratkevičius et al., 2014; Vignisdottir et al., 2019; Honarvar Nazari et al., 2021), as well as on road infrastructure, including vehicles. Man-made road elements such as bridges, pavements, traffic signs, sidewalks, reinforced concrete structures, electrical elements and sub-terrestrial means of transportation are also damaged by the corrosion provoked by these salts over the years (Sajid et al., 2022; Petkuviene and Paliulis, 2009). Among the different salts available (e.g. NaCl, $CaCl_2$, NaCl:$CaCl_2$), sodium chloride is by far the most widely used given its low price and ease of application. The use of NaCl also influences the presence of lead leached from paints, pigments and generated by the automotive industry in soil samples (Wu and Kim, 2017). Current efforts are therefore aimed at accurately determining the amount of salt required to avoid any excess (Hatamzad et al., 2022) and performing lifecycle assessments of these materials (Saxe and Kasraian, 2020; Vignisdottir et al., 2020).

Sugar-derived molasses (beet or sugar cane) (Garcia Serrada and Vara Pazos, 2017; Ossian and Behrens, 2008; Garcia Serrada and Parrado Nuñez, 2015; Bloomer, 2000; Higgin-Botham et al., 2014; Petkuviene and Paliulis, 2009; Augsburger and Darlington, 1985; Maslow et al., 2013; Mertz and Gall, 2000; Chandler et al., 2002), lees (Janke George and Johnson, 1998), both of which are rich in carbohydrates (Hartley and Wood, 2001; Bytnar, 2007; Toth et al., 1987) as well as other plant extracts (Umoren and Solomon, 2015; Y and Rao, 2019; Amitha Rani and Basu, 2012; Xhanari et al., 2017; Abd-El-Nabey et al., 2020; Khan et al., 2015; Lebrini et al., 2020), nanocomposite coatings (Honarvar Nazari et al., 2022) and even expired drugs (Sundaram et al., 2021) have all been studied as cost-effective, easily attainable and easy to extract green corrosion inhibitors. These materials are often treated as residues and all these studies consider them to be smart waste in terms of the circular economy. The use of beet molasses has already led to a commercial product known as Safecote, which is mixed with NaCl or $CaCl_2$ solutions to form a highly efficient de-icing agent (Higgin-Botham et al., 2014; Petkuviene and Paliulis, 2009). The use of Safecote reduces the amount of salt used to around 30%–50% and results in an almost 40% lower corrosive effect than when using neat brine (23% wt NaCl) (Burtwell et al., 2002; Burtwell and Transportation Research, 2004). A previous study (Garcia Serrada and Parrado Nuñez, 2015) also proved that the addition of molasses to brine formulations resulted in a decrease in the nucleation temperature of ice crystals (-4.06 °C) compared to neat brine (23% wt NaCl) (-3.61 °C) as well as an increase in the ice melting capacity.

The addition of a small amount of ammonium cations (1–2 wt%) to these de-icing agents increased their ability to act as corrosion inhibitors, leading to a decrease in corrosion of close to 70% (Garcia Serrada and Vara Pazos, 2017). There is much circumstantial evidence suggesting that the presence of amines in corrosion inhibitor mixtures is beneficial (Garcia Serrada and Vara Pazos, 2017; Kucinskas and Sviklas Alfredas, 2015; Luo et al., 1998; Sathiyanarayanan et al., 2005; de Damborenea et al., 1997). Indeed, heteroatoms in organic compounds containing lone electron pairs are known to interact with metallic surfaces, thereby potentially functioning as corrosion inhibitors (Abd El-Maksoud, 2008). These heteroatoms contribute by donating electron density to Fe^{2+} cations released from the steel surface, thereby leading to the development of a passive film that can protect the steel surface against corrosive species such as chloride ions and oxygen (Umoren and Solomon, 2015; Luo et al., 1998).

Herein we describe the benefits of amine addition to de-sugared beet molasses ; ; and wine-derived lees as part of anti-freezing and de-icing formulations in terms of corrosion inhibition. In our search for environmentally benign substances to mitigate corrosion while maintaining the anti-freezing and de-icing properties, two materials related to byproducts from industrial activity in the Castilla y León region in the northern part of Spain were selected. Thus, de-sugared beet molasses and winery lees are undervalued byproducts that contain a high percentage of carbohydrates which, when combined with brine (aqueous solution with 20–23% wt. sodium chloride), do not alter the anti-freezing and de-icing properties of brine but decrease undesired corrosion phenomena. As such, the goal of this work was to find amine candidates that will enhance the de-icing properties of brine and molasses/lees mixtures while minimizing the corrosion process triggered by brine that weakens metallic structures. The key findings are as follows. First, amines such as triethylamine, triethanolamine, mono- and diisopropanolamine and mono- and diisopropylamine improve the corrosion inhibition behavior in mixtures based on molasses and lees. Second, the ice-melting capacity when using amine-containing molasses or lees as part of the de-icing formulation is similar to that for neat brine (23% wt NaCl), thus allowing us to conclude that these formulations are advantageous as environmentally friendly corrosion inhibitors as well as good de-icing agents.

2. Materials and methods

2.1. Materials

Chemicals were purchased from Sigma-Aldrich, Inc. and Acros Organics and used without purification. Amines such as diGluEDA (*N*,*N*′-di-β-D-glucopyranosylethylenediamine) (Tabassum et al., 2014; Liao et al., 2011) and BBPA (*N*-benzyl-*N*,*N*-*bis*[(3,5-dimethyl-1*H*-pyrazol-1-yl)methyl]amine) (Tebbji et al., 2007) were synthesized according to literature procedures. Steel probes were donated by COLLOSA, which purchased them from Thyssenkrupp Materials Ibérica. According to the Certificate of Analysis, the carbon steel composition (not including iron) is C (0.48%), Si (0.20%), Mn (0.65%); P (0.011%); S (0.004%); Cr (0.040%); Cu (0.040%); Ni (0.030%); Mo (<0.005%); Ti (<0.005%); Al (0.026%) and N (0.0080%). Galvanized steel consists of the aforementioned carbon steel with a zinc layer deposited on the metal surface (see scanning electron microscopy (SEM) image and electron dispersive X-Ray (EDS) experiments in Fig. S1). Molasses was provided by Azucarera (Toro, Valladolid) while the lees were generated at the Emilio Moro vineyards (Ribera del Duero, Peñafiel, Valladolid). ^1H and ^{13}C NMR experiments were performed using a 500 MHz DD2 Three Channel Console equipped with a cryoprobe from Agilent Technologies. The spectrometer operates at 499.81 MHz for ^1H and at 125.69 MHz for ^{13}C. All NMR experiments were performed at 25 °C in the Laboratory of Instrumental Techniques (LTI) Research Facilities, University of Valladolid.

2.2. *Characterization of molasses and lees*

Molasses (Fig. S2): ion exchange chromatography, amperometric detector 850 Professional IC 1. Hamilton RCX-30 250 × 4.6 mm column. Recording time 30.0 min. Eluent composition NaOH 150 mM. Flow 1.1 mL/min. Pressure 11.81 MPa. Temperature 30 °C. Lees (Fig. S2): ion exchange chromatography, amperometric detector 850 Professional IC 1. Hamilton RCX-30 250 × 4.6 mm column. Recording time 60.0 min. Eluent composition, NaOH 150 mM. Flow 1 mL/min. Pressure 9.90 MPa. Temperature 30 °C.

2.3. *Weight loss experiments*

(a) Indoor experiments. Metal plates of galvanized steel and carbon steel with dimensions 5.5 × 3.0 × 0.2 cm were used. These plates were initially washed with distilled water and 95% ethanol, scrubbed to remove possible impurities from the turning process, then allowed to dry overnight between two sheets of absorbent paper. The following day, they were weighed three times using an analytical balance (4 decimal places). Each plate was then placed in a Petri dish with an internal diameter of 7 cm and the test solution was added. The Petri dish was covered with the lid and, after 96 h, the test solution was removed, the metal plates were washed with distilled water and 95% ethanol, scrubbed to remove any impurities, and allowed to dry between two sheets of absorbent paper overnight. A second weighing (in triplicate) was performed the following day. (b) Outdoor experiments performed at COLLOSA (Dueñas, Palencia, Spain). This study involved selecting three groups of steel plates (12 × 6 cm). The first group comprised six carbon steel and six galvanized steel plates, which were treated with conventional brine (23% wt NaCl solution). A second group consisted of an identical number of plates that were treated with test solution. In this case, the test solution comprised 91.5% v/v brine (23% wt NaCl), 7.5% v/v molasses and the equimolar amount of triethanolamine equivalent to 1% v/v triethylamine. This amount of amine was used based on the optimized results reported previously (Garcia Serrada and Vara Pazos, 2017). Triethanolamine was chosen based on its affordability, lack of toxicity, low vapor pressure and high boiling point (335 °C) as well as the results reported in this work. The third group also comprised six carbon steel and six galvanized steel plates, which were left unaltered to act as control experiment and test oxidation outdoors under similar atmospheric conditions. The experiment began by placing the plates outdoors and applying the aforementioned procedures to them each time it was necessary to add brine to the road due to adverse cold conditions and/or ice.

2.4. *Surface morphology studies*

Microscopy experiments were performed at the Advanced Microscopy Unit of the Scientific Park at University of Valladolid. SEM images were obtained using an FEI Quanta 200 FEG SEM instrument. AFM images were obtained using an AFM Asylum Research, model MFP-3D Bio, model tip AC160TS-R3 Asylum Research (OTESPA) at a frequency of 300 Hz and stiffness of 26 N/m. Samples for both instruments were prepared by following the washing and immersion methodologies explained in the weight loss section.

2.5. *Electrochemical measurements*

Electrochemical studies were carried out using a conventional three electrode pyrex cell with a double external wall for the thermostatic circuit. The cell has a hermetic lid adapted to insert the electrodes, a nitrogen cannula and a glass thermometer to verify the actual temperature of the cell. Galvanized steel and carbon steel probes were used as working electrodes, a cylindrical platinum (Pt) bar (1 mm diameter, submerged approximately 5 cm) was used as counter-electrode and silver/silver chloride (Ag/AgCl) as reference electrode (Bard and Faulkner, 2001). The potentiostat was a PAR EG&G Model 273A from Princeton Applied Research. This unit was connected to a computer by means of a GPIB card, which allows control of the potential switching using ECHEM in PAR EG&G M270 software, version 4.23, and RUN352 software (Potentiodynamic, Tafel curves and Linear Polarization). Polarization studies were performed after the specimen had reached a steady-state potential. Open-circuit potential experiments were performed as a control experiment and showed that the OCP values remain stable for a minimum of 5 days (Fig. S3a). Cyclic voltammograms were recorded to check the difference in electroactivity between carbon steel and galvanized steel electrodes as well as the residual current for both systems (Fig. S3b). Polarization was carried out from a cathodic potential of −0.2 V to an anodic potential of +0.2 V with respect to the corrosion potential, at a sweep rate of 0.1–0.5 mV/s. E *versus* log I curves were plotted (Fig. S4). The linear TAFEL segments of the anodic and cathodic curves were extrapolated to corrosion potential to obtain the corrosion current densities. For linear polarization measurements, a sweep from −0.02 to +0.02 V versus open circuit potential at a sweep rate of 0.5 mV/s was used. The polarization resistance, R_p, is obtained as the slope of the I *versus* E curve in the vicinity of the corrosion potential E_{corr}.

2.6. *Melting capacity measurements*

Experiments were performed at the CARTIF Technology Center, Parque Tecnológico de Boecillo (Valladolid, Spain). SHRP Ice Melting Test (H-205.1 for solid deicers and H-205.2 for liquid deicers) methods (Chappelow et al., 1992) were chosen based on two standard procedures: ASTM (C702-87 Standard Practice for Reducing Field Samples of Aggregate to Testing Size) and (E440-90 Method for Analysis of Calcium Chloride). The experimental procedure was as follows: two petri dishes (closed lid) containing 25 mL of ultrapure water were frozen 24 h prior to the experiment. The different instrumentation was allowed to cool for 4 h at the target temperature in a climate chamber. The two frozen petri dishes with their ice content were then introduced and 2 additional hours were allowed to reach the desired temperature. A known volume of neat brine (0.9 mL) or test solution (0.9 mL) was then added to the ice samples in the petri dishes. The melting volume was measured at different times. This test was repeated in triplicate at different temperatures. Two sets of experiments were performed with two test solutions: test solution 1 was prepared with brine (23% wt NaCl aqueous solution) 91.5% v/v, molasses 7.5% v/v and the equimolar amount of triethanolamine equivalent to triethylamine 1% v/v, whereas in test solution 2, lees replaced the molasses in similar amounts.

2.7. *Differential scanning calorimetry (DSC) experiments*

Samples were frozen in a closed aluminum pan in a DSC Q20 equipment (TA instruments, calibrated with indium). Nitrogen gas (flow rate, 50 mL/min) was used for the cell purge. Specimens were cooled to a temperature of between −30 and −50 °C followed by an isotherm lasting 30 min. A heating step was finally performed at a rate of 5 °C/min to obtain the DSC thermogram.

3. Results and discussion

3.1. *Characterization of molasses and lees*

De-sugared beet molasses and lees are byproducts of the sugar and wine industries, respectively. Beet molasses contain 45–55% wt. carbohydrates, 3–5% wt. proteins and 10–15% wt. of different mineral salts. These constitute the dry material of the molasses, which accounts for 72–78% of the total (Garcia Serrada and Vara Pazos, 2017). Lees is a low density matrix mainly comprising microorganisms (yeasts and bacteria) related to the winemaking process and is currently an undervalued byproduct. This material is also rich in carbohydrates, therefore its sugar content was analyzed by chromatographic methods, as was the corresponding carbohydrate content in beet molasses (chromatograms in Fig. S2 and Table S1). The main difference is the much higher percentage of sucrose in molasses (74.86%) compared with lees (16.98%). Sucrose is a non-reducing disaccharide whereas the remaining components are reducing mono- or disaccharides. The term reducing sugar means that the substance gives a positive test with Fehling's solution. The amount of reducing sugar is thought to be an important parameter as a high concentration of complex non-reducing sugars may have a negative effect on the extent of the freezing point depression caused by the de-icing agent (Montgomery and Yang Byung, 2003).

3.2. *Weight loss method*

Corrosion studies were performed with galvanized and carbon steels by immersing each metal plate in the test solution for 96 h. The initial test solution contained brine (23% wt NaCl aqueous solution) 91.5% v/v, molasses 7.5% v/v and triethylamine 1% v/v. This formulation was chosen based on optimized results obtained in a previous study (Garcia Serrada and Vara Pazos, 2017). The subsequent experiments aiming at optimizing the amine used involved replacing triethylamine with an equimolar amount of the new amine and substituting molasses for lees when necessary. The steel plates were weighed before and after the experiment. All experiments were performed at least in triplicate to study the reproducibility of the results, reporting the mean value and the corresponding standard deviation. The corrosion rate was determined using the following equation (Tebbji et al., 2007):

$$Norm.\ Weight\ Loss\ \% = \frac{W_0 - W_f}{W_{0blank} - W_{f\,blank}}\ x\ 100$$

where W_0 and W_f are the weight of the steel plates before and after the corrosion experiment, respectively, and $W_{0\text{-blank}}$ and $W_{f\text{-blank}}$ are the mass of the steel plates before and after being treated with neat brine (23% wt), respectively. As such, our control experiments were the different steel plates immersed in a solution of pure brine in the absence of inhibitor. A histogram was elaborated using these data to determine the most efficient amine in the deicing formulations for both steels.

Fig. 1 shows a histogram of the normalized corrosion rates for each amine used. The 100% value refers to the weight loss that took place in neat brine after 96 h (an average of 3.00 mg for a 25.713 g carbon steel plate and 2.97 mg for a 24.895 g galvanized steel probe). Various amines, ranging from simple primary, secondary and tertiary amines to more complex amines containing hydroxyl groups, were studied. Two main conclusions can be derived from the above figure. Firstly, galvanized steel is more sensitive to corrosion than carbon steel when immersed in neat brine (23% wt NaCl) solution. This unexpected result is due to an insufficient thickness of the zinc coating (Denison and Romanoff, 1952) as well as the aggressive experimental conditions (Karthick et al., 2020; Padilla et al., 2013). Dissolution of the zinc coating increased the corrosion of the metal underneath. After washing the steel probes, it

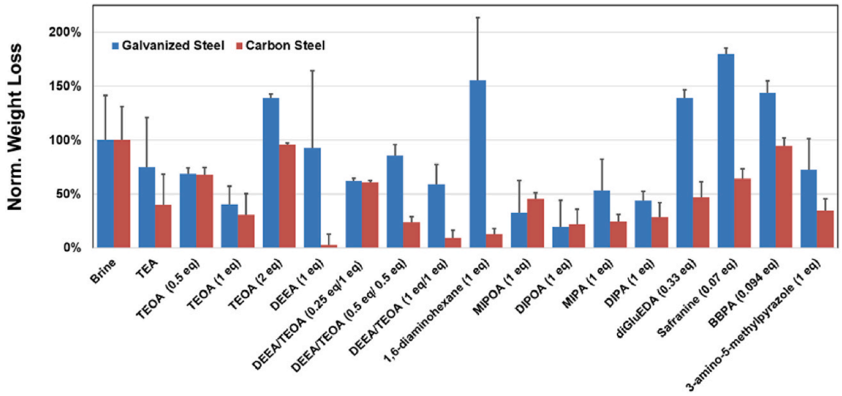

Fig. 1. Normalized weight loss histogram using molasses and different amines as additives in de-icing formulations. Abbreviations: TEA (triethylamine), TEOA (triethanolamine), DEEA (diethylethanolamine), MIPOA (isopropanolamine); DIPOA (diisopropanolamine); MIPA (isopropylamine); DIPA (diisopropylamine); diGluEDA (*N,N′*-di-*β*-D-glucopyranosylethylenediamine) and BBPA (*N*-benzyl-*N,N-bis*[(3,5-dimethyl-1*H*-pyrazol-1-yl)methyl]amine).

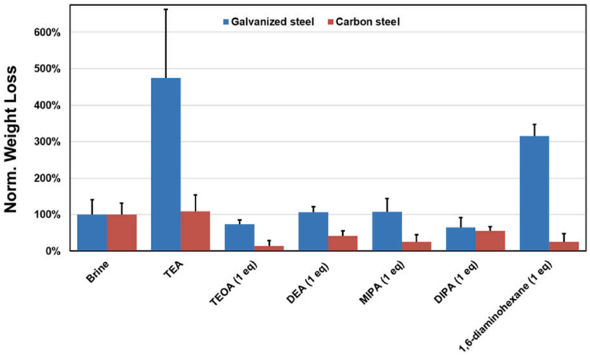

Fig. 2. Normalized weight loss histogram using lees and different amines as additives in brine-based de-icing compositions.

was noticed that, for some amines, the galvanizing coating had completely vanished, with the plate losing its distinguishing metallic luster and the base metal being fully exposed to the action of NaCl. Fig. S5 shows how the amine can lead to a marked and visible difference in the anti-corrosive effect. This is especially relevant when working with primary amines with a structure capable of chelating Zn^{2+} ions. The presence of these amines may inhibit the formation of simonkolleite ($Zn_5Cl_2(OH)_8 \cdot H_2O$), the product formed upon corrosion of galvanized steel in the presence of chlorides. This insoluble compound is thought to be responsible for preventing the permeation and retention of oxygen and water (Ikeda et al., 1991; Hosking et al., 2007). Secondly, amines such as triethylamine, triethanolamine, mono- and diisopropanolamine and mono- and diisopropylamine showed good corrosion inhibition behavior. Some of these amines contain chromophores with luminescent properties that may be used as markers (Hatamzad et al., 2022), such as safranine (Ebenso and Oguzie, 2005). BBPA (*N*-benzyl-*N*,*N*-bis[(3,5-dimethyl-1*H*-pyrazol-1-yl)methyl]amine) was synthesized as reported (Tebbji et al., 2007) and was expected to exhibit an efficient behavior based on the presence of three aromatic rings that could interact with the metal surface. However, under our conditions, the corrosion inhibition displayed by BBPA was quite poor. Another interesting compound is diGluEDA (*N*,*N*′-di-*β*-D-glucopyranosylethylenediamine) (Tabassum et al., 2014; Liao et al., 2011), which contains a high number of heteroatoms with lone electron pairs. When an equimolar amount of this compound related to triethylamine (1% v/v) was used, the result with galvanized steel showed a higher corrosion rate (three times higher, data not shown) than with just brine. However, decreasing the amount of this compound to 0.33 equivalents gave a better corrosion inhibition. This suggests that comparing amines with very different numbers of donor atoms may be risky. For this reason, far less than one equivalent of organic molecules containing several donor groups was employed (calculated in relation to the moles of TEA used in a previous study) (Garcia Serrada and Vara Pazos, 2017). The negative effect when working with ethylenediamine (EDA) as additive is also remarkable, with a much higher corrosion rate (15 times, data not shown) compared to conventional brine being observed. This result agrees with a previous observation (Garcia Serrada and Vara Pazos, 2017) and may be related to the ability of EDA to act as a good chelating agent that can extract Fe^{2+} ions from the surface (Maxwell, 2004; Micskei, 1987).

Fig. 2 shows the corrosion rate when lees was used in the de-icing compositions instead of molasses. The test solutions contained brine (23% wt NaCl aqueous solution) 91.5% v/v, lees 7.5% v/v and the equimolar amount of amine equivalent to triethylamine 1% v/v. Thiazole was also tested and found to lead to an even higher corrosion rate (10 times more than brine, data not shown). The fact that lees was previously milled until a homogeneous and viscous material similar to molasses was obtained should be noted. An absence of milling led to a lack of reproducibility. Among the amines tested, triethanolamine gave the most promising results. Unexpectedly, triethylamine did not work as a good corrosion inhibitor. The previous observations, together with the interesting features of triethanolamine, especially its affordability, lack of toxicity, low vapor pressure and high boiling point, led us to choose this amine for electrochemical measurements, open-field weight loss experiments as well as assessment of the ice-melting properties.

3.3. Electrochemical experiments

These assays were performed using brine (23% wt NaCl aqueous solution) 91.5% v/v, de-sugared beet molasses 7.5% v/v and the equimolar amount of triethanolamine with respect to triethylamine 1% v/v as test solution. This amine was chosen in view of the promising results obtained in the weight loss corrosion experiments. The potentiodynamic polarization curves allowed us to discern the associated electrochemical parameters such as corrosion potential (E_{corr}), corrosion current density (I_{corr}), and the anodic and cathodic Tafel slopes (b_a and b_c), which were obtained from the intersection of the anodic and cathodic Tafel lines (see plots in Fig. S4). The criterion for performing the experiments requires a steady-state potential to be achieved. Indeed, OCP vs time experiments showed that the open-circuit potential was stable for several days (Fig. S3a). The polarization resistances, R_p, were obtained as the slope of the I *versus* E curves in the vicinity of the corrosion potential (E_{corr}). Corrosion inhibition efficiencies IE(%) were calculated using the following equation (Mourya et al., 2016):

$$\boldsymbol{IE}\ \% = \frac{\boldsymbol{R_p} - \boldsymbol{R_p^0}}{\boldsymbol{R_p}}\ \boldsymbol{x}\ 100$$

where R_p^0 and R_p (k Ω) are the polarization resistance values for uninhibited and inhibited solutions, respectively. The corrosion current

Table 1
Electrochemical data obtained using brine or brine with molasses and TEOA as additive.

Solution	Working electrode	E (V)	R_p/kΩ	$I_{corr}/\mu Acm^{-2}$	b_a mV·dec^{-1}	b_c mV·dec^{-1}	B	IE%
Neat brine	Carbon Steel	−0.587	7.91	2.71	78.19	180.1	22.30	
	Galvanized Steel	−1.052	0.78	19.88	21.35	255.3	8.69	
Molasses and TEOA	Carbon Steel	−0.464	8.79	3.31	103.27	156.3	25.66	10.0
	Galvanized Steel	−0.977	2.40	14.23	19.84	206.3	7.60	67.5

density (μA·cm^{-2}) is derived from the Stern-Geary equation (Stern and Geary, 1957) as follows:

$$I_{corr} = k/R_p$$

$$k = \frac{-b_a \cdot b_c}{2.303(b_a - b_c)}$$

Table 1 shows the electrochemical data obtained under our conditions (electrodes submerged in neat brine solution or in brine and molasses containing TEOA). The inhibiting action of the molasses and TEOA is reflected in the less negative corrosion potential, which implies a higher resistance to oxidation. The galvanized specimen is easily oxidized under our conditions, thus concurring with the results obtained in the weight loss experiment. The zinc coating is fully oxidized, very likely leading to zinc corrosion products on the coating surface and preventing the zinc from acting as a sacrificial anode. The presence of inhibitor gives rise to a displacement in the corrosion potential of 123 mV when using TEOA with carbon steel electrodes (a 75 mV displacement was observed when working with galvanized steel probes).

3.4. *Surface topology experiments*

The scanning electron microscopy (SEM) images (Fig. 3) show that specimens dipped in the neat NaCl solution were severely corroded (for comparison, see pristine galvanized and carbon steel samples, Fig. S6), whereas the corrosion of specimens immersed in solutions containing brine, molasses and TEOA was inhibited to some extent despite the fact that the immersion methodology implies an enormous excess of NaCl on the metal surface, as confirmed from the SEM images (Fig. S7). For the sample immersed in brine solution, holes are abundant as a result of severe corrosion attacks, particularly for the galvanized steel specimen. This is because dissolution of the zinc layer leads to micro voids and micro cracks on the metal surface (Karthick et al., 2020). Of the inhibitors tested, it is surprising that the samples protected with molasses and triethylamine did not show efficient protection (Fig. S8) compared to the results obtained with triethanolamine. Moreover, the corrosion experienced by the galvanized steel specimens was higher than the corrosion observed for carbon steel in every case, in agreement with the weight loss experiments. The protection against corrosion arising due to the presence of molasses and triethanolamine was studied in more detail using atomic force microscopy (AFM). Grooves and irregularities are noticeable in the specimens treated with neat NaCl solution, whereas the surface topology is highly preserved in samples containing molasses and triethanolamine (Fig. S9). This trend is also observed with carbon steel samples (Fig. S10), although to a lesser extent, as these samples are less readily corroded by brine under our conditions.

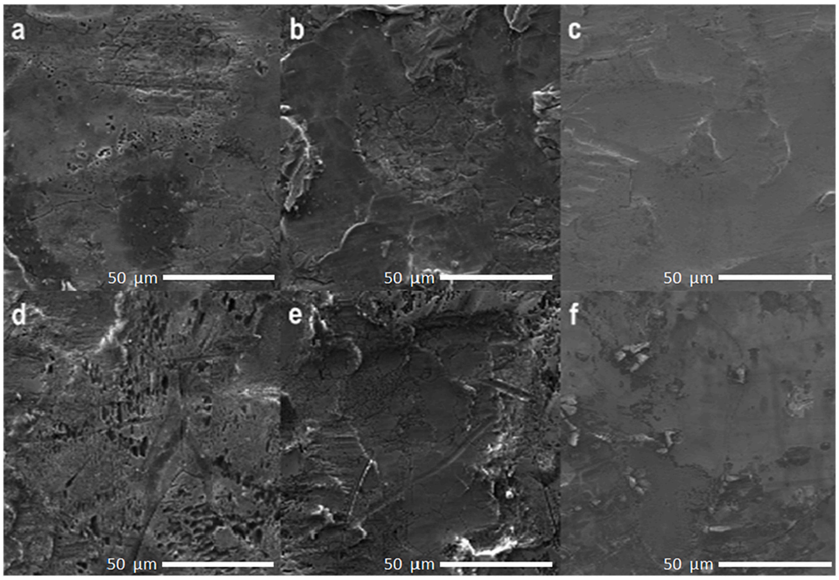

Fig. 3. Top. SEM images (1500x magnification) for carbon steel after incubation for 96 h with brine (a); with brine, molasses and TEOA (b); with brine, lees and TEOA (c). Bottom. SEM images (1500x magnification) for galvanized steel after incubation for 96 h with brine (d); with brine, molasses and TEOA (e); with brine, lees and TEOA (f).

3.5. Open-field corrosion test

The results obtained with molasses and triethanolamine encouraged us to perform outdoor tests (Fig. 4). These experiments were based on the aforementioned gravimetric weight loss method. Three groups of steel probes (six samples each) were tested in collaboration with COLLOSA (a Spanish company responsible for road maintenance and winter de-icing treatments). Two control groups of galvanized and carbon steel samples were prepared, one of which was left untreated under the environmental conditions and the second of which was treated with conventional brine solutions (23% wt. NaCl). A third group was treated with a solution containing 91.5% v/v brine (23% wt. NaCl), 7.5% v/v de-sugared beet molasses and an equimolar amount of triethanolamine that corresponds to 1% v/v triethylamine. The samples were treated each time the weather conditions required a winter de-icing treatment on the surrounding roads. This treatment consists of spraying the brine composition on the surface of the steel probes, thereby simulating truck performance when spreading the brine on the road surface. Samples were removed at different intervals, then washed and weighed. The samples removed to date (Pictures in Fig. S11) were obtained after: (a) 231 days and 9 winter treatments; (b) 339 days and 36 treatments; (c) 357 days and 44 treatments and (d) 453 days and 59 treatments, leaving behind two samples for the next winter season. The two plots in Fig. 5 were elaborated using these samples.

Fig. 5 shows the percentage weight loss for the steel samples after exposure to environmental conditions for a prolonged time and a finite number of winter treatments. In both samples (carbon and galvanized steel), use of the test solution (brine, molasses and TEOA) resulted in a marked decrease in the corrosion rate (88% for galvanized steel and 65% for carbon steel). Spraying the test solutions on the surface of the metals is a softer methodology than the immersion procedure performed previously, thereby possibly explaining why the inhibition phenomenon displayed by molasses/TEOA is enhanced under these conditions. The results achieved with galvanized steel are remarkable as they indicate that corrosion of the samples treated with the composition brine/molasses/TEOA was lower than for the control specimen subjected to no treatment. In this case, the zinc coating and the use of a green inhibitor minimized the corrosion to a marked extent. Indeed, the damage is minimum and the steel probes preserve their metallic luster (Fig. S11).

Fig. 4. Open-field experiments with carbon and galvanized steel probes.

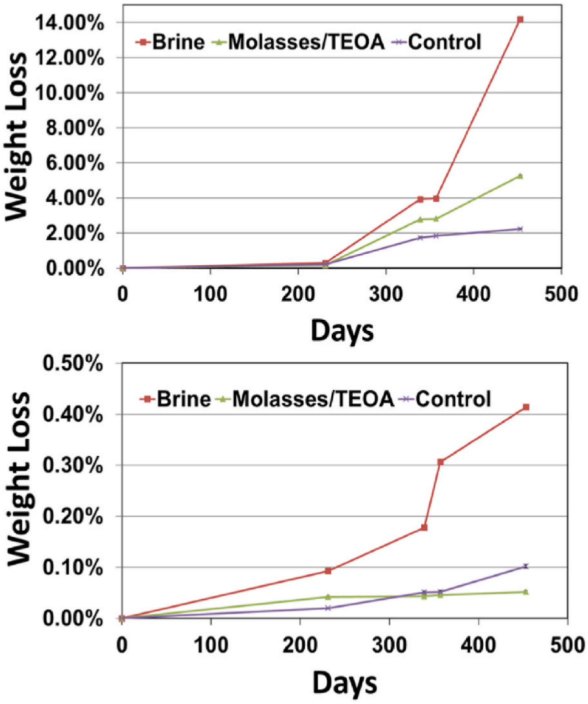

Fig. 5. Top. Plot of weight loss for carbon steel samples. Bottom. Plot of weight loss for galvanized steel samples.

3.6. *Ice-melting assessment*

Once the corrosion inhibition had been ascertained, the ice-melting capacity of the test solution was measured. To that end, the SHRP Ice Melting Test (H-205.1 and H-205.2) was employed at the CARTIF Technology Center (Fig. S12). This methodology is based on ASTM C702-87 (Standard Practice for Reducing Field Samples of Aggregate to Testing size) and E440-90 (Method for Analysis of Calcium Chloride) (Chappelow et al., 1992). In brief, it consists of freezing known volumes of water under controlled conditions in a climate chamber and allowing the different instrumentation to be used to reach the same temperature (Fig. 6). A known volume of neat brine and the test solution are then added to different ice samples. The melting volume is measured at different times. This test was repeated in triplicate at different temperatures.

Two sets of experiments were performed, one with molasses (test solution 1) and the other with lees (test solution 2), both being present in 7.5% v/v of the formulation and containing TEOA (1 equiv) in both cases (Table 2).

The results of these experiments clearly show that the ice-melting capacity of the brine solution was not altered by the addition of a known amount of molasses or lees together with triethanolamine. The volume of ice melted by our test solutions was comparable with that achieved using brine alone. In addition, DSC experiments were performed to record thermograms of frozen samples, which were slowly heated to determine the melting point. This temperature was defined as the sharpest tangent to the left-hand side of the endothermic event. The results are reported in Table S2. Formulations containing molasses/lees and TEOA provoked a drop in the melting point of 11% (−25.12 °C) and 5% (−23.73 °C), respectively, compared to neat 23% wt brine (−22.59 °C).

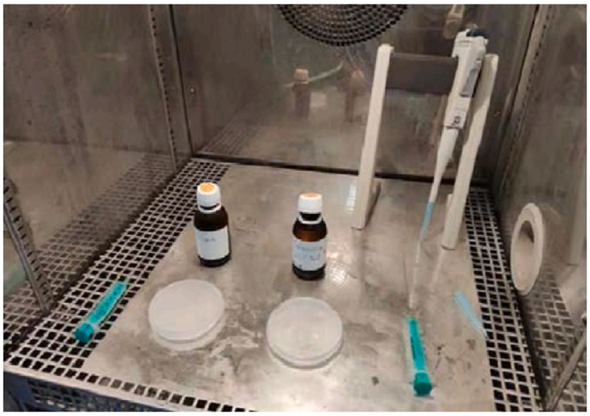

Fig. 6. Cooling the instrumentation and samples in the chamber before the experiment.

Table 2
Ice-melting volumes under temperature-controlled conditions using brine or spiked brine (molasses or lees plus triethanolamine).

			Temperature (°C)		
Additive	Time	Samples	−1	−5	−10
Molasses V(mL) melted	20 min	Brine	3.7 ± 0.6	2.0 ± 0.0	1.5 ± 0.0
		Test Sol.1	4.0 ± 0.5	2.0 ± 0.0	1.5 ± 0.0
	60 min	Brine	6.8 ± 0.3	2.2 ± 0.3	0.3 ± 0.3
		Test Sol.1	7.8 ± 0.6	2.2 ± 0.3	0.5 ± 0.0
Lees V(mL) melted	20 min	Brine	4.3 ± 0.3	3.2 ± 0.8	2.7 ± 0.3
		Test Sol.2	4.5 ± 0.0	3.2 ± 0.8	2.5 ± 0.0
	60 min	Brine	8.8 ± 2.4	8.0 ± 2.0	9.0 ± 2.2
		Test Sol.2	9.0 ± 2.2	7.8 ± 2.3	8.0 ± 2.0

4. Summary and conclusions

This work adds value to industrial byproducts such as molasses and lees as part of the formulation for ecofriendly de-icing agents. The interaction of molasses or lees with different aliphatic amines inhibits corrosion in galvanized and carbon steel in the presence of brine. We have shown by means of gravimetric methods, electrochemical studies and surface topology experiments that some modest amines exert an important inhibiting effect in terms of metal corrosion when mixed with molasses or lees and added to neat brine. Among the nitrogen-containing molecules, triethanolamine attracted our attention given its inhibiting properties as well as its physical features, namely that it is a liquid at room temperature and is fully miscible with water. The anti-corrosion properties that the mixture molasses/TEA conferred on a de-icing brine-based formulation was previously reported by some of us. (Garcia Serrada and Vara Pazos, 2017) The results reported herein represent an addition to our previous understanding by suggesting that molasses and lees containing an affordable, non-toxic and widely available amine such as triethanolamine are very useful green corrosion inhibitors. Indeed, the mixtures containing molasses/lees and triethanolamine exhibited better corrosion inhibition for carbon and galvanized steels than those containing triethylamine. More importantly, the addition of molasses/lees and triethanolamine to a de-icing agent such as brine solution (23% wt NaCl) does not alter the de-icing properties of the original neat brine solution. In light of the above, these solutions may be suitable as an environmentally friendly alternative to the brine solutions commonly used in road maintenance, thereby lowering the detrimental effects caused by sodium chloride and other common salts on roads and the surrounding vegetation and bodies of water.

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Author statement

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Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Francisco J. Pulido reports financial support was provided by ICE (business competitiveness institute, Castilla y León Government, Spain). Carlos Garcia Serrada reports a relationship with Construcciones y Obras Llorente, SA that includes: employment. Carlos Garcia Serrada has patent #ES2545931B1 issued to Construcciones y Obras Llorente, SA. Carlos Garcia Serrada has patent #ES2464693B1 issued to Construcciones y Obras Llorente, SA.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scp.2022.100789.

References

Abd El-Maksoud, S.A., 2008. The effect of organic compounds on the electrochemical behaviour of steel in acidic media. A review. Int. J. Electrochem. Sci. 3, 528–555.

Abd-El-Nabey, B.A., Abd-El-Khalek, D., El-Housseiny, S., Mohamed, M.E., 2020. Plant extracts as corrosion and scale inhibitors: a review. Int. J. Corros. Scale Inhib. 9, 1287–1328. https://doi.org/10.17675/2305-6894-2020-9-4-7.

Amitha Rani, B.E., Basu, B.B.J., 2012. Green inhibitors for corrosion protection of metals and alloys: an overview. Int. J. Corros. 2012, 380217 https://doi.org/10.1155/2012/380217.

Augsburger, J.J., Darlington, R.K., 1985. Corrosion Inhibition of Aqueous Brines. NL Industries Inc. Darlington, R. Keith, US 4536302 A.

Baltrenas, P., Kazlauskiene, A., Zaveckyte, J., 2006. Experimental investigation into toxic impact of road maintenance salt on grass vegetation. J. Environ. Eng. Landsc. Manag. 14, 83–88. https://doi.org/10.1080/16486897.2006.9636883.

Bard, A.J., Faulkner, L.R., 2001. Electrochemical Methods : Fundamentals and Applications/Allen J. Bard, Larry R. Faulkner, second ed. John Wiley & Sons, New York.

Bloomer, T.A., 2000. Anti-freezing and Deicing Composition and Method. Bloomer; Todd, A., US 6080330 A.

Burtwell, M., Transportation Research, B., 2004. Assessment of Safecote: New Deicer Product. Transportation Research Board, pp. 529–540.

Burtwell, M., Wilson, M., Alad, L., 2002. Safecote de-icer in UK winter maintenance. Highways 71, 13–15.

Bytnar, S.C., 2007. De-icing Composition and Method. Archer Daniels Mildland Co., US, 2007/0295932 A1.

Chandler, C., Kharslian, M., Furman, A., 2002. Sugar beets against corrosion. Corrosion Rev. 20, 379–390. https://doi.org/10.1515/CORRREV.2002.20.4-5.379.

Chappelow, C.C., McElroy, A.D., Blackburn, R.R., Darwin, D., Noyelles, F.G., 1992. Handbook of Test Methods for Evaluating Chemical Deicers.

de Damborenea, J., Bastidas, J.M., Vázquez, A.J., 1997. Adsorption and inhibitive properties of four primary aliphatic amines on mild steel in 2 M hydrochloric acid. Electrochim. Acta 42, 455–459. https://doi.org/10.1016/S0013-4686(96)00250-2.

Denison, I.A., Romanoff, M., 1952. Corrosion of galvanized steel in soils. J. Res. Natl. Bur. Stand. 49, 299–314.

Ebenso, E.E., Oguzie, E.E., 2005. Corrosion inhibition of mild steel in acidic media by some organic dyes. Mater. Lett. 59, 2163–2165. https://doi.org/10.1016/j.matlet.2005.02.055.

Garcia Serrada, C., Parrado Nuñez, C., 2015. Flux Composition to Eliminate or Prevent the Formation of Ice or Snow. Construcciones y Obras Llorente SA. ES 2464693 B1.

Garcia Serrada, C., Vara Pazos, E., 2017. Additive Anticorrosive Composition for De-icing and Anti-freezing Products, Product Comprising Same and Method for the Preparation Thereof. Construcciones y Obras Llorente SA. WO 2017/017295 A1.

Hartley, R.A., Wood, D.H., 2001. Deicing Solution. Sears Petroleum & Transp Corp. US 6299793 B1.

Hatamzad, M., Polanco Pinerez, G.C., Casselgren, J., 2022. Using deep learning to predict the amount of chemicals applied on the wheel track for winter road maintenance. Appl. Sci. 12, 3508. https://doi.org/10.3390/app12073508.

Higgin-Botham, J., Grimshaw, V., Fisher, L., 2014. De-icing, Anti-freezing and Anti-corrosion Compositions. Safecote Ltd.. EP 1680476 B1.

Honarvar Nazari, M., Mousavi, S.Z., Potapova, A., McIntyre, J., Shi, X., 2021. Toxicological impacts of roadway deicers on aquatic resources and human health: a review. Water Environ. Res. 93, 1855–1881. https://doi.org/10.1002/wer.1581.

Honarvar Nazari, M., Zhang, Y., Mahmoodi, A., Xu, G., Yu, J., Wu, J., Shi, X., 2022. Nanocomposite organic coatings for corrosion protection of metals: a review of recent advances. Prog. Org. Coating 162, 106573. https://doi.org/10.1016/j.porgcoat.2021.106573.

Hosking, N.C., Ström, M.A., Shipway, P.H., Rudd, C.D., 2007. Corrosion resistance of zinc–magnesium coated steel. Corrosion Sci. 49, 3669–3695. https://doi.org/10.1016/j.corsci.2007.03.032.

Ikeda, K., Nishimoto, H., Satoh, H., Kawafuku, J., Katoh, J., Toyama, M., 1991. Properties of Zinc Alloy Coated Steel Sheets Obtained by Continuous Vapor Deposition Pilot-Line. SAE International.

Janke, George A., Johnson Jr., Warren D., 1998. Deicing composition and method. Janke, George A. Johnson Jr., Warren D., US 5709813 A.

Karthick, S., Muralidharan, S., Saraswathy, V., 2020. Corrosion performance of mild steel and galvanized iron in clay soil environment. Arab. J. Chem. 13, 3301–3318. https://doi.org/10.1016/j.arabjc.2018.11.005.

Khan, G., Kazi, S.N., Basirun, W., Binti, H., Ali, M., Faraj, F., Khan, G., 2015. Application of natural product extracts as green corrosion inhibitors for metals and alloys in acid pickling processes-A review. Int. J. Electrochem. Sci. 10, 6120–6134.

Kucinskas, V., Sviklas Alfredas, M., 2015. Snow and Ice Melting Composition. UAB Baltkalis. WO 2015/092600 A1.

Lebrini, M., Suedile, F., Salvin, P., Roos, C., Zarrouk, A., Jama, C., Bentiss, F., 2020. Bagassa guianensis ethanol extract used as sustainable eco-friendly inhibitor for zinc corrosion in 3% NaCl: electrochemical and XPS studies. Surf. Interfaces 20, 100588. https://doi.org/10.1016/j.surfin.2020.100588.

Liao, Q.Q., Li, Y.J., Xiang, B., 2011. Synthesis and characterization of an aminated D-glucose and its stability of Cu2+Complex. Adv. Mater. Res. 197–198, 65–68. https://doi.org/10.4028/www.scientific.net/AMR.197-198.65.

Luo, H., Guan, Y.C., Han, K.N., 1998. Corrosion inhibition of a mild steel by aniline and alkylamines in acidic solutions. Corrosion 54, 727–731.

Maslow, W., De Jong Edwin, R., Demmer Rene Lodewijk, M., 2013. Deicing Composition, Akzo Nobel Chemicals Int BV. WO 2013/068299 A1.

Ethylenediamine and chelating agents. In: Maxwell, G.R. (Ed.), 2004. Synthetic Nitrogen Products: A Practical Guide to the Products and Processes. Springer US, Boston, MA, pp. 325–331.

Mertz, S.F., Gall, J.A., 2000. Corrosion Inhibited Chloride Salt De-icers. Dow Chemical Co., CA 2287582 A1.

Micskei, K., 1987. Equilibria in aqueous solutions of some iron(II) complexes. J. Chem. Soc., Dalton Trans. 255–257. https://doi.org/10.1039/DT9870000255.

Montgomery, R.E.X., Yang Byung, Y.U.N., 2003. Biodegradeable Deicing Composition. Univ. Iowa Res. Found.. US 6605232 B1.

Mourya, P., Singh, P., Rastogi, R.B., Singh, M.M., 2016. Inhibition of mild steel corrosion by 1,4,6-trimethyl-2-oxo-1,2-dihydropyridine-3-carbonitrile and synergistic effect of halide ion in 0.5M H2SO4. Appl. Surf. Sci. 380, 141–150. https://doi.org/10.1016/j.apsusc.2016.01.263.

Ossian, K.C., Behrens, K., 2008. Processed Raffinate Material for Enhancing Melt Value of De-icers. Ossian, Inc., US, 2008/0128651 A1.

Padilla, V., Ghods, P., Alfantazi, A., 2013. Effect of de-icing salts on the corrosion performance of galvanized steel in sulphate contaminated soil. Construct. Build. Mater. 40, 908–918. https://doi.org/10.1016/j.conbuildmat.2012.09.077.

Petkuviene, J., Paliulis, D., 2009. Experimental research of road maintenance salts and molasses (“safecote”) corrosive impact on metals. J. Environ. Eng. Landsc. Manag. 17, 236–243. https://doi.org/10.3846/1648-6897.2009.17.236-243.

Ratkevičius, T., Laurinavičius, A., Tuminienė, F., Bradulienė, J., 2014. Reduction of Negative Impact of Salts Used for Winter Road Maintenance on the Environment. The 9th International Conference “Environmental Engineering” Vilnius, Lithuania.

Sajid, H.U., Jalal, A., Kiran, R., Al-Rahim, A., 2022. A survey on the effects of deicing materials on properties of Cement-based materials. Construct. Build. Mater. 319, 126062 https://doi.org/10.1016/j.conbuildmat.2021.126062.

Sathiyanarayanan, S., Marikkannu, C., Palaniswamy, N., 2005. Corrosion inhibition effect of tetramines for mild steel in 1M HCl. Appl. Surf. Sci. 241, 477–484. https://doi.org/10.1016/j.apsusc.2004.07.050.

Saxe, S., Kasraian, D., 2020. Rethinking environmental LCA life stages for transport infrastructure to facilitate holistic assessment. J. Ind. Ecol. 24, 1031–1046. https://doi.org/10.1111/jiec.13010.

Shi, X., Jungwirth, S., 2018. The Search for "Greener" Materials for Winter Road Maintenance Operations, Sustainable Winter Road Operations. John Wiley & Sons, New York, pp. 378–401.

Stern, M., Geary, A.L., 1957. Electrochemical polarization: I. A Theoretical Analysis of the Shape of Polarization Curves. J. Electrochem. Soc. 104, 56–63. https://doi.org/10.1149/1.2428496.

Sundaram, R.G., Vengatesh, G., Sundaravadivelu, M., 2021. Surface morphological and quantum chemical studies of some expired drug molecules as potential corrosion inhibitors for mild steel in chloride medium. Surf. Interfaces 22, 100841. https://doi.org/10.1016/j.surfin.2020.100841.

Tabassum, S., Afzal, M., Arjmand, F., 2014. New modulated design, docking and synthesis of carbohydrate-conjugate heterobimetallic CuII–SnIV complex as potential topoisomerase II inhibitor: in vitro DNA binding, cleavage and cytotoxicity against human cancer cell lines. Eur. J. Med. Chem. 74, 694–702. https://doi.org/10.1016/j.ejmech.2013.09.036.

Tebbji, K., Bouabdellah, I., Aouniti, A., Hammouti, B., Oudda, H., Benkaddour, M., Ramdani, A., 2007. N-benzyl-N,N-bis[(3,5-dimethyl-1H-pyrazol-1-yl)methyl] amine as corrosion inhibitor of steel in 1 M HCl. Mater. Lett. 61, 799–804. https://doi.org/10.1016/j.matlet.2006.05.063.

Terry, L., Conaway, K., Rebar, J., Graettinger, A., 2020. Alternative deicers for winter road maintenance—a review. Water Air Soil Pollut. 231, 394 https://doi.org/10.1007/s11270-020-04773-x.

Toth, J., Szeles, J., Egenhoffer, O., 1987. Anti-freeze Composition Suitable for Making Surfaces Free of Snow and Ice. Alkoto Ifjusag Egyesueles, US 4676918 A.

Umoren, S.A., Solomon, M.M., 2015. Effect of halide ions on the corrosion inhibition efficiency of different organic species – a review. J. Ind. Eng. Chem. 21, 81–100. https://doi.org/10.1016/j.jiec.2014.09.033.

Vignisdottir, H.R., Ebrahimi, B., Booto, G.K., O'Born, R., Brattebø, H., Wallbaum, H., Bohne, R.A., 2019. A review of environmental impacts of winter road maintenance. Cold Reg. Sci. Technol. 158, 143–153. https://doi.org/10.1016/j.coldregions.2018.10.013.

Vignisdottir, H.R., Ebrahimi, B., Booto, G.K., O'Born, R., Brattebø, H., Wallbaum, H., Bohne, R.A., 2020. Life cycle assessment of winter road maintenance. Int. J. Life Cycle Assess. 25, 646–661. https://doi.org/10.1007/s11367-019-01682-y.

Wu, J., Kim, H., 2017. Impacts of road salts on leaching behavior of lead contaminated soil. J. Hazard Mater. 324, 291–297. https://doi.org/10.1016/j.jhazmat.2016.10.059.

Xhanari, K., Finšgar, M., Knez Hrnčič, M., Maver, U., Knez, Ž., Seiti, B., 2017. Green corrosion inhibitors for aluminium and its alloys: a review. RSC Adv. 7, 27299–27330. https://doi.org/10.1039/C7RA03944A.

Y, S., Rao, P., 2019. Material conservation and surface coating enhancement with starch-pectin biopolymer blend: a way towards green. Surf. Interfaces 16, 67–75. https://doi.org/10.1016/j.surfin.2019.04.011.